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**Patterning and Structural Engineering of Dimensionally Constrained Functional Oxide
Nanostructures**

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ABSTRACT

Patterning and Structural Engineering of Dimensionally Constrained Functional Oxide Nanostructures

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The current trend of ceramic nanotechnology has motivated an ever-increasing need to achieve exquisite control over *size*, *shape*, and *spatial confinement* for functional oxide architectures, in an equivalent manner demonstrated for semiconductors. However, the unique nature of ceramics has posed major challenges for most traditional nanofabrication technologies, putting the development of innovative oxide nanopatterning schemes under the spotlight. Dimensional and spatial confinement of functional oxides has also raised extensive intellectual interests since it carries a profound bearing upon their microstructure variation and leads to often superior performances. This further underlines the need for exploring the “*materials science and engineering*” of nano-constrained oxides, i.e., to fabricate nanopatterns with precise geometrical control at various dimensionalities, and to tailor their microstructural and functional characteristics. This dissertation presents one strategy to achieve such objectives.

We have developed a versatile nanofabrication approach, termed variable pressure-soft-electron beam lithography (VP-soft-eBL) that successfully resolves the generic challenges in patterning oxides and enables high resolution fabrication of diverse materials on a multitude of substrates. A strategy based on VP-soft-eBL was derived for microstructural and morphological

control on the nanostructures, particularly that of ferroelectrics and ferrimagnets. The effect of pattern aspect ratio on the microstructure evolution has been investigated for CoFe_2O_4 and BaTiO_3 nanodiscs on single crystal substrates with appropriate lattice matching. Following this strategy, high quality epitaxial patterns can be readily achieved from amorphous form during annealing.

VP-soft-eBL portfolio was then expanded significantly towards multi-dimensional patterning capability to facilitate systematic study on the confinement phenomena. We investigated the beam skirt effect on electron energy deposition profile in VP-eBL and demonstrated successful fabrication of architectures spanning 0-dimensional dots, 1-dimensional lines, 2-dimensional high density grids, and 3-dimensional heterostructures. Embedded in these efforts were varied site-specific characterizations on the nanostructures. Our initial study using x-ray microdiffraction indicated localized deformation field induced in the substrate at vicinity of epitaxial pattern edges.

Our approach of building and tailoring nano-constrained functional oxides is highly flexible, serving for a wide variety of materials and diverse types of architectures. The protocol reported in this dissertation lays the groundwork for in-depth exploration of the rich phenomena related to spatial/dimensional confinement. Further refinement of our strategy may provide an effective tool to harness the technological opportunities of diverse functional materials and pave the way for innovative applications which require nanopatterned architectures.

Dedicated to my parents, Wei Xiong and Chengwen Pan, who offered me unconditional love and support throughout my venture in graduate school

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CHAPTER 1

INTRODUCTION

1.1 FUNCTIONAL OXIDE NANOSTRUCTURES

During the past two decades, ever-increasing research attention has been paid to the design and realization of functional oxide nanostructures of various types. The family of functional oxides possesses a very broad spectrum of technologically significant linear and non-linear properties in response to electric, magnetic, stress field, or combinations of them. These properties are inclusive of, but not limited to, ferroelectricity,^{1, 2} ferromagnetism,³ ferroelectromagnetism,⁴ colossal magnetoresistance,⁵ abnormal thermal expansion,⁶ fast ionic conductivity,⁷ and high T_c superconductivity.⁸ Many of these properties show remarkable size dependency as well as interesting synergistic coupling when materials with different functionalities are positioned in close proximity. Therefore, the ability to manipulate and measure oxides at the nanometer and atomic levels has led to the discovery of surprising materials behaviors and patenting of new products and processes based on nanostructure control of these functional oxides.

Depending on their architectures, functional oxide nanostructures that are currently under study can be categorized into three types, namely i) freestanding nanostructures; ii) nanocrystalline ceramics or nanocomposites; and iii) spatially and dimensionally constrained

nanopatterns. Figure 1.1 schematically illustrates the typical morphology of these three types of nanostructures. The following paragraphs will briefly summarize the potential applications and typical fabrication methods for each type.

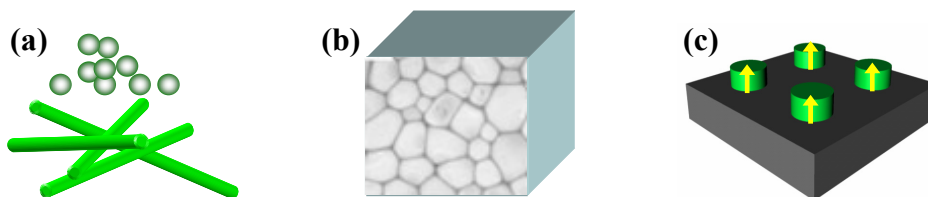


Figure 1.1: Schematic illustration of typical functional oxide nano-architectures. (a) free-standing; (b) nanocrystalline ceramics or nanocomposites; (c) spatially and dimensionally constrained nanopatterns.

1. Freestanding nanostructures

Freestanding materials include isotropic structures such as zero-dimensional (0D) nanoclusters and nanoparticles, and anisotropic one-dimensional (1D) structures such as nanowires, nanorods and nanobelts in dispersion form. Due to the high surface-to-volume ratio and the quantum confinement effect at low dimensions, the freestanding functional oxide nanostructures are showing great potentials both in catalysis, battery electrodes and electrochemical capacitors⁹ and in fabricating nanosized electrical junctions, optoelectronic and electromechanical devices.¹⁰ Various chemical methods have been developed for making 0D and 1D freestanding oxide nanostructures from a wide range of materials with well-controlled morphologies. These methods include, but not limited to, sol-gel approach,⁹ electrophoretic deposition,¹¹ and hydrothermal synthesis.¹² A generic character of these methods is: they are wet

chemistry routes that utilize the self-organization of material precursors to form the preferred phase and morphology in liquid environment, or otherwise known as “bottom-up” approaches.

2. *Nanocrystalline ceramics and nanocomposites*

Nanocrystalline oxide ceramics are known to possess unique physical and mechanical properties, including enhanced ductility and superplasticity even in traditionally brittle materials; superior strength; and optical transparency in usually opaque ceramics.¹³ Nanocomposites, i.e., ceramics containing at least one phase with constituents of less than 100 nm in size, exhibit enhanced mechanical, magnetic, high-temperature, and optical properties, as well as excellent catalytic properties.¹⁴ The fabrication of nanocrystalline or nanocomposite oxide ceramics usually rely on synthesis of single phase nanopowders or composite powders with nano-embedments, followed by consolidation of these powders into bulk-sized components while preserving their nanostructures. Traditional sintering methods such as cold pressing, hot pressing, and hot isostatic pressing have strong limitations of not being able to retain the nanoscale grain size due to excessive grain growth during processing. Unconventional consolidation techniques that employ non-equilibrium mass transfer under high energy or high pressure have been explored to solve this problem. These techniques include transformation-assisted consolidation,¹⁵ spark plasma sintering,¹⁶ dynamic consolidation using shock waves,¹⁷ microwave sintering,¹⁸ and laser-based techniques.¹⁹

3. *Spatially and dimensionally constrained nanopatterns*

In the context of this dissertation, *spatial confinement* refers to inevitable attachment of materials to a substrate or an overlayer(s). *Dimensional* constraint arises from the ubiquitous

need for materials to be confined in different dimensionalities to enhance aerial density and possible novel properties. For example, a blanket thin film is spatially confined by the underlying substrate in two in-plane directions, and its vertical size is constrained dimensionally at a given thickness. To be succinct, the term “spatially and dimensionally constrained nanostructures” is sometimes replaced with definitions readily used to describe freestanding structures hereafter, i.e., 0-dimensional nanopatterns represent nanodots or nanodiscs confined on a substrate, whereas 1-dimensional nanopatterns refer to lines with sub-100 nm width lying in-plane on a substrate, etc.

Compared with the freestanding form, the dimensionally constrained nanopatterns possess the following unique characteristics:

- i) Due to the atomic bonding between the nanostructures and the underlying substrate, the crystallinity of the nanostructures can be dictated by the substrate, akin to what has been demonstrated in thin film technology. Furthermore, through proper chemical modification of the substrate, the morphology and orientation of the patterned nanostructured can be tuned.^{20, 21} This provides a new degree of freedom to engineer the nanostructures.
- ii) The lattice mismatch and thermal mismatch between different materials involved in the system (including the nanopattern, the substrate, and in some cases capping layer or matrix) provide constraint on the nanostructures in terms of stress or strain field. This may lead to surprising property change or interesting synergistic coupling phenomena at the small length scale. It is particularly palpable for materials that are

sensitive to the strain field, e.g., electrostrictive or magnetostrictive or a heterostructure of both. Simulation results indicate that the strain condition varies drastically with the geometry of the patterns,^{22, 23} making it possible to harness the functional performance of materials by changing the design of fabrication.

- iii) Substrate-integrated patterns usually have similar size, shape and geometric anisotropy. For functional oxides that are responsive to external actuations (e.g., photoelectric, ferroelectric or magnetic), a uniform response over all patterns can be expected under the applied external field. This makes them very suitable for nanoelectronic or nanomagnetic device applications.

Nano-constrained structures can be fabricated via either “top-down” or “bottom-up” route. Utilizing the state-of-the-art thin film deposition and lithography capability, “top-down” approaches ensure precise shape, size and separation of the pattern. However, “top-down” processes usually involve destructive steps such as etching or ion beam milling, which may cause structural damage to the nanopatterns. “Bottom-up” approaches have been demonstrated for simple oxide systems such as ZnO^{20, 21} and TiO₂,²⁴ by nucleation control and self-assembled patterning. For multi-cation oxides, nanometer size structures can be achieved by utilizing the microstructural instability of ultra-thin films.²⁵ However, nanostructures obtained in this way have random distribution and non-uniform size and shape. It is generally difficult to achieve precise geometric control while maintaining the preferred microstructure, particularly for multi-cation oxides. The challenges of preparing dimensionally constrained nanostructure of functional oxides will be addressed in detail in chapter 2.

1.2 FERROIC OXIDES: EXAMPLES, STRUCTURE AND PROPERTY

Among various functional oxide materials, nanopatterning of ferroic oxides are of particular fundamental science interests and great technological importance. Ferroic is the generic name given to ferro/ferrimagnets, ferroelectrics and ferroelastics. Because of their sensitivity to magnetic, electric or elastic fields, nanopatterned architectures of ferroic oxides have a considerable bearing on the manner in which the materials can be integrated in to micro- and nanoscale devices. Specifically, this dissertation focuses on patterning and microstructural tuning of ferroelectric oxide barium titanate (BaTiO_3) and ferrimagnetic oxide cobalt ferrite (CoFe_2O_4) systems. The structures and properties of the two materials are briefly introduced below.

1.2.1 BaTiO_3 : Ferroelectricity and piezoelectricity

BaTiO_3 (BTO) is one of the most studied ferroelectric materials and can serve as an excellent example to illustrate the ferroelectricity associated with its perovskite structure. Typical perovskite structure has a general formula of ABO_3 . It is characterized by a close-packed cubic structure formed by A^{2+} and O^{2-} ions combined with highly charged B^{4+} ions in octahedral interstices. Each A^{2+} is surrounded by twelve nearest-neighbor O^{2-} ions; each B^{4+} ion is surrounded by six O^{2-} ions. In BaTiO_3 the large Ba^{2+} ions and O^{2-} ions form an *f.c.c.*-like lattice with Ti^{4+} ions fitting into octahedral interstices. A schematic illustration of BaTiO_3 lattice structure is shown in figure 1.2.

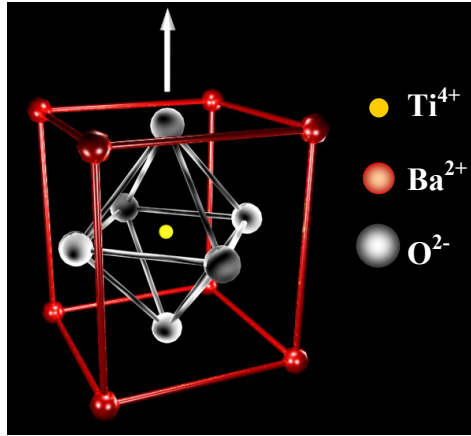


Figure 1.2: BaTiO₃ lattice structure

Below the Curie temperature $T_c = 120\text{ }^{\circ}\text{C}$, the octahedral structure changes from cubic to tetragonal symmetry with Ti^{4+} in an off-center position corresponding to a net electrical dipole moment. Such a spontaneous alignment of electric dipoles which can be reoriented by the application of an electric field is the origin of ferroelectricity in perovskite structures. The behavior of the spontaneous polarization is explained using Landau-Ginzburg-Devonshire theory by expansion of the free energy as a function of the polarization P .²⁶ Minimization of free energy gives the form of P in thermal equilibrium for first-order and second-order transitions.

Another important characteristic of ferroelectric oxides is piezoelectricity. Piezoelectricity is the ability of materials to produce electrical charge when stress is applied (direct piezoelectric effect), and to produce strain when an electric field is applied (converse piezoelectric effect). The direct and converse piezoelectric effects can be described as the following coupled equations:

$$\{S\} = [s^E]\{T\} + [d_t]\{E\} \quad (1.1)$$

$$\{D\} = [d]\{T\} + [\varepsilon^T]\{E\} \quad (1.2)$$

where S is strain, s is compliance, T is stress, d is piezoelectric coefficient, E is electric field, ε is permittivity. The superscript E indicates a zero, or constant, electric field; the superscript T indicates a zero, or constant, stress field; and the subscript t stands for transposition of the piezoelectric coefficient matrix.

For a poled piezoelectric material with cylindrical symmetry, equations 1.1 and 1.2 are usually shown in the matrix notation below (for 4mm class):

$$\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} = \begin{bmatrix} s_{11}^E & s_{12}^E & s_{13}^E & 0 & 0 & 0 \\ s_{12}^E & s_{11}^E & s_{13}^E & 0 & 0 & 0 \\ s_{13}^E & s_{13}^E & s_{33}^E & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44}^E & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{44}^E & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{66}^E = 2(s_{11}^E - s_{12}^E) \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} + \begin{bmatrix} 0 & 0 & d_{31} \\ 0 & 0 & d_{31} \\ 0 & 0 & d_{33} \\ 0 & d_{15} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \quad (1.3)$$

$$\begin{bmatrix} D_1 \\ D_2 \\ D_3 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \\ T_5 \\ T_6 \end{bmatrix} + \begin{bmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{11} & 0 \\ 0 & 0 & \varepsilon_{33} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \quad (1.4)$$

Table 1.1 lists structural details and some physical properties of BaTiO₃ and another widely used ferroelectric material PbZr_xTi_{1-x}O₃ (PZT), including their Curie temperature T_c , piezoelectric coefficient d and dielectric constant ε_r at room temperature.

Table 1.1 Structure and properties of BTO and PZT²⁷

Material	Structure	Lattice constant	Space group	T_c (°C)	ϵ_r	d (10^{-12} V/m)
BaTiO₃	Tetragonal	a=3.99 Å c=4.03 Å	P4mm	130	$\epsilon_{r\ 11} = 1600$ $\epsilon_{r\ 33} = 1900$	$d_{31} = -79$ $d_{33} = 190$ $d_{15} = 270$
PbZr_{0.44}Ti_{0.56}O₃[⊕]	Tetragonal	a=4.02 Å c=4.14 Å	P4mm	380	$\epsilon_{r\ 11} = 1130$ $\epsilon_{r\ 33} = 2800$	$d_{31} = -234$ $d_{33} = 480$ $d_{15} = 335$

⊕- A typical composition of PZT with tetragonally distorted perovskite structure.

Based on their unique physical characteristics, BaTiO₃ and other ferroelectric oxides show three main technological niches. First, as a result of spontaneous polarization which can be switched by external electric field, the binary data “0” and “1” can be encoded by the two directions of the ferroelectric polarization. This is the working principle of non-volatile ferroelectric random access memories (NVFRAM). Second, the coupling between a material’s mechanical and electrical behaviors enables the conversion between the two different energy formations. This is the basis for wide application of perovskite-structured oxides in high voltage and power sources, sensors, actuators and piezoelectric motors. Finally, the large dielectric permittivity leads to applications in capacitors.

1.2.2 CoFe₂O₄: Ferrimagnetism and magnetostriction

CoFe₂O₄ (CFO) is a spinel-structured ferrimagnetic oxide. The general formula of spinel structures is AB₂O₄ where A stands for divalent cations and B trivalent. The oxygen ions are in face-centered cubic close packing. In a unit cell, which contains 32 oxygen ions, there are 32 octahedral sites and 64 tetrahedral sites. For “normal spinel”, all 8 A²⁺ ions are on the tetrahedral sites (*a* sites) and all 16 B³⁺ ions on the octahedral sites (*b* sites); whereas in the “inverse spinel”, 8 of the 16 B³⁺ ions fill tetrahedral sites and the rest 8 B³⁺ and 8 A²⁺ ions together fill the 16 octahedral sites. A schematic illustration of normal spinel structure is shown in figure 1.3.

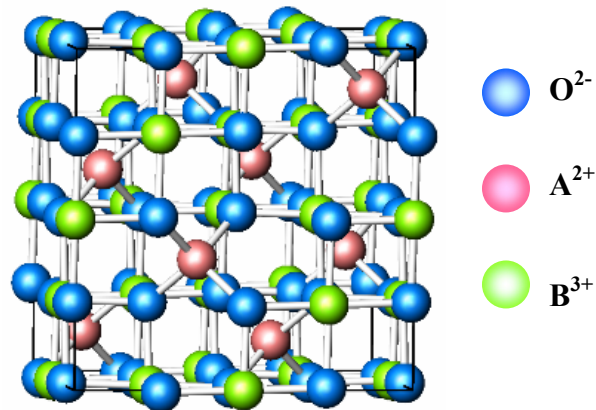


Figure 1.3: Schematic illustration of normal spinel structure

The magnetic properties of spinel ferrimagnets are rich and complex. The term “ferrimagnetism” was first used by Néel²⁸ to describe the properties of ferrites, which combine the resistivity of good insulators with high permeability. Ferrimagnets behave similar to ferromagnets, in that they exhibit a spontaneous magnetization below some critical temperature (Néel temperature) even in the absence of an applied magnetic field. In a ferrimagnet, the

exchange coupling between adjacent magnetic ions leads to anti-parallel alignment of the localized moments. The overall magnetization occurs because the magnetization of one sublattice is greater than that of the other sublattice. Magnetic ordering in spinels can be described by mean field theory, which considers the exchange interactions between cations.²⁹

CFO is ideally a complete inverse spinel. It shows extremely high magnetocrystalline anisotropy, which means its magnetic properties vary depending on the crystallographic direction in which the magnetic moments are aligned. Magnetization of CFO is easier along $\langle 100 \rangle$ directions, compared with other crystalline directions. In addition to magnetocrystalline anisotropy, CFO also shows strong magnetostrictive property i.e., shape change when subjected to an external magnetic field. It arises from the strain dependence of the anisotropy constants. The microstructural explanation of magnetostriction is the magnetic domain shift and rotation causing the dimension change of the material upon a magnetic field. For CFO, the fractional change in dimension at saturation magnetization is as high as the order of 10^{-4} , more than 10 times larger than many other ferrite oxides and about 100 times larger than ferromagnets such as Co and Ni.

Table 1.2 summaries the properties of several spinel ferrites, including the number of Bohr magnetons per molecule μ_B (measured and calculated), the Néel temperature T_N , the room-temperature resistivity ρ , the saturation magnetization M_s , the magnetostrictive constant λ , and the magnetocrystalline anisotropy constant K_1 . Due to their high resistivity, ferrites find applications in situations where the electrical conductivity shown by most ferromagnetic materials would be detrimental. For example, they are widely used in high-frequency

applications, because an *ac* field does not induce undesirable eddy currents in an insulating material. Among those ferrites CFO has favorable hard magnetic property, relatively high T_N and extraordinary high magnetostrictive constant. These properties are enticing for integration of CFO with other field-sensitive materials for novel functional devices.

Table 1.2 Summary of properties of some spinel ferrites^{30, 31}

Materials	Lattice Parameters (Å)	ρ ($\Omega\cdot\text{cm}$)	T_N (°C)	M_s (emu/cm³)	K_I (erg/cm³)	λ (10⁻⁶)
CoFe₂O₄	8.391	10 ⁷	520	425	2×10 ⁶	-110
MnFe₂O₄	8.499	10 ⁴	312	400	-3×10 ⁴	-5
CuFe₂O₄	8.370 (quenched)	10 ⁵	447	135	-6.3×10 ⁴	-17
NiFe₂O₄	8.337	10 ^{3~10} ⁴	585	270	-6.9×10 ⁴	-10

1.3 FERROIC NANOPATTERNS AT MULTI-DIMENSIONS

Research focuses on ferroic oxide nanostructures constrained at multi-dimensionality are introduced in this section. Because dimensional or spatial confinement is embodied in form of patterned architectures in the context of this dissertation, the term “nanopatterns” is used to indicate the nanostructures under substrate constraint with uniform geometry and regular distribution, as mentioned earlier.

1.3.1 Planar nanopatterns: Zero-dimensional (0D) and one-dimensional (1D) systems

Zero-dimensional (e.g., nanodots) and one-dimensional (e.g., nanorods or nanolines) architectures are the most well-studied planar nanostructure systems for ferroic oxides mainly because they exhibit tantalizing potentials in field- or stress-sensitive devices. For example, nanopatterns of ferroelectric oxide $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ in the form of 80nm-thick capacitor has been employed in non-volatile memory devices. Storage density as high as 10 Giga-Bit (GB) can be prospectively achieved in the non-volatile memory device by reducing the lateral dimensions of the ferroelectric capacitors to less than 100 nm.³² Ferroelectric nanorods with diameters as small as 5 to 60 nm were obtained by a solution phase decomposition.³³ Ferroelectric switching was proved for PZT or BTO nanotubes³⁴ and nanorods.³⁵ These ferroelectric rods or tubes can be used as building block of miniaturized electromechanical devices. For instance, the piezoelectric tubes with diameters in the micron range and a higher aspect ratio than the bulk counterpart will enable extreme miniaturization of scanners.

There are several fundamental questions related to the size shrinking in 0D and 1D ferroic nanopatterns that must be taken into consideration. For instance, it has long been believed (on the basis of empirical evidence) that there is a critical correlation volume on the order of hundreds of angstroms below which the total energy payoff associated with dipole formation and alignment is outweighed by the entropic desire to disorder.^{36, 37} The intrinsic size effect therefore poses a fundamental limit on the stability of spontaneous electric polarization in a material and would render ferroelectrics useless for applications at sizes below this cutoff. Recent first-principles theoretical work has indicated that the critical size is orders of magnitude smaller than previously thought.^{38, 39} However, the extensive array of experimental data available from

different groups still indicates that down-sizing strongly influence the performance of ferroelectric materials within tens of nm to submicron size range.⁴⁰ The physical nature of the size effect can be rather complicated. It may involve intrinsic phenomena such as depolarization⁴¹ as well as extrinsic phenomena related to oxygen vacancy gradient and charge injection,⁴² both of which strongly correlate to the property of ferroelectric/electrode interface.

Another intensely studied area particularly focused on the nanopatterned architectures is: what are the effects of the constrained geometries on the order parameters? Compared with their thin film counterparts, substrate-integrated nanopatterns may experience significantly different strain conditions which are determined not only by the pattern/substrate material system (i.e. the misfit stress/strain), but the geometric factors such as the lateral size, thickness, aspect ratio and shape. For example, it has been predicted theoretically⁴³ and demonstrated experimentally^{44, 45} that patterning ferroelectrics into discrete islands greatly enhanced the piezo-response than thin film forms due to less clamping from the substrate. Another example through finite element analysis suggests significantly different phenomena in stress distribution in the 1D nanostructure compared with 0D, due to the large aspect ratio of longitudinal versus transverse dimensions in the former.⁴⁶ This may lead to an interesting research direction, i.e., to prepare a series of 0D, 1D and even 2D nanopatterns (e.g., grids or networks) under the same processing protocol and use them as test structures to probe the size- or geometry-dependence at sub-micron length scales.

One may expect from the above argument, that the intrinsic material properties of ferroic oxides are strongly correlated with various extrinsic factors, which complicate the behavior of miniaturized structures.⁴⁷ Except for the strain effects from substrates (or electrodes), these factors also include surface/interface properties⁴⁸ and sometimes patterning process control.⁴⁹ It

is worth pointing out that the current experimental approaches to understand the fundamental influences of reduced dimensionality and spatial constraint are mainly limited to scanning probe microscopy (SPM), due to the practical difficulty of detecting polarization or magnetization from a tiny, discrete pattern. The SPM-based method exceeds in its high site-specificity, yet this approach is generally difficult to disentangle the intrinsic material properties from various extrinsic factors, e.g., strain distribution in and around the nanostructures. Experimental methods that allow direct mapping or measurement of strain contribution are highly favorable to understand the behavior of nano-constrained ferroic materials.

1.3.2 Non-planar stacking: Three-dimensional (3D) heterostructures

In comparison to planar arrays of functional oxides that are interesting for their intrinsic properties, non-planar stacking of more than two types of functional oxides may lead to fascinating “product behavior” due to the interaction between different order parameters. For example, it has been reported that arrays of magnetic dots can constitute effective ordered pinning centers for the vortex lattice when they interact with type II superconducting films.⁵⁰ It has also been demonstrated that the transport properties of ordered $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ nanostructures can be tuned through a mechanical coupling with the surrounding MgO matrix.⁵¹

In the context of ferroelectric and ferrimagnetic oxides, multilayer structures for the magnetoelectric coupling effect (the “ME effect”) have long been investigated.⁵²⁻⁵⁴ Most recently, 3D heterogeneous nanostructures of ferroelectrics and ferrimagnets have attracted considerable attention, as the unique geometry significantly enhances such interactions.⁵⁵ Currently, the materials systems studied most for the multiferroic 3D heterostructures are perovskite

ferroelectrics (e.g., BaTiO_3) and spinel ferrite (e.g., NiFe_2O_4 and CoFe_2O_4).⁵⁶⁻⁵⁸ This is because both structures are built on the basis of octahedral oxygen coordination and that perovskites and spinels have very little solid solubility between each other.⁵⁹ BTO can form eutectic with CFO due to the reasonably commensurate lattice parameters ($a_{\text{CFO}} \approx 2a_{\text{BTO}}$)⁶⁰. This innate structural compatibility enables them to self-assemble into vertically aligned heterostructures during sputtering process. The so-called multiferroic nanostructures are in the form of nanopatterned film on commensurate substrate, with nanopillars of one phase embedded in the matrix of the other phase. The coupling between the two order parameters is through a stress mediation, i.e., a magnetic field induces a distortion of the magnetostrictive phase, which in turn distorts the piezoelectric phase in which an electric field is generated. It is believed that the downsizing of at least one phase, the vertical hetero-epitaxy and the three-dimensional constraint on the nanopillars played very important roles in the enhanced coupling.⁶¹ This suggested that new properties can be expected by patterning novel 3D heterostructures of functional oxides.

Compared with single phase multiferroics, the advantages of 3D constrained multiferroic heterostructures are: (i) the ME effect in the heterostructure patterns is much higher than single phase ferroelectromagnets in existence; (ii) the physical properties of the materials can be tailored by the selection of different constituent phases and their size and volume ratios in order to meet specific requirements. From this perspective, a real patterning technique that affords controlled dimensions and periodicity of such minaturized structures is highly desirable. The emerging area of 3D magnetic/ferroelectric heterostructure fabrication and characterization is well worth investigation.

1.4 RESEARCH OBJECTIVES OF THE DISSERTATION

The remarkable potential of miniaturization in functional oxides in the above three categories has been revolutionizing traditional ceramic materials design in many existing and emerging applications. Particularly, the capability endowed by the dimensional and spatial confinements of tailoring material properties via structural control becomes increasingly important as the device packing density ascends. Developing and advancing of this capability serves as an ideal platform to investigate the unique structure-property relationship at miniature size scale and the critical issues related to close juxtaposing of different functional oxides.

Endowed with this information, materials scientists are now disposed to develop innovative design strategies to: (1) manipulate functional ceramic materials at nanometer length scales; (2) control the dimensions and morphology of the substrate-integrated oxide nanofeatures at multi-dimensionalities and (3) engineer their internal microstructure. This has become the major motivation for this thesis work.

This PhD project tightly revolves around dimensionally and spatially confined functional oxide nanopatterns. The central theme of the project is to develop a generic nanofabrication scheme that can solve challenges in patterning ceramics, to tackle different pressing issues related to nanofabrication at diverse dimensions, and to provide excellent control over the geometric characteristics of 0D to 3D architectures. Towards this goal, a novel nanofabrication approach termed variable pressure-soft-electron beam lithography (VP-soft-eBL) is developed. The efficacy of this new approach has been validated through patterning a wide variety of oxide materials. On this basis, we explore the effects of pattern geometry on their microstructure

development at reduced size scales, aiming at achieving preferred crystallinity and orientation on the as-prepared nanopatterns. The nanofabrication and structural controlling protocol will then serve as enabling tools for investigation on the constraint-related phenomena. Probing such phenomena using site-specific characterization at appropriate resolutions will help establish the structure-property correlation for functional oxides in nanometer regime. Figure 1.4 below illustrates the critical issues involved at multi-levels in achieving this objective, and how this project expands in terms of pursuing nanofabrication capability, microstructure controllability and probing of the oxide nanostructures at appropriate resolution.

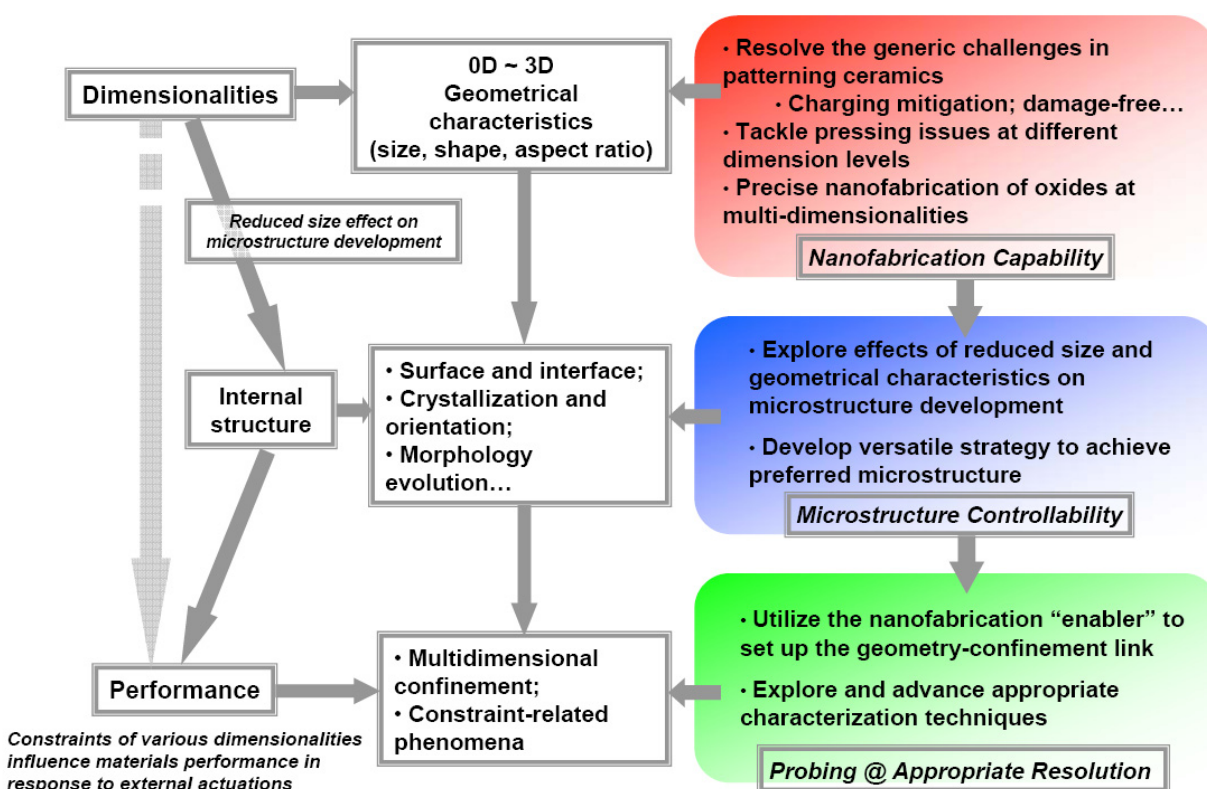


Figure 1.4: “Materials science and engineering” of nano-constrained functional oxides—Scheme of the research objectives and organization of the dissertation.

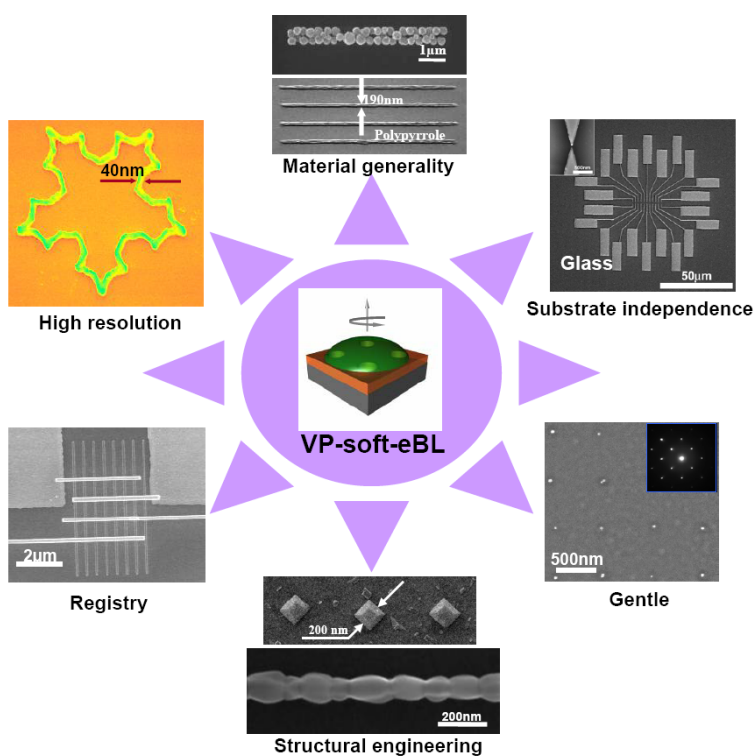
1.5 SCOPE OF THE DISSERTATION

Chapters in this dissertation are organized as following. **Chapter 2** first reviews challenges in ceramic nanopatterning and various high resolution ceramic nanofabrication techniques reported in literature. It then describes the VP-soft-eBL approach that we have developed and employed as the key nanopatterning scheme. The procedures of VP-soft-eBL are introduced, and its unique capabilities suitable for oxide nanofabrication are demonstrated through multitude examples of nanopatterned structures. **Chapter 3** reports a strategy incorporated with VP-soft-eBL scheme to control the microstructure of sol-gel-derived complex oxide nanopatterns. Particularly, epitaxial single crystal 0D and 1D patterns of barium titanate and cobalt ferrite with preferred orientation are fabricated using this strategy. The patterning-controlled morphology development is also discussed. Efforts to expand the VP-soft-eBL portfolio into patterning 2D high density grids are presented in **chapter 4**, focusing on understanding the beam skirting effect in VP-eBL which exacerbates proximity effect and pattern infidelity. The chapter describes an analytical method to predict the distribution of the energy deposited by the beam skirt, which allows for dose compensation during VP-eBL patterning. **Chapter 5** introduces two routes for 3D heterostructures fabrication. Particularly, using self-assembled monolayers modification, radially-stacked multiferroic oxide heterostructures are directly patterned without painstaking feature-alignment procedure. The epitaxial nanostructures fabricated with VP-soft-eBL serve as ideal test-beds for investigation of the dimensional constraint in the oxide-on-oxide nanopatterned systems. Our exploration towards this direction is presented in **chapter 6**. It reports our initial study on patterning-induced substrate deformation at vicinity of the pattern

edges using x-ray microdiffraction technique. **Chapter 7** summarizes the work presented in this dissertation and suggests on the future work.

CHAPTER 2

DEVELOPMENT OF VARIABLE PRESSURE-SOFT-ELECTRON BEAM LITHOGRAPHY



This chapter describes the generic challenges in ceramic nanopatterning, and introduces a unique nanofabrication technique, VP-soft-eBL, that is particularly suitable for patterning functional oxide nanostructures. Its key attributes are demonstrated through diverse patterning examples.

The work presented in this chapter was published in **Nano Lett.**, **5**, 1710 (2005), **Appl. Phys. Lett.**, **89**, 163117 (2006), and **IEEE Trans. Nanotech.**, **7**, 1 (2008). Other parts were presented at **2006 Materials Research Society (MRS) Spring Meeting** and **2006 Microscopy and Microanalysis Meeting**.

The ability to rapidly pattern functional oxide materials into miniature architectures without deleterious effects on microstructure is a major concern in study of size-dependent properties of the materials and in applications of these materials as capacitors, sensors, memory cells and MEMS devices.⁶² However, traditional nanofabrication techniques that have been proved very successful in semiconductor industry are severely challenged by the inherent nature of most ceramics. Myriad alternative approaches of patterning functional oxide materials at micrometer or nanometer scale have been developed and practiced on various material systems.

In this chapter, we first describe the generic difficulties of nanopatterning functional oxides, particularly multi-component oxides. Various patterning methods that have been demonstrated successful for oxides at 20 nm to 200 nm scale are briefly reviewed. Emphasis will then be laid on our effort in developing a ceramic nanopatterning approach that combines the state-of-the-art electron beam lithography and using of liquid material precursors, termed “soft”-electron beam lithography (hereafter soft-eBL for short). We show that this hybrid technique is capable of addressing advantages of both lithography method (high resolution and registry) and wet chemistry (versatility and etch-free), at the same time. In the following, the procedure of soft-eBL in regular high vacuum condition is first demonstrated. Using of soft-eBL in variable pressure mode for patterning on insulating substrates is then reported. The capabilities of the variable pressure-soft-electron beam lithography (VP-soft-eBL) approach are discussed in detail through patterning examples.

2.1 CHALLENGES FOR NANOPATTERNING FUNCTIONAL OXIDE CERAMICS

According to the way nanostructure is generated, patterning methods can be generally categorized into bottom-up approaches and top-down approaches. Bottom-up methods are based on building structures from the bottom using atoms and molecules, whereas top-down approaches is characterized by trimming-off extra material from thin films or bulk formations. Photolithography is a traditional top-down approach that has been most well studied and widely employed in semiconductor industry. The process of photolithography-based technique is shown in figure 2.1. For many materials, the process of blanket film deposition, photolithographic resist patterning, and subtractive etching is an effective patterning method. The removal of materials is usually carried out using chemical etching (wet etching) or reactive ion etching (RIE) and both procedures are well-developed for Si and related materials. However, the inherent chemical stability and refractory nature of many ceramics often presents significant difficulty for this conventional process. First, etching rate for many oxides is much lower compared with Si.⁶³ For multicomponent oxides, wet etching also raises concerns of maintaining stoichiometry since different components usually have different reaction mechanisms with the same etchant, or different removal rates. For example, ferroelectric oxide $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ can be regarded as $\text{PbO} \cdot (1-x)\text{ZrO}_2 \cdot x\text{TiO}_2$. While hydrochloric acid can etch PbO and TiO_2 easily, hydrofluoric acid is necessary to dissolve ZrO_2 . Due to the complexity of reaction mechanism, stringent control over the etching condition is required to ensure that the nanopatterns inherit the exact same chemical composition and microstructure from the thin film. Compared with wet etching, RIE is more desirable since it has very little damage and good side wall definition. However, RIE of multicomponent oxides is in its infancy and further work in this area needs to be done.⁶⁴ The

future trend in pure top-down method is to develop more general etching protocols for diverse ceramics, or to employ unconventional, etch-free lithography.

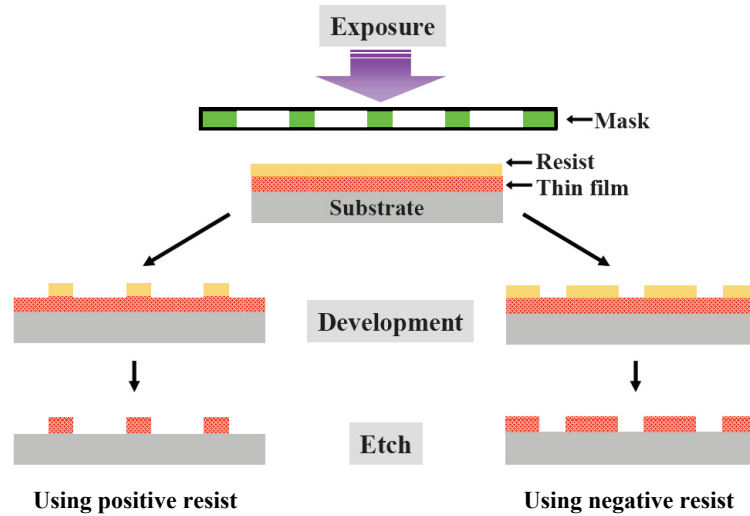


Figure 2.1: Schematic diagram of photolithography-based patterning procedure

Another challenge of patterning functional oxides from top-down direction stems from their high electrical resistivity. Furthermore, many times patterning needs to be done on insulating substrates, for a number of different applications in both existing and emerging technologies. Insulating oxide substrate having small lattice mismatch with the patterned material is of particular interest since it offers a template for the pattern to grow with better microstructural control. However, the low conductivity of the material/substrate system has limited the application of conventional electron beam lithography (eBL) or focused ion beam (FIB) milling, because bombarding the insulating sample with electron or ion will induce significant charging problem and pattern distortion.

To circumvent the problems in top-down approaches involving etching or charging, a number of bottom-up methods have been demonstrated for certain oxide systems. Various high-quality ceramic one-dimensional nanostructures can be fabricated using solution-based methods.⁶⁵⁻⁶⁷ However, these methods usually render free-standing nanostructures rather than patterns with well-defined size and separation, and the control of crystallinity and orientation of these nanostructures still remains a challenge compared to substrate-based approaches. Catalytic growth from vapor or liquid phase on lithography pre-determined sites has been demonstrated successful for single component oxides such as ZnO⁶⁸ and SnO₂.⁶⁹ However, there has not been much success in applying the similar method to multi-component oxide systems. A more general approach that can be applied to diverse material systems is characterized by employing anodic aluminum oxide (AAO) membrane⁷⁰ or self-assembled microbeads^{71, 72} as masks and filling the liquid precursor into the templates. After filling, masks need to be removed and the patterns are subjected to thermal treatment in order to convert into crystalline structure. However, it only enables certain size, shape and organization of patterns due to limitation of the mask geometry.

In short, the inherent chemical stability and high electrical resistivity have made it very hard to manipulate functional oxide ceramics, particularly multi-component ceramics, at sub-micron and nanometer size scale from both pure top-down and pure bottom-up directions. The miniaturization trend for functional ceramics calls for development of unconventional patterning method and structural engineering strategy to achieve ceramic nano-elements with well-defined dimensions and controlled internal structure.

2.2 PATTERNING APPROACHES FOR SUB-200 NM OXIDE NANOSTRUCTURES

In this section, various state-of-the-art ceramic patterning methods are briefly reviewed. These methods have been demonstrated successful for multi-component functional oxides (particularly ferroelectrics and ferrimagnets) at 20 ~ 200 nm scale. They include: focused ion beam (FIB) milling, electron beam direct writing (EBDW), nanoimprint lithography (NIL), soft lithography, spontaneous self-patterning, and dip-pen nanolithography (DPN).

2.2.1 Focused ion beam (FIB) milling

FIB milling is a fabrication method that employs focused gallium ion beam to do micromachining on thin film sample. So far individual ferroelectric capacitors with lateral dimension ranging from 1 μm to 100 nm have been patterned by FIB milling.^{73, 74} The great advantage of FIB is the possibility of using an established method to produce high-quality thin films, including epitaxial films. Therefore, it enables a comprehensive macroscopic characterization of the film before patterning, avoiding the potential compositional or structural deviations which might be involved in other nanofabrication techniques based on bottom-up approaches. This has actually opened the possibility of direct comparisons between the properties of a patterned structure and the original film.⁷⁵

The major drawback of the method is associated with the high damage that occurs during milling and imaging.^{76, 77} Previous work has shown FIB patterning induced gallium impregnation and associated creation of amorphous layers in a surface region of the single crystal materials some 20 nm thick.⁷⁷ While most of the structural defects can be healed by a high-temperature thermal annealing after milling, a gallium doping is basically unavoidable and in special cases

might be relatively harmful to the final electrical properties. Gallium has a strong tendency to segregate into nanosize droplets during the milling and additionally might precipitate and diffuse along the grain boundaries of the film, creating local conducting channels and increasing the leakage current. For instance, Stanishevsky *et. al.*⁷⁸ discovered composition change of PZT film at near-surface layer due to gallium deposition which leads to a modification of the ferroelectric properties. In order for FIB-based patterning technique to become more suitable for patterning multicomponent oxides, multi-stage post-FIBing treatment has to be applied with care.

Another inherent limitation of FIB milling is the difficulty of patterning highly insulating substrate due to the severe charging effect. In our attempt to pattern on single crystal MgO substrate, direct exposure of ion beam causes strong charge-induced contrast that prevents proper imaging, and pattern distortion due to the strong static field built on top of the substrate surface. Deposition of a grounding metal layer alleviates the charging problem at the price of introducing foreign material to the system which can be detrimental for the physical property of the pattern.

It is worth pointing out that there are a few interesting variants of FIB-based nanofabrication techniques. They include FIB assisted etching (FIBAE for short, also known as chemical-assisted or gas-assisted ion etching), and FIB-induced deposition (FIBID). Therefore FIB can be adapted for both subtractive and additive routes. FIBAE has been demonstrated for fabrication of semiconductors (such as Si and GaAs) and metals.⁷⁹⁻⁸¹ According to the gas precursors used, FIBID can be used to deposit metals (e.g., W, Au, Al and Pt) and simple oxide such as SiO₂.⁸² However, due to the availability of etch chemicals and restriction of the gas precursors, FIBAE and FIBID techniques for most multi-component metal oxides are not yet demonstrated.⁸³

2.2.2 Electron beam direct writing (EBDW)

Electron beam lithography (eBL) has been used for over 40 years in microelectronics industry, predominantly for mask design.⁸⁴ Conventional eBL process is similar to photolithography, involving patterning on polymeric resists and fabricating subsequent inorganic structures by lift-off and etching. It has the main advantages of very high resolution and versatile pattern formation. The ultimate resolution on electron beam resist, polymethyl methacrylate (PMMA), has been demonstrated to be less than 10nm.⁸⁵ A variation of this process being explored to circumvent etching step is to replace regular resist with e-beam sensitive resist which contains the right proportion of elemental components of the final inorganic material. This e-beam direct writing (EBDW) technique allows to pattern ferroelectric cells with lateral size down to 75nm.³² Arrays of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and PZT with individual cells of 100 ~ 150 nm lateral size were prepared and shown to display ferroelectric properties.⁸⁶⁻⁸⁸

This approach circumvents the etching problems and it highlights the advantages of making use of maskless lithography combined with metalorganic precursors. However, in order to crosslink the metalorganic precursor at the exposed area, very high electron dose has to be used. The regular area dose used in EBDW is between 1200 to 6000 $\mu\text{C}/\text{cm}^2$, much higher than the dose required to expose PMMA (a few hundred $\mu\text{C}/\text{cm}^2$). Therefore the EBDW technique is very time-consuming. A single pattern, ca. $20 \times 20 \mu\text{m}$ in size, takes 24 hours to fabricate.⁸⁹ To overcome this problem, e-beam sensitive agent can be added to the precursor system. The other trend is to develop a more generic eBL technique that can still take advantages of using metalorganic precursors but avoid high exposure dose.

2.2.3 Nanoimprint lithography (NIL)

NIL is considered to be potentially suitable for mass industrial production for its ability in preparing large area arrays at low cost. It implies the use of a thermoplastic resist which becomes a viscous liquid above its glass transition temperature and thus deforms easily. First, a thickness contrast pattern is created in the resist layer by pressing a mold with the negative of the desired pattern into it. After the removal of the mold, the pattern is transferred by anisotropic etching to remove the residual resist which usually remains in the compressed area. The pattern can be further transferred into the substrate using selective etching. A schematic illustration of NIL procedure is shown in figure 2.2. Arrays of mesoscopic ferroelectric PZT with lateral size from several micrometers to below 300 nm were fabricated using NIL method from metalorganic precursor and sol-gel precursor.⁹⁰

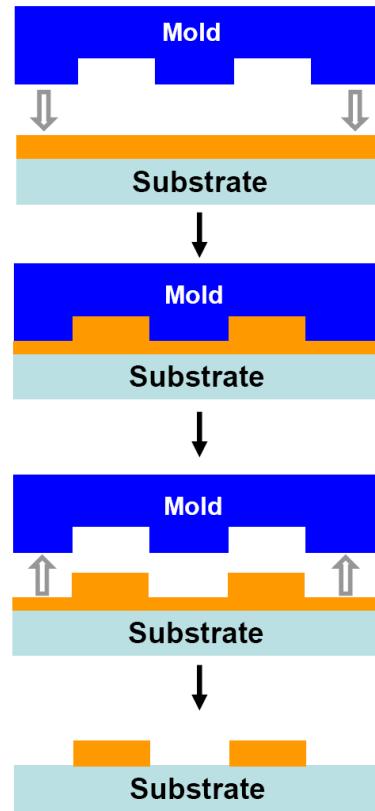


Figure 2.2: Key steps in NIL procedure. From top to bottom: pressing the mold into the polymer film; embossing the topographic features into the polymer and cooling down; removing the mold; etching to remove the residual polymer in the pressed regions.

The main drawback of NIL stems from the etching procedure which complicates the process. Another problem is that the patterned material may stick to the mold and smear the pattern fidelity in the next round of patterning. The overlay alignment in NIL can be more difficult than photolithography, in which the gap between the wafer and mask can be fixed to perform the alignment. In NIL, one needs to do alignment while bringing the mold in contact with the resist on the wafer and imprint into it. This can be hard since the gap is changing from

tens of micrometers to zero during the imprint process and may not be uniform over the whole substrate. Therefore NIL does not present high site-specificity as compared with ion beam or electron beam based lithography methods. Developing accurate and reliable overlay registration and alignment methods has been a subject of intense research in NIL process.^{91, 92} The main niche of NIL will be low-cost, large-area, etch-free, and substrate-general patterning of oxide structures in mesoscopic range for microelectronmechanical systems or optical applications.

2.2.4 Soft lithography

A similar strategy that utilizes mold with micrometer or sub-micron topographic features is soft lithography. Soft lithography represents a family of patterning approaches characterized by transferring patterns from a soft, elastomeric mold to the substrate using liquid phase precursors (usually monomers or prepolymers). Typical soft lithography techniques include micro-transfer molding (μ TM), micromolding in capillaries (MIMIC), embossing and micro-contact printing (μ CP), among many others. Figure 2.3 shows the schemes of these four soft lithography approaches. The review article published by Whitesides group is an excellent source for more detailed description on these techniques.⁹³

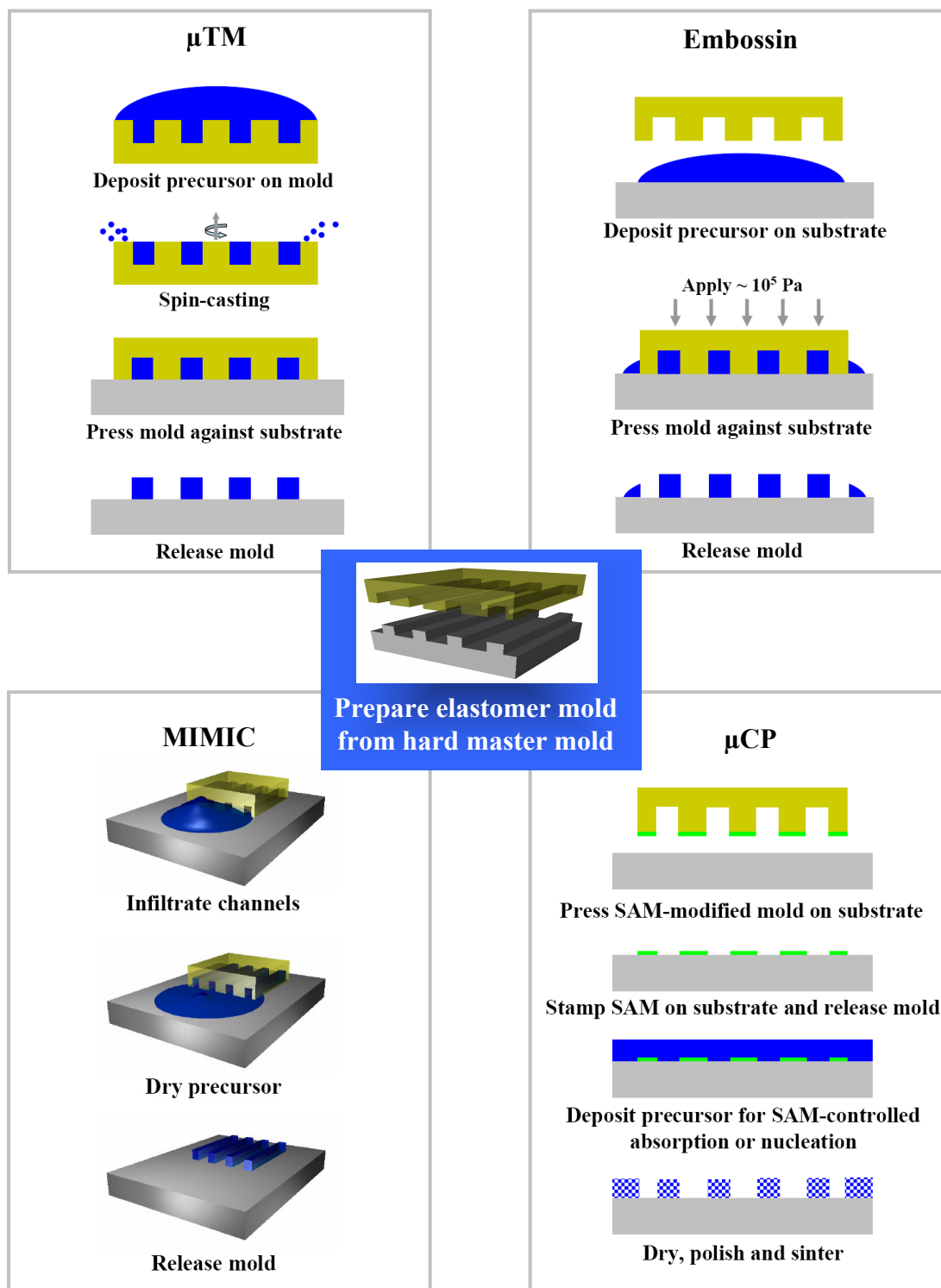


Figure 2.3: Schematic diagram of four typical soft lithography procedures: μ TM, embossing, MIMC and μ CP.

Due to its low cost and superb compatibility with liquid precursors, soft lithography has been widely used to pattern a large variety of materials, including polymers,^{94, 95} ceramic powders⁹⁶ and inorganic salt.⁹⁷ It is particularly suitable for patterning sol-gel precursors of simple oxides as well as multi-component oxides. For example, Moran and Lange⁹⁸ patterned monoclinic zirconia lines orientated epitaxially from a zirconyl 2-ethylhexanoate precursor solution with 500 nm lines widths, using μ TM technique. Kim *et. al.*⁹⁹ demonstrated the use of μ TM by patterning 50 μ m-wide $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) lines on (001) SrTiO_3 substrate. Using MIMIC, PZT and $\text{Sr}_2\text{Nb}_2\text{O}_7$ patterns with micron feature width were fabricated.^{96, 100}

The feature size of oxide structures fabricated with soft lithography typically ranges from a few micrometers down to 500 nm. The limitation on the spatial resolution stems from the softness of the mold, causing features to deform or distort which are severe detriments at smaller size scale. The practical difficulty in maintaining the conformal contact between mold and substrate also hinders patterning at sub-200 nm scale.¹⁰⁰ However, by incorporating substrate modification methods such as self-assembled monolayers (SAMs), recent efforts in developing soft lithography have shown its potential in generating feature size of ~ 150 nm.^{101, 102} Therefore we still include soft lithography in this section, and highlight its advantages including capability of forming large area pattern during short period of process and great versatility in material and substrate selection. These advantages are endowed by the so-called “confinement-based” philosophy,¹⁰³ that the pattern is imparted to the thin film by using physical boundaries to define where the liquid precursor rigidifies. This suggests that combining wet chemistry with lithography may facilitate patterning a wide diversity of functional ceramics and beyond.

2.2.5 Self-organized patterning

FIB, EBDW and NIL represents typical top-down approaches that are very well suited to fabricate structures with extremely good spatial resolution. Aiming at smaller feature size and less structural damage introduced during fabrication, there is also a considerable interest in other methods that are not based on carving thin films, but rather on building structures from the bottom using atoms and molecules. These bottom-up methods have shown promises in obtaining self-patterned very fine features. For example, BaTiO₃ nanoparticles on SrTiO₃ substrates have been deposited using pulsed laser deposition.³² Single crystalline PZT nanoparticles with an average diameter of about 7 nm and a standard deviation of 5.4% have been obtained via pulsed laser ablation.¹⁰⁴ Chemical solution deposition (CSD) was also applied to obtain epitaxial PZT nano-islands with 50nm lateral dimension on SrTiO₃ substrate.¹⁰⁵ There are also other chemical routes such as microemulsion route for synthesis of phase-pure ceramic nano-crystals under low temperature.^{105, 106}

The nature of self-organized patterning is a parallel approach for inexpensive preparation of structures with sizes of 10-20 nm, below the resolution limit of the state-of-the-art lithography. However, it does not provide control over the patterning sites. The nanostructures are randomly distributed, with non-uniform shape and size. Bimodal volume distribution of nanocrystals prepared from liquid precursor has been observed, showing the coexistence of pyramid and dome shapes.¹⁰⁷ For self-organized patterning with liquid precursors, the formation of nanoislands is based on the “microstructural instability” of ultra thin film. Therefore, nanostructures rendered this way usually have a very low thickness.

2.2.6 Dip-pen nanolithography (DPN)

DPN is a recently developed method capable of deposition of materials with very high resolution and precision. It is characterized by coating precursor “ink” on the tip of atomic force microscope (AFM). Scanning the ink-coated tip on a flat substrate enables transporting the ink material to the substrate via the spontaneous water meniscus formed between the tip and the surface. The scheme of DPN is shown in figure 2.4. It is first used to generate nanostructures of simple organic and biomolecules with down to a few tens of nanometer.¹⁰⁸⁻¹¹¹ Su *et. al.*¹¹² further expanded the scope of DPN by using sol-gel precursors as ink. Using sol-ink, various solid-state oxide materials have been patterned with DPN including ZnO, SiO₂, TiO₂, Al₂O₃ and BaFe₁₂O₁₉.¹¹²⁻¹¹⁶ Single-tip DPN is an inborn serial writing method and can be time consuming. Recently the development of multiple-pen “nanoplotter”¹¹⁷ has enabled DPN parallel patterning capability. However, DPN patterning of sol-gel based materials still faces problems such as unknown ink transfer mechanism and tip contamination by sticky sol. These problems pose great challenges on the DPN performance in terms of consistency and reproducibility for nanopatterning inorganic materials.

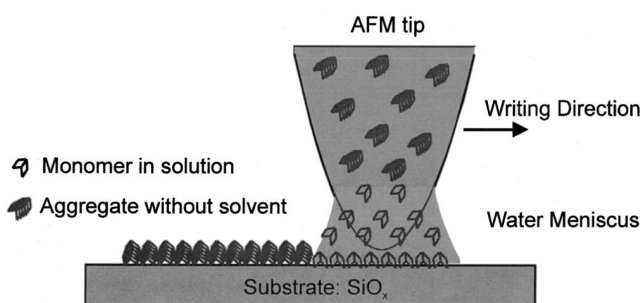


Figure 2.4: Scheme of DPN (adapted from literature¹¹³)

2.2.7 Summary of the above nanopatterning approaches

To better compare the above ceramic nanopatterning approaches, table 2.1 summarizes their capabilities in terms of their spatial resolution for ceramic patterning, generality for patterned materials and substrates, site-specificity and capability of etch-free patterning, etc. One may find that, when dealing with ceramic nanofabrication, each of these routes possesses unique advantages and disadvantages, both determined by the nature of the processing steps involved. For instance, nanoimprint lithography, self-organized patterning and soft lithography are characterized by utilizing liquid phase precursors, which ensures the capability of etch-less patterning a very wide variety of oxides on a multitude of substrates; their general disadvantage is lacking of registry and difficulties of generating patterns with complex shape. As a comparison, electron beam direct writing and focused ion beam technique provide precise control over the patterning sites and shapes; however, the material/substrate systems can be patterned with these routes are quite limited by their nature of using charged electron or ion beam. It suggests that no single technique has all the desirable attributes and further underscores the importance of developing new approaches as mergers of multiple well-developed techniques. This task is of particular importance for the interest in dimensionally constrained ferroic nanopatterns that requires multiple test structures with miniature size, controlled geometry and microstructure simultaneously. Bearing this in mind, combining deposition of organic precursors and the state-of-the-art lithography has been attempted in our laboratory. In section 2.3 through 2.6, a patterning scheme termed “variable pressure-soft-electron beam lithography” (VP-soft-eBL) will be presented. Its unique attributes in nanofabrication of ceramics will be demonstrated.

Table 2.1 Comparison of unconventional ceramic nanofabrication techniques

Patterning technique	FIB milling	EBDW	Self-organized patterning	DPN	NIL	Soft lithography
Category	Subtractive		Additive			
	Mask-free				With mask	
Resolution	Sub-100 nm ⁷³	10~100 nm ¹¹⁸	< 50 nm ¹⁰⁵	150 nm ¹¹²	<100 nm ¹¹⁹	~ 400 nm ¹⁰³
Etch -free	No	Yes	Yes	Yes	No	Yes (except for embossing)
Compatible with Sol-Gel	Milling can be done on sol-gel prepared thin film	Yes, but requires either electron-sensitive sol or very high dose	Yes	Yes, but lacks reproducibility for sol-ink	Sticky sol may damage mold ¹¹⁹	Yes
Registry capability	Good	Good	Very poor	Good	Poor	Poor
Substrate generality	Not suitable for insulating materials	Not suitable for insulating substrates	Yes (difficult on fragile substrates)	Limited by ink chemistry	Yes	Yes
Material generality		Demonstrated mainly for simple oxides	Good		Good	Good
Comments	Capable of generating 3D structures. Time consuming.	Very time consuming	High throughput. Poor control over size, shape and site of patterns.	Ink transfer mechanism for sols under exploration.	Viable for volume production. Advances required in overlay registration.	High throughput. Difficulties in patterning oxides at sub-200 nm scale.

2.3 SOFT-ELECTRON BEAM LITHOGRAPHY PATTERNING SCHEME

Soft-electron beam lithography (soft-eBL) is a hybrid technique characterized by deposition of organic solution precursors at pre-defined position on a substrate. The deposition positions are determined by the patterned polymeric e-beam resist as mold in the electron beam lithography process. The crucial steps involved in soft-eBL approach are schematically illustrated in figure 2.5. These steps include:

1) *e-beam lithography on polymeric resist*: Electron beam exposure is carried out on substrate coated with polymeric positive resist film. The e-beam exposure causes chain scission in the resists and increases their solubility in developer. After developing, the resist film contains trenches with shape and size defined by the e-beam exposure.

2) *Substrate functionalization*: The developed substrates are subjected to chemical functionalization or plasma cleaning to tune the hydrophilicity of the exposed substrate area.

3) *Spinning liquid precursor*: Liquid phase precursors (such as sols and colloidal solution) are dropped onto the e-beam patterned substrate and the substrate is spun to remove the excess liquid. By this we eliminate the need for etching or additional steps to remove excess precursors from the substrate.

4) *Lift-off*: Precursor-spun substrates are baked to solidify the patterns. Subsequently the substrates are soaked in acetone to dissolve resist and lift-off extra material from un-patterned area.

5) *Heat treatment*: For patterns made with sol precursors, the as-deposited materials are amorphous dry gels. Further pyrolysis and annealing at elevated temperature are carried out on the pattern to decompose the organic residues and crystallize the structures.

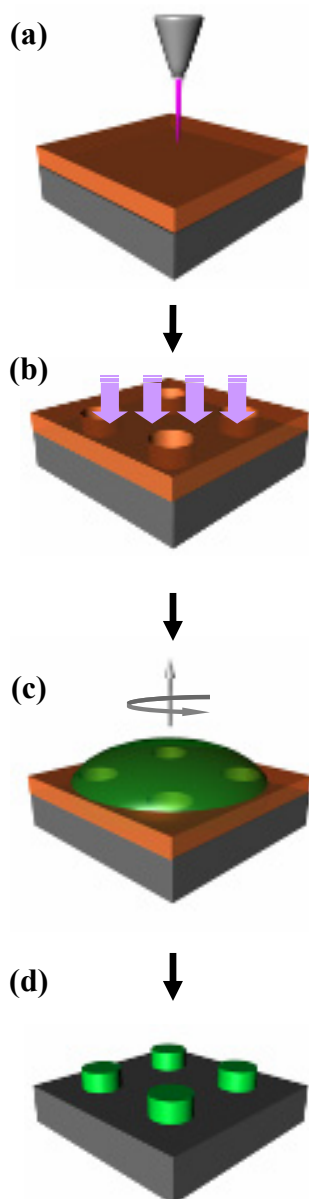


Figure 2.5: Schematic illustration of Soft-eBL procedure. (a) e-beam lithography; (b) development and surface functionalization; (c) spinning of sol precursor; (d) lift-off, pyrolysis and annealing

2.4 EXPERIMENTAL DETAILS OF SOFT-EBL PATTERNING PLANAR NANOSTRUCTURES

In this section, experimental details for patterning single phase planar nanostructures (e.g., dot and line arrays, etc.) in high vacuum SEM chamber are reported. Specific patterning conditions for high density two-dimensional grids and three-dimensional vertically-stacked heterostructures will be presented in chapters 4 and 5.

2.4.1 Preparation of sol precursors

Liquid precursors that are mostly used in this project are synthesized via sol-gel method. For example, CoFe_2O_4 sol with 0.05 ~ 0.2 M concentration is prepared by dissolving 1:2 mol portions of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 2-methoxyethanol, with 10 vol.% ethanolamine as complexing agent. The solution is refluxed at 70 °C for 4 hrs, cooled down, filtered and applied to soft-eBL. To make 0.1 M BaTiO_3 sol, titanium isopropoxide ($\text{Ti}((\text{CH}_3)_2\text{CHO})_4$) is dissolved in 2-methoxyethanol, while proportional amount of barium acetate ($\text{Ba}(\text{CH}_3\text{COO})_2$) is dissolved in a mixture of acetic acid and de-ionized water (1:1 volume ratio). The solution containing barium source is then added dropwise to the solution containing titanium source under vigorous agitation at 60 °C. The final mixture solution is refluxed at the same temperature for 8 hrs to form a clear sol. Both BaTiO_3 and CoFe_2O_4 sols remain stable for more than 6 months. We also prepared $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ sol (0.1 M concentration), using a modified method based on the report by Kim *et. al.*¹²⁰ Lead acetate trihydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) is dissolved in a mixture of isopropanol and methanol (5:1 volume ratio) at 80 °C with constant

agitation. Titanium isopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$) and zirconium n-propoxide ($\text{Zr}(\text{OC}_3\text{H}_7)_4$) are then added to the mixture solution. The whole mixture is heated under constant stir at 100 °C for 1 hr, let cool down and filtered. All chemicals are obtained from Alfa-Aesar and Sigma-Aldrich.

The viscosities of the sols studied in this work are measured in stress controlled mode. The change of viscosity with shear rate is plotted in figure 2.6, using 0.05 M CFO as an example. Viscosities of various sols used in this project are found to be around 0.3 Pa.s at shear rate higher than 100 s^{-1} . The sol precursors are gelated and annealed in air between 850 °C and 1000 °C for 1 hr to obtain crystallized powders. Chemical composition and crystalline phase expected for these materials are proved by x-ray diffraction on these powders.

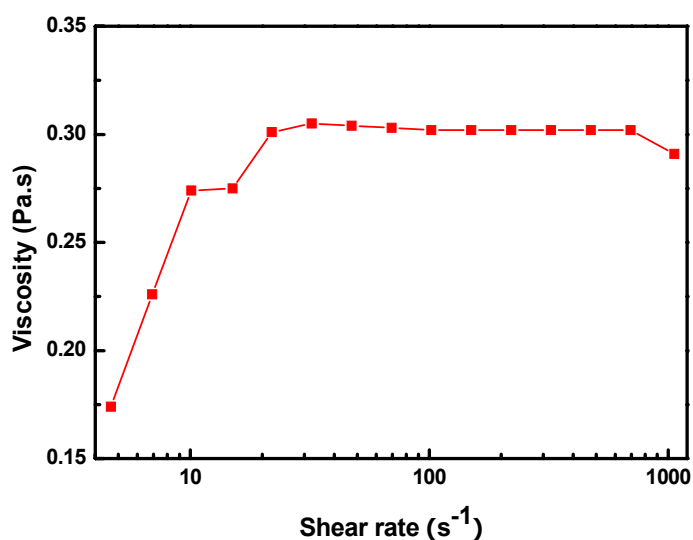


Figure 2.6: Viscosity of 0.05 M CFO sol.

2.4.2 Substrate treatment and coating of resist

The substrates are first cleaned using oxygen plasma (Model 1020 Plasma Cleaner, Fischione) for 1 ~ 3 minutes to remove any contamination and facilitate the spinning of resist. Two types of regular electron beam positive resists are used in this project, i.e., MMA (methyl methacrylate) – MAA (methacrylic acid) copolymer (hereafter “copolymer” for short) and PMMA (polymethylmethacrylate, hereafter “PMMA” for short). The copolymer resist (MMA(8.5)MAA EL6) and the PMMA resist (950PMMA A3) are purchased from MicroChem. Due to the different electron dose sensitivity of the resists, bi-layer resist with copolymer at bottom and PMMA on top can be used to facilitate lift-off, or to form radially stacked heterostructures introduced in chapter 5. Each layer is spin-coated at 3000 rpm for 45 sec to give a nominal thickness of about 150 nm, which gives 300 nm total thickness of the bi-layer resist. PMMA resist can be used alone to ensure uniform trench width across the depth after development. Followed by spinning each layer, the substrate is heated at 175 °C for 1 min and cooled at room temperature for 1 min, before the next layer is applied.

2.4.3 Electron beam lithography

Electron beam exposure is carried out in QUANTA 600F environmental SEM (FEI Co.) equipped with Nanometer Pattern Generation System (NPGS) and integrated beam current measurement capability. Typical instrumental parameters used for patterning on Si wafer are: primary beam energy = 30 keV, area dose = 200 – 400 $\mu\text{C}/\text{cm}^2$, working distance = 7 – 10 mm, beam current = 150 pA. The exposed substrate is developed in a mixed solution of one volume of methylisobutylketone (MIBK) and three volumes of isopropanol (IPA) for 75 sec and then rinsed in IPA for 60 sec. The substrate is then blown dry with N_2 gas.

In order to remove any organic residue after development, the patterned substrate is subjected to oxygen plasma treatment prior to spinning precursors. The plasma treatment is carried out under the condition of 75 W power, 50 sccm O₂ flow rate and 75 mTorr operating pressure for 20 sec. Immediately after plasma cleaning, the liquid precursors are spun onto the substrate using 4000 – 6000 rpm for 45 sec, and are then baked on hot plate at 150 °C for 1 min. The spinning speed is chosen based on the concentration of the precursor and the design of the pattern. For example, higher speed is required to lift-off the excess materials for a higher concentrated sol or a higher density of pattern geometry. Considering that the sols with different concentrations show similar viscosity values at high shear rate, we suspect that other factors such as the solvent evaporation speed may be the main contribution to this correlation between lift-off effectiveness and the sol concentration.

In this step, we utilize the patterned resist as mold to define the size and shape of the nanostructures. Given proper spinning condition, the approach eliminates the need for additional steps such as back polishing or reactive ion etching to remove excess precursors from the substrate.

2.5 PATTERNING ON INSULATING SUBSTRATES IN VARIABLE PRESSURE MODE

Soft-eBL is first employed on grounded conducting substrates or semiconducting substrates such as Pt and Si wafer. In many cases, electrically insulating substrates are required for a number of different applications. These include conventional materials in semiconductor processing such as SiO_2 and Si_3N_4 , materials for optoelectronics such as GaN and glass as well as polymers for applications including so-called flexible plastic electronics. Particularly, single crystal oxide substrates are widely used for epitaxial growth of high quality oxide thin films and micro- or nano-structures. These include MgO, SrTiO_3 , MgAl_2O_4 and sapphire, among many others. Despite the importance of using insulating substrates for the above purposes, efforts on direct patterning these substrates using eBL have been scarce due to the severe charging effect.

In a typical run of soft-eBL process, the resist layer is about 300 nm thick in order to optimize the exposure profile in the resist. Given the thin resist layer and the high energy beam energy (30 kV), the vast majority of the electron dose is deposited in the substrate. Because insulating substrates lack a means of charge dissipation, using conventional eBL to directly pattern on insulators can result in significant astigmatism and pattern distortion.¹²¹ Methods have been developed to minimize the charge-induced pattern distortion by creating pathways for the charge to dissipate. For example, a thin metal grounded layer can be deposited on top of the resist.¹²² This method introduces additional process steps such as film deposition prior to exposure and film removal by wet etch after exposure but prior to development. Other methods include using ion shower and using conductive polymer resists.^{123, 124} However, these methods may raise concern regarding chemical compatibility with the resist as well as the liquid precursor

used in soft-eBL. It is highly favorable to develop a widely applicable method for eliminating substrate charging effects without additional processing steps or the use of nonstandard materials.

An effective solution to this problem was developed and demonstrated in our laboratory two years ago, using the capability of variable pressure SEM (VP-SEM) for in-situ charge dissipation in eBL process.^{125, 126} In the following section, the principle of charge dissipation in VP-SEM is introduced briefly. The effectiveness of minimizing charging-induced pattern distortion in eBL is then demonstrated. The optimized patterning condition in variable pressure mode is discussed.

2.5.1 Charge dissipation mechanism in VP-SEM

Since its inception in 1990s, VP-SEM has been used for imaging of electrically insulating materials in pristine condition, without the need for conductive coatings or lengthy and difficult dehydration processes.¹²⁷ The charge dissipation is realized by introducing a low pressure of gas (typically water vapor, N₂, Ar, or He) into the SEM chamber. Differential pumping system is normally used to maintain high vacuum (10^{-11} Torr) in the electron column. The gas molecules can be ionized by electron beam. Due to the positive bias (about +600 volts) applied on the gaseous secondary electron detector (GSED), the positive ions in the sample chamber may migrate to the negatively charged surface and balance the surface charge, as shown in figure 2.7.

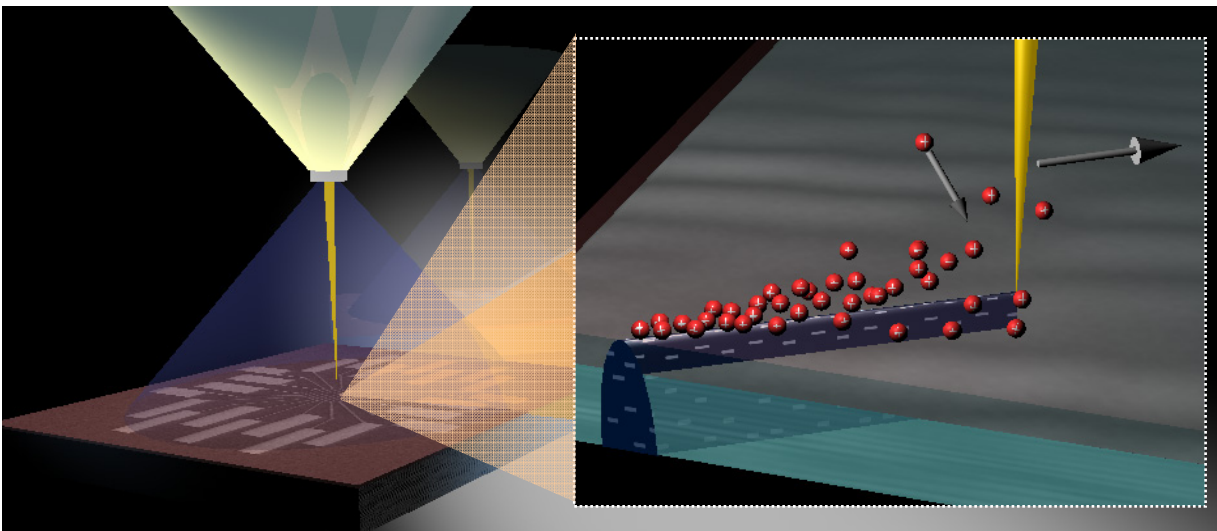


Figure 2.7: Schematic illustration of ionization of gas molecules and charge compensation in VP-SEM. Courtesy: Benjamin Myers

The presence of gas molecules in the SEM chamber has several other important consequences. For example, secondary electrons (SEs) released from the sample encounter gas molecules once they exit the surface. The gas molecules, when struck by these SEs, produce SEs themselves, which in turn produce SEs from adjacent gas molecules. Thus the gas functions as a cascade amplifier for the original secondary electron signal from the sample. The so-called “gas cascade” effect may lead to different contrast mechanism in VP-SEM.¹²⁸ Further, the primary beam will be scattered to some extent by collisions with the gas molecules resulting in the formation of a beam “skirt” around the focused primary beam at the sample surface, as illustrated in figure 2.8. The beam skirt deteriorates the spatial resolution for x-ray spectroscopic analysis in VP-SEM and eBL patterning capability, which will be discussed in detail in chapter 4.

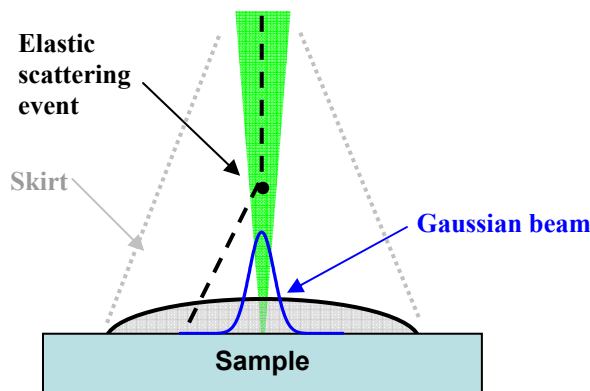


Figure 2.8: Schematic diagram illustrating formation of electron scattering “skirt” around the focused beam in VP-SEM

2.5.2 Application of VP-SEM in eBL patterning on insulators

In spite of the effectiveness of VP-SEM in imaging and microanalysis of electrically insulating materials, very few attempts have been made so far on its application in eBL. The charge-balance concept has been applied in a recurrent-eBL process for the production of MEMS devices.^{129, 130} However, to our knowledge the technique of variable pressure eBL (VP-eBL) has not yet been systematically applied to the fabrication of nanostructures. As a result, understanding towards the influence of instrumental parameters on the patterning capability has been limited.

During the past two years, our laboratory has applied the charge-balance mechanism of the VPSEM to the fabrication of nanometer-scale features on insulating substrates with a technique called VP-eBL. The effects of water vapor gas pressure, working distance (beam-gas path length), beam energy and detector bias on proximity dose, linewidth and exposure dose have been systematically investigated.¹²⁵ Figure 2.9 shows a proof-of-concept example demonstrating

the effectiveness of VP-eBL in eliminating the charging-induced pattern distortion. The distortion-free electrode pattern in figure 2.9(b) is fabricated using VP-eBL under the same condition as that in figure 2.9(a), with exception of a chamber pressure of 1 Torr.

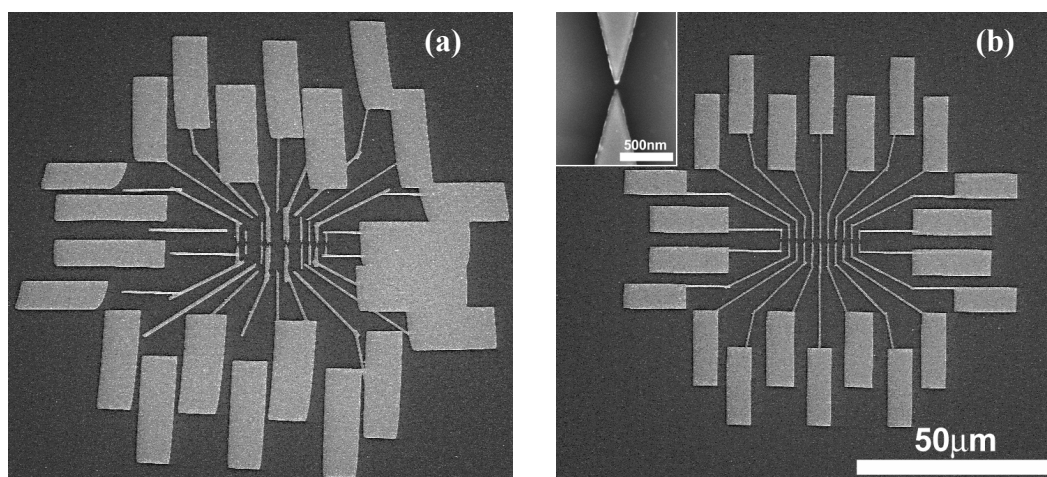


Figure 2.9: VP-SEM images of Au/Pd electrodes patterned via eBL and lift-off processing in PMMA on glass with a 30 kV beam in high vacuum (a) and with the VP-eBL using 1 Torr of water vapor (b), at the same magnification. The inset in (b) is a close-up of the ~30 nm electrode gap. Courtesy: Benjamin Myers

2.5.3 Optimization of VP-eBL parameters

In conventional eBL (high vacuum), change of instrumental parameters (kV, working distance, probe current, etc.) does not influence the primary beam profile (i.e., the energy density deposition profile in the resist), and consistent pattern size can be achieved under the same designed dose profile. However, in VP-eBL, the real received dose at exposed area is strongly dependent on SEM instrumental parameters. This is the most significant distinction between VP-eBL and the conventional eBL.

The reason for the dose-instrumental parameter dependence is because the electron-resist and electron-substrate interactions are made more complicated by the scattering of the gas molecules. For example, the development of beam skirt has been described as¹²⁷:

$$r_s = \left(\frac{364Z}{E}\right)\left(\frac{P}{T}\right)^{1/2} L^{3/2} \quad (2.1)$$

where

r_s = skirt radius (m)

Z = atomic number of the gas

E = primary beam energy (eV)

P = pressure (Pa)

T = temperature (K)

L = beam path length in gas (m).

Obviously the radius of beam skirt increases with higher gas pressure, causing undesirable influences on the VP-eBL performance including: (1) the effective size of the focused beam may be altered and limit the resolution of eBL; (2) the received dose at e-beam addressed area may be re-distributed by the skirt and deviate from the designed value. This causes lower dose contrast between patterned and un-patterned areas, and poor pattern definition with increasing developing time or developer concentration. In fact, changes of pattern size have been observed at different gas pressure for small beam currents.¹²⁹ It can be expected that the above phenomena are more

prominent for conditions such as low primary beam energy, high working distance, and high chamber pressure, all of which increase the number of gas-electron scattering events.

Based on the above argument, one needs to be very careful choosing VP-eBL patterning condition to (1) effectively reduce the charging-induced pattern distortion; and (2) avoid the undesirable influences of beam skirt on pattern dimension definition. We discuss the proper range of primary beam energy and the chamber gas pressure, while keeping the working distance fixed at 7 mm.

In the previous study in our laboratory, qualitative assessment of the VP-eBL patterns has determined a chamber pressure threshold for pattern distortion elimination on highly insulating substrate is near 0.6-0.7 Torr (water vapor) at 30 keV beam energy for the minimum dwell time required to completely expose the resist. This threshold value corresponds well with experimental evidence for minimum pressures to achieve charge balance during imaging (0.1-0.6 Torr).¹³¹ Up to 2 Torr vapor pressure has shown a more significant effect in reducing the charging-induced distortion, without degrading the patterning resolution.

However, this does not suggest that higher gas pressure is more preferred for VP-eBL patterning. Myers *et. al.*¹²⁶ have shown decreasing trench size as a function of increasing gas pressure due to the dose attenuation, particularly at low primary beam energy (e.g., 5 keV). A modification of the trench shape can also be visualized with increasing gas pressure, indicating a modification of the sub-surface space charge distribution. This size change is significantly subdued when 30 keV beam energy is used even for gas pressure as high as 2 Torr, due to the higher kinetic energy carried by the incident electrons and much smaller scattering cross section.

It can be seen from the above experimental observations that there exists a trade-off between charge dissipation and pattern definition, i.e., higher gas pressure ensures better charge elimination up to 2 Torr, but may cause weaker control over the ultimate pattern dimension. Using higher beam energy is an effective way to reduce the beam skirt-induced pattern size alteration. Therefore, we finalize the gas pressure to be 1~1.5 Torr and the primary beam energy to be 30 keV. The patterning conditions for highly insulating substrates in VP-eBL are summarized in table 2.2 below.

Table 2.2 Experimental conditions for patterning on insulating substrates in VP-eBL

Primary beam energy	30 keV
Gas pressure (water vapor)	1~1.5 Torr
Working distance	7 mm
Probe current	~150 pA
Resist thickness	~ 300 nm

Using the above conditions, direct patterning of oxide nanostructures on insulators can be achieved without any extra processing step in eBL. The next section will cover examples of oxide nanostructures on either single crystal oxide substrates for high quality epilayer formation, or on Si_3N_4 thin membranes for direct observation under transmission electron microscopy. The expansion from soft-eBL to variable pressure soft-eBL (VP-soft-eBL) has significantly broadened the scope of this patterning approach. It further paves the way for microstructural engineering on these nanostructures through invoking substrate effect, as discussed in chapter 3.

2.6 VP-SOFT-EBL CAPABILITIES

In this section, the key attributes of VP-soft-eBL are summarized and demonstrated through multiple patterning examples.

2.6.1 Etch free fabrication of ceramic nanostructures

One unique characteristic of VP-soft-eBL technique is the combination of the state-of-the-art lithography and wet chemistry. Using eBL-patterned resist as mold, the materials are deposited by spinning of liquid precursors. Therefore the definition of the pattern size and shape is realized in eBL patterning on polymeric resist, not directly on the oxide materials. When proper spinning condition is employed for certain sol system, the extra material left on top of unexposed areas forms a very thin layer after spinning that can be readily removed along with the underlying resist in lift-off step. This approach eliminates the application of chemical etching or ion beam milling which may introduce sidewall re-depositions, contaminations and structural damage.¹³² Therefore it is particularly suitable for patterning refractory and chemically inert ceramics, or delicate organic systems that otherwise are difficult to pattern through top-down routes.

2.6.2 High spatial resolution

The VP-soft-eBL inherits very high spatial resolution of the electron beam lithography. We have demonstrated its capability of patterning ceramic structures such as ZnO and SnO₂ as small as 30 nm. This is possibly the smallest size reported for ZnO fabricated with a lithography

approach. Figure 2.10 shows a few examples of the ZnO patterns made on Si wafer (with 600 nm thick thermal oxide) after annealing at 700 °C in air. It clearly demonstrates the precise control on the size and shape at sub-100 nm scale. The preparation of ZnO sol used in this experiment is introduced in an earlier publication of our group.¹³³

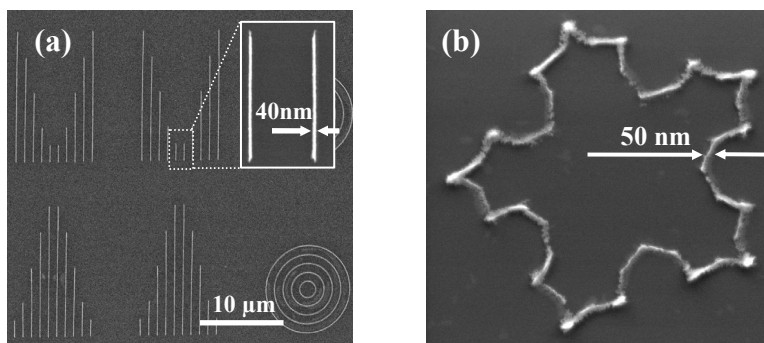


Figure 2.10: ZnO line patterns on Si wafer after annealing showing the high spatial resolution of VP-soft-eBL patterning.

Nanostructures of other ceramic materials with lateral dimension ranging from sub-100 nm to a few microns can also be readily fabricated. Since the patterned resist is used as a mold, the thickness of resist provides an upper bound for the vertical dimension of the pattern. That is, the height of the patterns made in this work is less than 300 nm. In fact, patterns made using single layer 300 nm-thick PMMA resist normally show a height less than 150 nm before annealing. This suggests the sol precursor only fills in a portion of the 300 nm-deep trench, probably due to the high spinning speed used.

The sol precursors used in this work are normally very low in mass content. Therefore the as-deposited patterns are in the form of amorphous dry gel containing a large amount of organic residue. During annealing, the pattern dimension decreases, resulting from both the elimination

of organic component and the phase change from an open-structured amorphous state to a dense crystalline structure. Atomic force microscope (AFM) measurements (not shown here) have disclosed that most sol-derived patterns shrink about 30% ~ 40% in lateral dimension and about 50% in vertical dimension. Taking into account the shrinkage in both width and height of a typical disc pattern, these values translate to about 70.5% ~ 82% volume shrinkage. Such large volume shrinkage contributes to the stress evolution in sol-derived nanostructures and leads to interesting phenomena regarding morphologic development as discussed in detail in chapter 3. On the other hand, the large volume shrinkage also suggests that much smaller nanostructures can be achieved than the eBL defined trench size in the resist. For example, CoFe_2O_4 line patterns with width as small as 70 nm can be achieved by patterning 120 nm-wide trenches in eBL resist followed by spinning 0.1 M CoFe_2O_4 sol and annealing in air at 900 °C.

2.6.3 Material/substrate generality

2.6.3.1 Versatility in patterned materials

The VP-soft-eBL can be in principle applied to patterning any liquid precursor that shows good chemical compatibility with the resist system. It is well known that PMMA and copolymer resists dissolve easily in ketone and toluene, but stay fairly stable in many alcohol and water solution environments. The sol precursors in this study are prepared in alcohol solutions and therefore very compatible with the resist. Our experiments further show that the 300 nm thick resists have fairly good resistance to diluted acetic acid (~50% volume ratio in de-ionized water) environment. This is the maximum concentration used in this study to prepare CoFe_2O_4 and BiFeO_3 sols. The sol systems that have been applied to VP-soft-eBL include, but not limited to,

ZnO, SnO₂, BaTiO₃, (Ba, Sr)TiO₃, Pb(Zr, Ti)O₃, BiFeO₃ and CoFe₂O₄. The spinning condition should be adjusted based on the concentration, gelation speed of particular sol system and the geometry of the designed pattern. However, we have noticed that spinning speed of 3000 ~ 6000 rpm typically render satisfactory lift-off for the above sol systems. Therefore, unlike other “top-down” patterning methods, the materials deposition process does not require significant adjustment for different precursors. Examples of sol-derived VP-soft-eBL patterns are shown in figures 2.11(a) to 2.11(c).

The robust VP-soft-eBL technique can also be combined with multiple other wet chemistry routes. For example, ZnO colloidal solution with particle size of 200 nm is spun on eBL patterned PMMA resist. After baking at 100 °C to evaporate the solvent, the sample is soaked in acetone for lift-off. The ZnO particles that have filled in the eBL-determined trenches can withstand the lift-off and even slight ultra-sonication. The final patterns on the substrate are arrays of nanoparticles aligned inside the predetermined areas. The line pattern formed by ZnO colloidal particles on Si wafer is shown in figure 2.11(d). Further explorations also demonstrate that the VP-soft-eBL can be used to fabricate arrays of well-aligned ZnO nanorods by first spinning the ZnO seed solution on patterned resist, followed by soaking the as-spun sample in Zn-rich liquid environment for room temperature growth.

Another interesting attempt has been made by using polymeric solutions as precursors. For example, nanostructures of polypyrrole, a conducting polymer, are patterned on Si wafer. The precursor is prepared by diluting the as-purchased polypyrrole solution (5 wt.% in water) to 1:3 ratio of polypyrrole to water. The SEM image of the polypyrrole pattern is shown in figure 2.11(e). The chemical identity of these patterns are proved to be consistent with polypyrrole

using secondary ion mass spectrometry by Donthu et al.¹³³ Given the difficulty in milling or etching polymers from thin films without significant damage to the nanostructures, the VP-soft-eBL can be particularly useful for patterning polymeric structures.

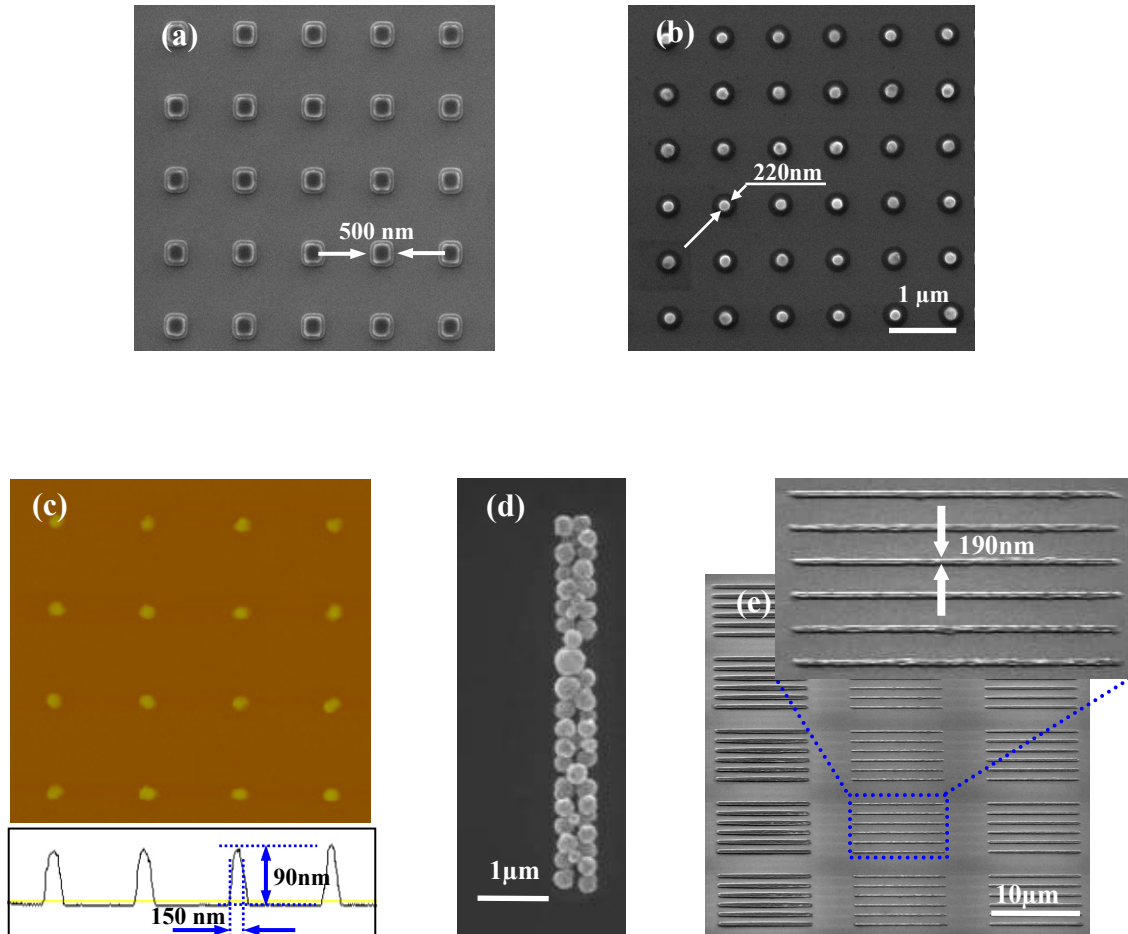


Figure 2.11: Versatility of VP-soft-eBL demonstrated through multitude of materials patterned with various liquid phase precursors. (a) SEM image of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ discs on $\text{Nb}:\text{SrTiO}_3$ single crystal substrate, before annealing. (b) SEM image of BiFeO_3 discs on Si wafer, annealed in air at 600 °C for 30 min. (c) AFM image and cross section profile of CoFe_2O_4 discs on SrTiO_3 single crystal substrate, annealed in air at 1000 °C. (d) SEM image of ZnO line pattern formed by colloidal particles on Si wafer. (e) SEM image of polypyrrole line patterns on Si wafer.

2.6.3.2 Substrate generality

Besides the high versatility in material systems that can be patterned, VP-soft-eBL approach also exhibit remarkable generality on substrate selection. The impact of this generality can be viewed from two aspects, i.e., fabrication control capability and compatibility with multiple characterization techniques.

First, the incorporation of variable pressure mode has significantly expanded the scope of the soft-eBL approach by enabling direct patterning on highly insulating substrates that are important for microstructural control over the patterned oxide materials. For example, BaTiO₃ nanodisc arrays are patterned on different substrates after annealing. The substrates are: 1 wt.% Nb doped SrTiO₃ (001) single crystal (Nb:STO), 50 nm-thick epitaxial SrRuO₃ thin film coated SrTiO₃ (001) single crystal (SRO/STO) and pure SrTiO₃ (001) single crystal (STO). The experimental conditions are the same for patterning all three types of substrates, with the exception of the gas pressure in VP-eBL process. The room temperature resistivity of the above substrates and the chamber gas pressure used in VP-soft-eBL are listed in table 2.3. It can be inferred from the table that VP-soft-eBL is capable of patterning on a wide substrate resistivity range from 10^{-3} to $10^9 \Omega\cdot\text{cm}$ under proper patterning conditions. Due to the different lattice parameters of STO (or Nb:STO) and SRO, the edges of annealed BaTiO₃ pattern on these substrates align with different crystalline orientations accordingly, as shown in figure 2.12. Further study has demonstrated that the VP-soft-eBL allows exquisite control over the internal microstructure as well as the external morphology of multiple oxide nanostructures by invoking the substrate effect (see chapter 3 for detail). The substrate generality therefore has become the critical capability to ensure high quality oxide nanopatterns.

Table 2.3 Room temperature resistivity and gas pressure used for VP-soft-eBL patterning on Nb:STO, SRO/STO and STO substrates

Substrate	Resistivity	Chamber pressure (Water vapor)
Nb:STO	0.0035 $\Omega\cdot\text{cm}$	High vacuum (10^{-11} Torr)
SRO/STO	$\sim 0.21 \Omega\cdot\text{cm}^{134}$	High vacuum (10^{-11} Torr) if SRO film is grounded or low vacuum (1.2 Torr) if SRO film is not grounded
STO	$4 \times 10^9 \Omega\cdot\text{cm}$	Low vacuum (1.5 Torr)

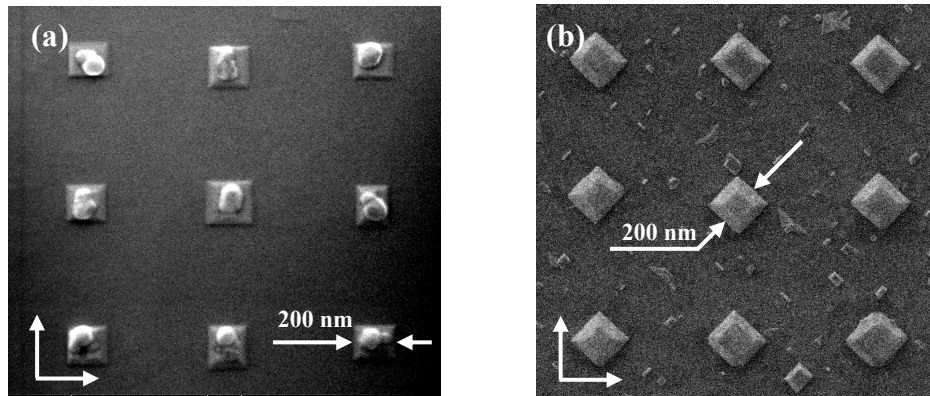


Figure 2.12: Patterning of BaTiO₃ on substrates with significantly different electrical resistivities. (a) VP-SEM image of BaTiO₃ discs patterned on pure STO substrate. (b) SEM image of BaTiO₃ discs patterned on SRO/STO substrate. The white arrows in the left corner of both images indicate the <100> orientations of the substrate. Please note the different edge alignment in (a) and (b).

Second, the VP-soft-eBL employs spinning of liquid precursor for materials deposition. Therefore it is a gentle technique that can be applied on fragile substrates. This is demonstrated by patterning various oxide nanostructures directly on SiN_x membrane as thin as 50 nm. The thin, electron-transparent membranes (SPI Supplies, Structure Probe, Inc.) are fabricated by deposition of SiN_x thin film on Si wafer followed by back etching through the wafer to produce a "membrane window" with desired thickness. Using the thin membrane window as substrate, nanostructures can be directly viewed and characterized under transmission electron microscope (TEM). This saves great effort and time on painstaking traditional TEM sample preparation procedures including cutting, polishing, dimpling and ion beam thinning. On the other hand, direct patterning on the membrane also prevents structural damage to the samples introduced by conventional TEM sample preparation, which can be of particular detrimental for miniaturized structures. Figure 2.13(a) shows SEM images of the Si_3N_4 membrane (image obtained from SPI Supplies website), and figure 2.13(b) shows a schematic illustration of VP-soft-eBL direct patterning on the opposite side of such membrane.

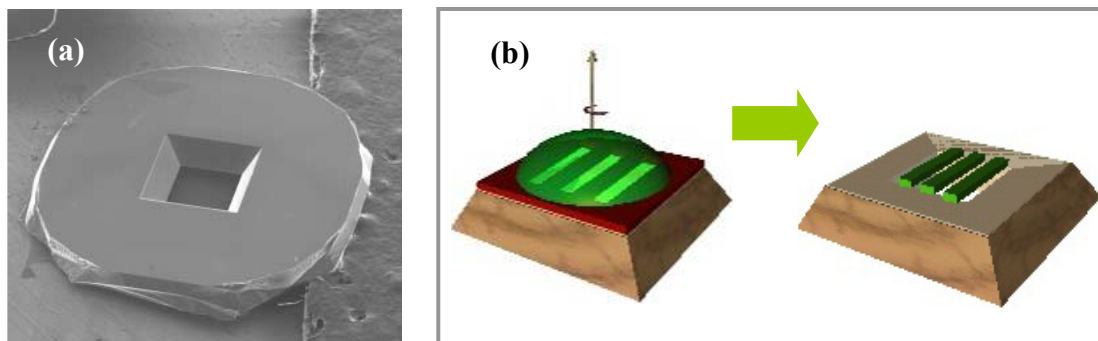


Figure 2.13: VP-soft-eBL direct patterning on thin membrane window. (a) SEM image of the membrane window with surrounding silicon support. Total dimension is 3.0 mm diagonally. (b) Schematic illustration of spinning liquid precursor on VP-eBL patterned resist on top of the membrane window, followed by lift-off.

It should be pointed out here that a few modifications have been made for patterning on SiN_x membrane windows compared with regular VP-soft-eBL process for bulk sample. The windows as manufactured tend to be highly hydrophobic, causing difficulties in coating resist with desired thickness as well as retaining proper amount of liquid precursor in the trenches during spinning. This problem is solved by using oxygen plasma treatment immediately before spinning resist and spinning the liquid precursor. Also, we have noticed that area dose almost twice as high as that on Si wafer is needed for patterning on the 50 nm-thick SiN_x membrane to achieve effective exposure. This is probably because the very thin sample produces lower density of backscattered electrons compared with bulk substrate. Several examples of nanostructures patterned using the modified procedures are shown in figure 2.14. Figures 2.14(a) to 2.14(c) are scanning transmission electron microscopy (STEM) images of CoFe_2O_4 nanodisc patterns annealed in air at 1000 °C and energy dispersive x-ray (EDX) analysis result from this sample. The STEM mode is very sensitive to mass and thickness variation. The dark field STEM image

in figure 2.14(b) therefore clearly shows thickness variation across the 50 nm-diameter CoFe_2O_4 disc. Inset of figure 2.14(b) is an electron diffraction pattern obtained from one individual CoFe_2O_4 disc (the SiN_x membrane is amorphous). The diffraction pattern demonstrates the single crystallinity of the disc and is indexed to the $[001]$ zone axis of the spinel structured CoFe_2O_4 . The EDX spectra obtained from the disc and the plain membrane in figure 2.14(c) confirm the chemical constituents of the patterns. Figure 2.14(d) shows the STEM image of a BaTiO_3 disc pattern on the SiN_x membrane annealed at 1000 °C and the electron energy loss spectroscopy (EELS) line scan profile across such disc at 10 nm intervals. The relative intensity variations in the Ti $L_{2,3}$ edges and Ba $M_{4,5}$ edges originate from the thickness variation of the nanostructure across its diameter. The spectra clearly identify the chemical constituents of the nanopattern, and demonstrate no significant diffusion of Ba and Ti on the SiN_x membrane outside the patterned area. The oxygen K edge showing in and outside the pattern indicates that the SiN_x membrane is oxidized upon annealing in air. The examples in figure 2.14 demonstrate the feasibility of imaging as well as chemical analysis under TEM on VP-soft-eBL patterned nanostructures without requiring any additional sample preparation procedure.

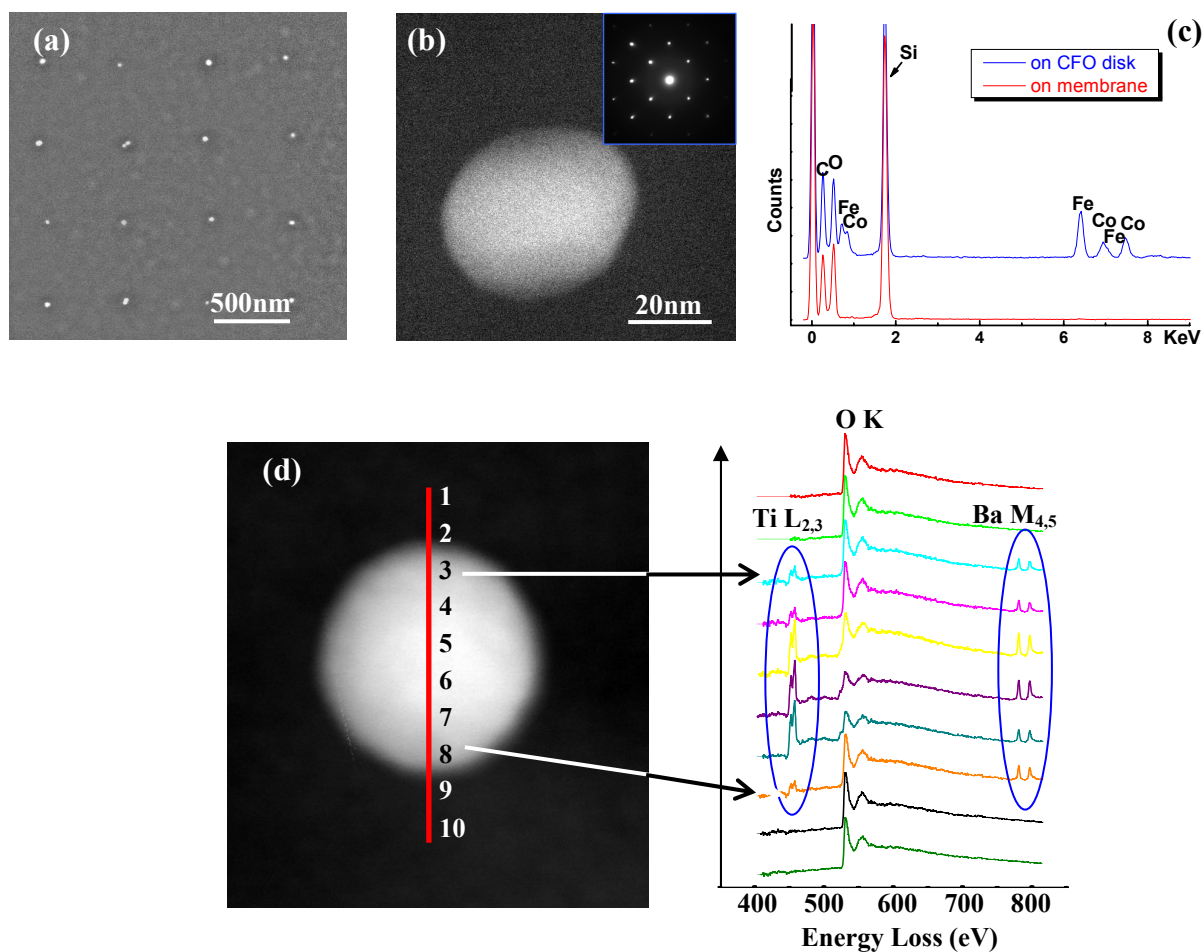


Figure 2.14: (a-b) STEM images of CoFe_2O_4 nanodiscs on SiN_x membrane; inset of (b) shows the diffraction pattern taken from the disc with $[001]$ zone axis, illustrating its single crystal nature. (c) EDS spectra taken on the disc and on the plain membrane. (d) STEM image of BaTiO_3 50 nm-diameter disc on SiN_x membrane and the point-by-point analysis of EELS spectra across the pattern.

The capability of patterning on SiN_x membrane not only enables direct observation under advance electron microscopy for structural/chemical characterization, it also provides a platform for applying multiple other analytical techniques on the nanopatterned system. For example, Donthu et al. have measured the photoluminescence property from ZnO (doped with Eu) nanodots patterned on membrane using near-field scanning optical microscopy (NSOM).¹³⁵ Figure 2.15 schematically illustrates the multiple characterization techniques that we have incorporated on the patterned membrane samples, along with the source used and the signal detected in each technique.

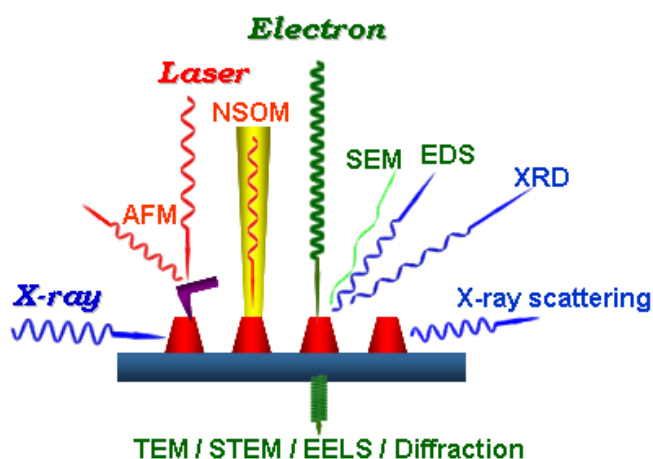


Figure 2.15: Capability of patterning on fragile membrane allows multiple characterizations on one individual sample. These characterization techniques include x-ray diffraction, x-ray scattering, SEM, TEM/STEM, AFM and NSOM.

As a short summary for section 2.6.3, the highly versatile nature of the VP-soft-eBL scheme is highlighted through fabrication of nanostructures of diverse materials (including ferroelectric, magnetic, optoelectronic and conducting polymeric materials) at different length scales and spatial density on a multitude of substrates (including highly insulating substrates and fragile electron transparent membranes). VP-soft-eBL enjoys remarkable attributes of independence of material systems and substrate choice and gentle nature of the process. These attributes can be extremely valuable to study the microstructural evolution and stress distribution in the sol-derived pattern systems by choosing proper substrates and using suitable characterization techniques.

2.6.4 Site-specificity

VP-SEM used in this work is equipped with fine stage movement control and superb NPGS system. Therefore patterning can be carried out at certain specific position on the substrate with high repeatability and precision. This ensures excellent site-specific patterning capability. Figure 2.16 shows an example of a group of ZnO lines patterned across two Au electrodes in order to measure their conductivity. To prepare this sample, the Au electrodes and alignment markers are first patterned using photolithography on the Si wafer. Then the patterned sample is spun with PMMA resist and patterned with line features using VP-soft-eBL, by aligning the entire sample with the aid of the alignment markers (not shown). This greatly facilitates the integration of nanostructures into device architectures.

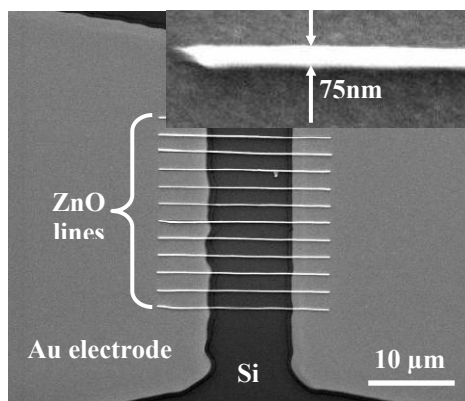


Figure 2.16: ZnO lines (75 nm-wide) patterned across two Au electrodes. Inset shows the detail at the end of one line.

2.7 EVALUATION ON EASE OF PRACTICE OF VP-SOFT-EBL

In general, VP-soft-eBL can be readily carried out for exploratory research in a lab setting. The ease of practice for VP-soft-eBL can be evaluated from the following aspects:

(1) *Precursor synthesis*: The sol-gel chemistry for the oxide precursors used in this work has been very well-developed. Modification on sol concentration or solvent systems can be readily conducted in lab. Synthesis of colloidal particle suspension has also been established in our laboratory.

(2) *eBL process*: eBL patterning condition on copolymer and PMMA resists has long been established and highly repeatable, particularly on semiconducting or conducting substrates. Patterning on insulating substrates under variable pressure mode can be less straightforward.

However, optimized VP-eBL condition in terms of gas pressure and primary beam energy has been established. Further knowledge regarding the beam skirt effect has been obtained through quantitative analysis (chapter 4) to obtain better control in VP-eBL.

(3) *Etch-free lift-off*: The lift-off effectiveness is dictated by an integrated effect of sol recipe, pattern geometry and spinning speed. Therefore precise estimation of the optimized lift-off condition can be very difficult. However, an empirically obtained spinning condition can achieve satisfactory lift-off effect for most of the sol systems used in this work.

(4) *Thermal treatment of as-deposited patterns*: Proper high temperature annealing condition has to be selected based on the sol property, pattern dimension, choice of substrate, and desired crystalline structure and density.

2.8 SUMMARY

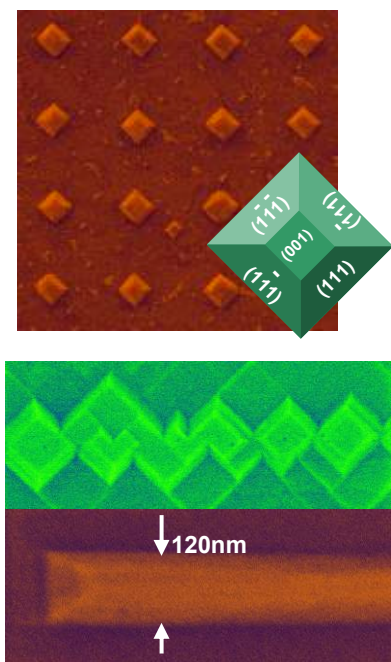
This chapter reports a facile yet effective nanopatterning approach for fabrication of nanostructures from a wide variety of solid state materials on diverse substrates, with controlled dimensions and locations. Combining the advantages of the state-of-the-art electron beam lithography and the highly versatile wet chemistry, the VP-soft-eBL possesses the four key attributes pertinent to patterning functional oxide nanostructures. These include: etch-free, high spatial resolution, registry and material/substrate generality.

With its remarkable versatility, VP-soft-eBL can be adapted to achieve various goals for ceramic nanopatterning. As a matter of fact, multiple developments and improvements to the

VP-soft-eBL have been achieved over the past two years. The scope of VP-soft-eBL has been greatly expanded in two regimes. One is to explore the patterning capability in fabrication of ceramic nanostructures under substrate constraint at multi-dimensionalities. The other is to employ the VP-soft-eBL as an enabler for exquisite control over morphology, shape evolution, and crystalline orientation of these nanostructures, akin to what has been possible in the past with semiconductor heterostructures by thin film approaches. The effort made in the above areas will be systematically demonstrated in chapters 3 to 5.

CHAPTER 3

MICROSTRUCTURAL AND MORPHOLOGIC CONTROL OF VP-SOFT-eBL PATTERNED 0D AND 1D NANOSTRUCTURES



This chapter details the microstructural control strategy incorporated with VP-soft-eBL scheme for sol-gel-derived complex oxide nanopatterns. Our observations show that, besides the elastic property matching of the substrate/material system, the original pattern aspect ratio has significant influence on the microstructural development of the 0D patterns during heat treatment. Particularly, epitaxial single crystal patterns with preferred orientation are obtained and confirmed by structural, chemical and functional characterizations using TEM and SPM. The chapter also highlights the capability of achieving “patterning-controlled morphology” for 0D and 1D nanostructures of materials with high surface energy anisotropy.

Part of the work presented in this chapter was published in **Nano Lett.**, **6**, 2344 (2006) and **Appl. Phys. Lett.**, **91**, 143105 (2007) (selected for the October, 2007 issue of Virtual Journal of Nanoscale Science & Technology). Other parts were presented at **2006 MRS Fall Meeting** and **2007 MRS Fall Meeting**.

Fabrication and assembly of zero-dimensional (0D) and one-dimensional (1D) functional oxide nanostructures, particularly of those with magnetic and/or ferroelectric order parameters, have attracted considerable research interest in recent decades.¹³⁶⁻¹⁴⁰ Properties and performances of such nanostructures are heavily influenced by their internal microstructure as well as external morphology. Such significant influences arise from two factors: 1) ferroelectricity and magnetism are intrinsic material properties that are extremely sensitive to parameters such as crystallinity, orientation, aspect ratio, and pattern-substrate interface structure; and 2) small alterations in chemistry,¹⁴¹ shape,¹⁴² and even surface roughness¹⁴³ of 0D and 1D nanostructures have a rather strong impact due to miniaturization. This has become the central driving force for the development of innovative design strategies to: (i) manipulate functional ceramic materials at nanometer length scales; (ii) control the dimensions and morphology of the nano-features and (iii) engineer their internal microstructure. The realization of the above capabilities, while appealing, is equally challenging for both pure “top-down” approaches^{132, 144-146} and pure “bottom-up” approaches.⁶⁵⁻⁶⁷ It is particularly difficult to fabricate single crystalline or uniformly textured functional ceramic nanopatterns in order to probe their intrinsic or enhanced properties.

We have introduced the VP-soft-eBL approach as a highly versatile patterning scheme suitable for fabrication of diverse oxide nanostructures. We also notice that VP-soft-eBL allows exquisite control over the internal microstructure of oxide nanopatterns. For example, Donthu *et al.*^{147, 148} have demonstrated that VP-soft-eBL enables grain size control of ZnO line patterns through changing the line width. The scope of structural engineering can be further expanded by utilizing the unique characteristic of VP-soft-eBL. Basically, its “top-down” feature implies that the microstructure of patterns can be dictated by the underlying substrate, akin to what has been

possible in the past with semiconductor heterostructures by thin film approaches. Its “bottom-up” quality, i.e., compatibility with sol precursors, has provided an etch-less and damage-free route for making miniaturize structures. Therefore, the behavior of the as-prepared patterns with different dimensions can be directly cross-compared to single out the influence of morphology.

In this chapter, we report a strategy incorporated with VP-soft-eBL scheme to control the microstructure of sol-gel-derived complex oxide nanopatterns, particularly to obtain epitaxial single crystal patterns with preferred orientation. The patterning-controlled morphology development for 0D and 1D nanostructures is also discussed.

3.1 MECHANICAL STABILITY OF SOL-GEL SYSTEMS AND MICROSTRUCTURAL ENGINEERING STRATEGY

The principle sol-gel-processing routes for oxide ceramics involve the gelation or the cross-linking between hydrolyzed metal alkoxides in an alcoholic solvent. The final conversion to the oxide is accomplished by heat-treating the gel. There are large shrinkages to accommodate at two stages: as the gel dries and as the dried gel sinters to dense ceramic. For a sol-derived blanket thin film system, the shrinkage induces residual tensile stresses in the film and causes film cracking when the film thickness is larger than a critical value. Cracking-related mechanical and microstructural instability of sol-derived thin films has become the focus of intensive research.¹⁴⁹⁻¹⁵³ For example, Atkinson and Guppy¹⁵⁴ proposed that the critical thickness h_c above which through-film cracking happens is dependent on the elastic properties of the systems as:

$$h_c = \frac{EG_f}{0.6\pi\sigma^2} \quad (3.1)$$

where E is the modulus of both the film and the substrate (assumed equal); G_f is the critical strain energy release rate for crack extension in the film which is related to the free surface energy of the film material; σ is the stress in the film.

Equation 3.1 implies that mechanical stability of a sol-derived system can be tuned by adjusting the strain energy in the system, i.e., the value of σ and G_f . For a blanket thin film, this can be practically realized by adjusting processing parameters like solvent-to-alkoxide ratio, pyrolysis temperature and heating rate.¹⁵⁵ For a nanopatterned system, another degree of freedom for tuning the strain energy is introduced due to the strong correlation between the pattern geometry and the constraint imposed by the substrate. It can therefore be expected that the mechanical stability and the microstructure of the discrete nanopatterns will change with their size and shape. On the other hand, the crystalline structure and orientation of the nanopatterns can be dictated by the underlying substrate with appropriate lattice matching. This has become the motivation of microstructural engineering on the as-deposited, amorphous nanostructures made from VP-soft-eBL.

3.2 EXPERIMENTAL DETAILS

In this study, nanodisc arrays of technologically important magnetic oxide CoFe_2O_4 (CFO) and ferroelectric oxide BaTiO_3 (BTO) are fabricated with various diameters using the VP-soft-eBL approach. Diverse single crystal oxide substrates are selected to provide different degrees of

lattice matching with CFO or BTO. These substrates include: (1) (001) SrTiO₃ (STO); (2) (001) MgO; (3) 50 nm-thick epitaxial SrRuO₃ film sputtered on (001) SrTiO₃ substrate (SRO/STO); (4) (110) GdScO₃ (GSO); (5) (110) DyScO₃ (DSO). The lattice constants and crystalline structures of substrates used in this study are listed in table 3.1. The lattice mismatch α between the patterned material and the corresponding substrate is defined as:

$$\alpha(BTO) = \frac{a(substrate) - a(BTO)}{a(BTO)} \times 100\% \quad (3.2)$$

$$\alpha(CFO) = \frac{2a(substrate) - a(CFO)}{a(CFO)} \times 100\% \quad (3.3)$$

where a stands for the lattice constant of the patterned material or the substrate. Please note that here a is the lattice spacing of (100) plane ($d_{(100)}$) for CFO, BTO, STO, SRO and MgO. For (110) DSO and GSO substrates, a takes the value of the in-plane lattice spacing of the nearly square surface mesh for comparison with the perovskite BTO.¹ The factor 2 is used in equation 3.3 because the lattice constant of spinel CFO is about twice that of the substrates used in this work.

Table 3.1 Lattice mismatch between different substrates with CFO and BTO

Patterned materials	Substrate	Substrate Parameters			α (%)
		a (Å)	Structure	Space group	
CFO	(001) SrTiO ₃	3.905	Perovskite	Pm3m	-6.9
Spinel (Fd3m) $a = 8.391$ Å	(001) MgO	4.212	Rock salt	Fm3m	0.39
BTO	(001) SrTiO ₃	3.905	Perovskite	Pm3m	-2.3
Perovskite (P4mm)	(001) SrRuO ₃ /SrTiO ₃	3.92	Perovskite	Pbnm	-1.9
$a = 3.997$ Å	(110) DyScO ₃	3.95	Distorted-perovskite	Pbnm	-1.2
$c = 4.03$ Å	(110) GdScO ₃	3.97	Distorted-perovskite	Pbnm	-0.68

VP-soft-eBL and scanning electron microscope (SEM) imaging are both conducted in Quanta 600F environmental SEM (FEI Co.). Patterning conditions for discrete 0D and 1D nanostructures in VP-eBL have been reported in chapter 2. In order to crystallize and fully densify the patterns, all patterned samples are annealed at 1000 °C using 80 °C/min heating rate and cooled down to room temperature with 30 °C/min. The CFO patterns are annealed in air, whereas the BTO patterns are annealed in 1 atm O₂ atmosphere to subdue the development of oxygen vacancies.¹⁵⁶ The crystalline structure and chemical constituents of the annealed nanopatterns are characterized in transmission electron microscope (TEM, JEM-2100F, JEOL, Japan), equipped with high angle annular dark field (HAADF) detector to provide high atomic number contrast under scanning transmission electron microscopy (STEM) mode. The external

morphology and the thickness of the nanopatterns are measured using atomic force microscope (AFM, Nanoscope III microscope, Digital Instruments). The site-specific characterizations on the magnetic and piezoelectric behavior of the patterns are conducted using scanning probe microscopy based technique, i.e., magnetic force microscopy (MFM) and piezo-force microscopy (PFM), separately. The experimental condition of MFM and PFM operations will be introduced in related sections.

3.3 VARIATION OF MICROSTRUCTURAL DEVELOPMENT WITH PATTERN SIZE: CoFe₂O₄ 0D DISC PATTERNS

In this section, we first demonstrate patterning of CFO discs on (001) STO substrate and site-specific characterizations on their chemical and functional identities. We then discuss the pattern size effect on microstructure development of CFO discs on STO substrate, and propose a strategy using which epitaxial single crystal disc patterns can be achieved.

3.3.1 Development of CoFe₂O₄ disc patterns on (001) SrTiO₃ substrate

Figure 3.1 shows typical AFM images of soft-eBL-patterned CFO arrays on STO substrate after annealing, illustrating the size uniformity of the CFO patterns. The cross-sectional profile shows that each disc has uniform diameter of about 150 nm and height of about 90 nm. In the following, samples with different pattern diameters on STO substrate are selected in order to understand the influence of pattern size on the morphology and crystallinity of CFO discs. The height of the final patterns for different samples generally falls in the range of 80~100 nm.

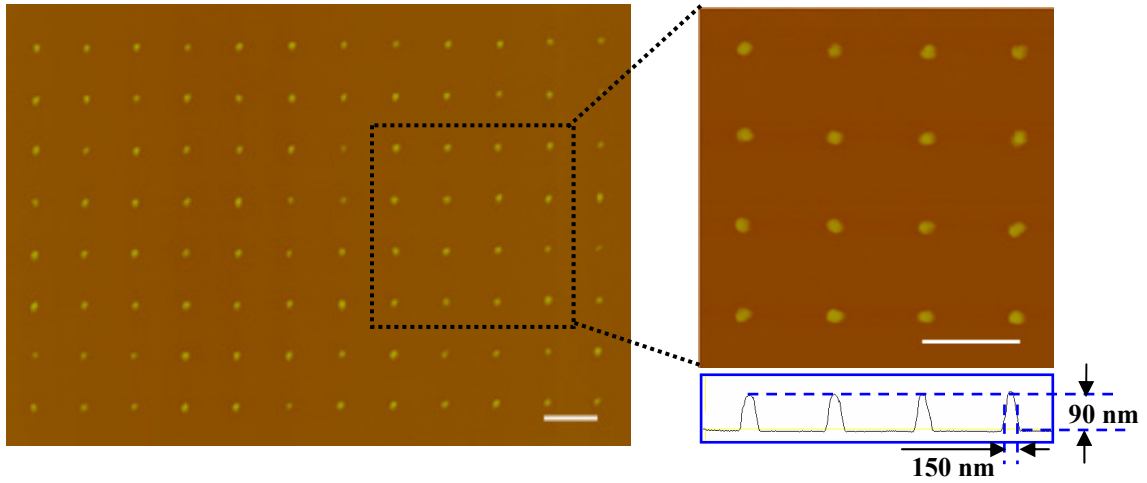


Figure 3.1: AFM images of CFO disc array on STO. Scale bar = 1 μm .

Figures 3.2(a) to 3.2(c) are SEM images of CFO discs with 500 nm, 200 nm and 100 nm diameters, respectively. In figure 3.2(a), the 500 nm-diameter patterns appear to break into several discrete crystallites. This tendency is significantly diminished for smaller patterns. In fact, two types of morphologies are observed to coexist for pattern diameter between 500 nm and 200 nm: one showing polycrystalline CFO network with small pores trapped inside, and the other with dense CFO discs. Patterns with 200 nm and smaller diameters (figures 3.2(b) and 3.2 (c)) are all developed into fully dense nanodiscs. In order to obtain explicit evidence for crystallinity of smaller patterns, tapping mode AFM phase images are taken on the 200 nm-diameter discs. AFM phase image can provide superior grain boundary contrast especially when grains are smaller than 20 nm.¹⁵⁷ Figures 3.3(a) to 3.3(b) show the typical phase images of 200 nm-diameter patterns, where no grain boundary features are observed. Although the original patterns in the e-beam resist are circular discs, a certain percentage of annealed CFO patterns present faceted shape which is consistent with the Wulff construction for cubic $m3m$ point group

symmetry (truncated octahedron with $\{100\}$ and $\{111\}$ facets¹⁵⁸), as illustrated in figure 3.3(c). The sharp angle between the side and bottom surfaces measured from cross-sectional profiles of figure 3.3(b) is around $56\sim 58^\circ$, corresponding well to the angle between cubic $\{001\}$ and $\{111\}$ planes (57.4°). It suggests the single crystal nature of the nanopatterns with less than 200 nm diameter and their uniform cube-on-cube epitaxial orientation with respect to the substrate.

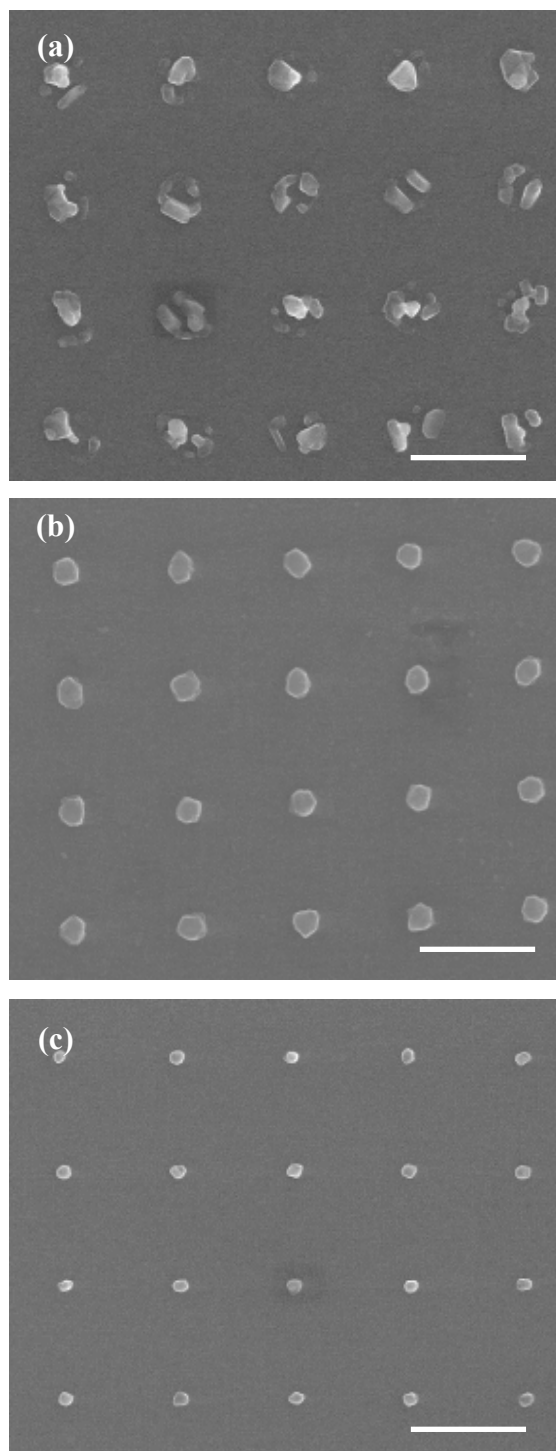


Figure 3.2: VP-SEM images of CFO disc arrays on STO substrate, with (a): 500 nm, (b): 200 nm, and (c):100 nm diameters, respectively. Scale bar = 1 μ m.

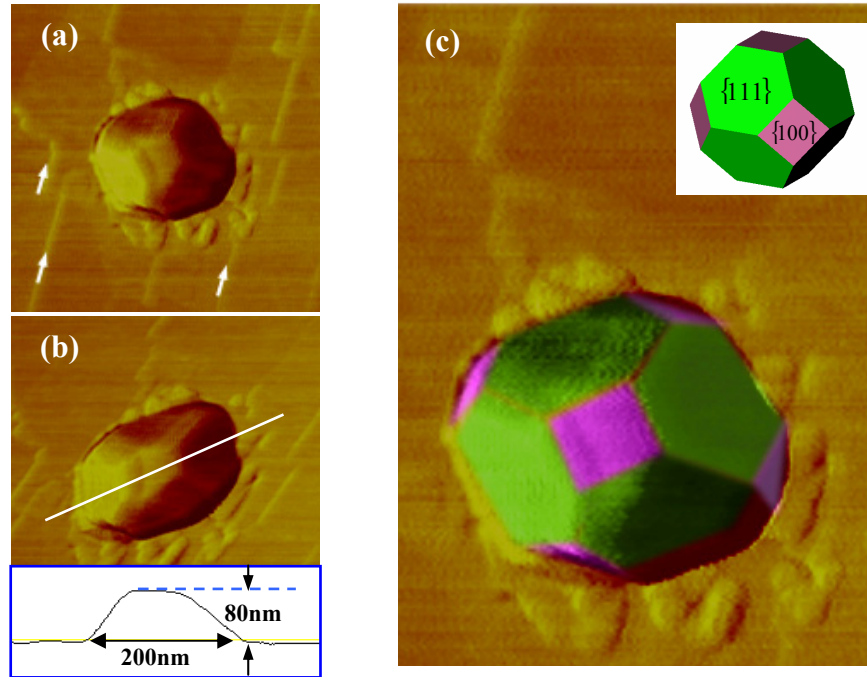


Figure 3.3: AFM phase images of CFO discs with 200 nm diameter and cross sectional profile. The line contrast on the substrate (indicated by arrows) comes from the terraces on (001) STO due to its surface reconstruction during annealing. Figure 3.3 (c) shows colored facets of one disc, illustrating the possible crystallographic orientations that are consistent with the Wulff construction for cubic $m\bar{3}m$ point group symmetry (inset).

TEM investigation on a plan view sample (CFO 200 nm-diameter disc arrays on (001) STO substrate after annealing) provides unambiguous evidence of the single crystal nature and detailed information on the orientation of the nanodiscs. Well-defined pattern shape can be readily observed from figures 3.4(a) and 3.4(b). Typical selected area diffraction (SAD) pattern obtained from one such disc (figure 3.4(c)) further reveals the cube-on-cube heteroepitaxy between the single crystal CFO nanodiscs and the STO substrate. This heteroepitaxy implies that one magnetocrystalline easy axis (i.e., $\langle 100 \rangle$) of CFO nanopatterns is aligned normal to the

substrate plane, which is highly favorable to harness the magnetization direction of such nanopatterns. While current attempts for fabrication of textured or epitaxial ferrite thin films or miniaturized structures are mainly focused on high energy deposition (e.g., pulsed laser deposition, magnetron sputtering, and molecular beam epitaxy)¹⁵⁹ with careful monitoring of the film growth, the approach we demonstrate here can serve as an attractive alternative to fabricate highly textured ferrite nanostructures and heterostructures.

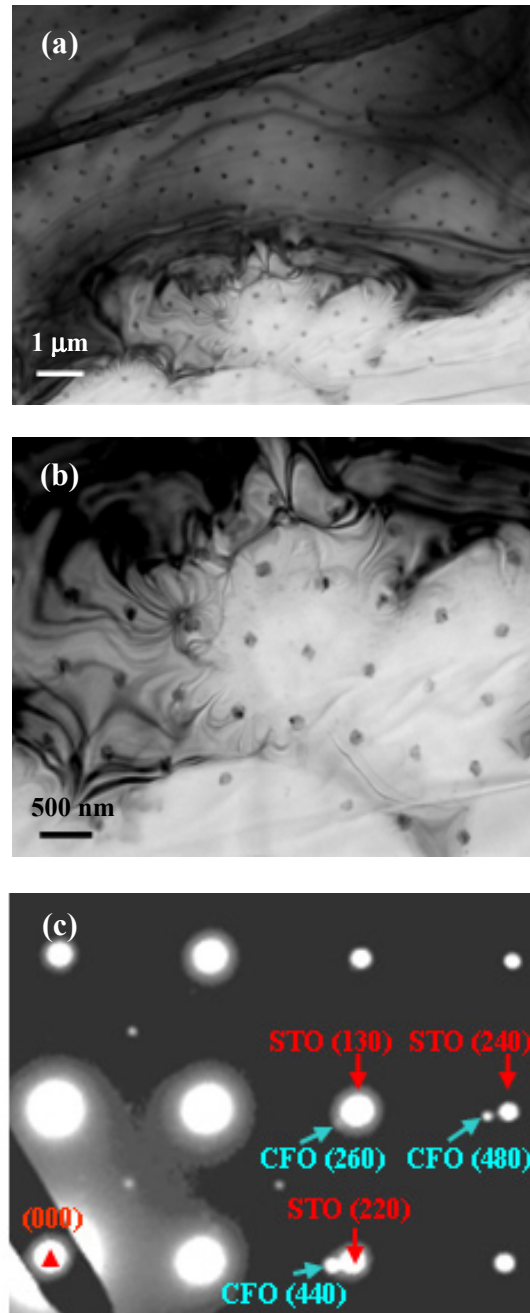


Figure 3.4: (a-b) TEM plan view images of 200 nm-diameter CFO discs on (100) STO substrate. (c) SAD pattern obtained from one CFO disc pattern illustrating the cube-on-cube heteroepitaxy between the pattern and the substrate.

To probe the localized chemical information of the nanostructures, energy dispersive x-ray (EDX) spectra are collected using STEM mode. Figure 3.5 shows the HAADF-STEM image of a CFO pattern, where the faceting and thickness variation can be observed across the pattern. An electron probe with nominal size of 1 nm is used to obtain point-by-point EDX spectra across the CFO pattern. The yellow box on the image indicates the area for spatial drift correction while collecting the EDX data. The EDX analysis confirms the coexistence of Fe and Co elements on the pattern, but not outside on the STO substrate. The peak intensity change in Fe and Co signals is due to the thickness variation.

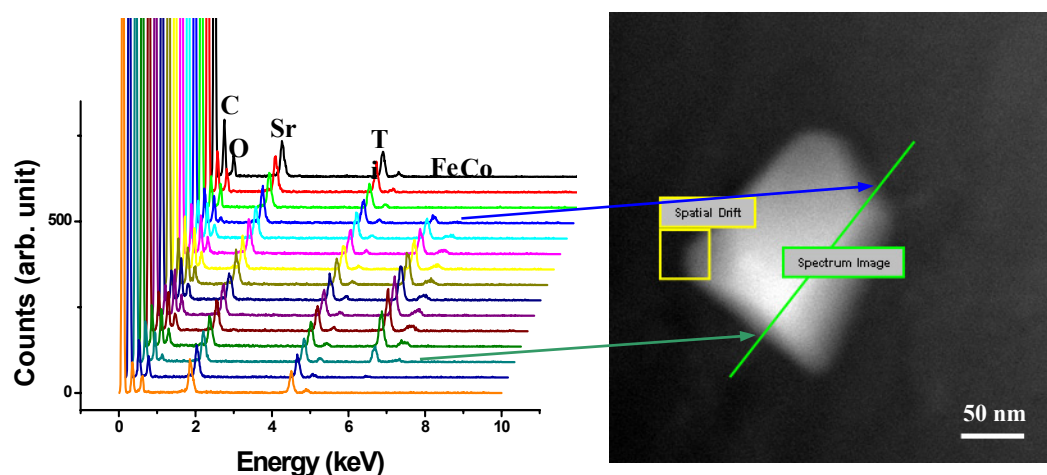


Figure 3.5: STEM image of 200 nm CFO nanodiscs (right) and point-by-point EDX spectra analysis (left) taken on the disc and on the STO substrate.

The fact that majority of the 200 nm-diameter CFO nanopatterns exhibit heteroepitaxy with respect to the STO substrate suggests that their magnetocrystalline easy axes (i.e., $\langle 100 \rangle$) are aligned normal to the substrate plane. To study the spontaneous magnetization of the CFO

patterns, lift-mode MFM is employed. The AFM tip used is coated with cobalt thin film and magnetized before scanning. The lift height in MFM operation is 40 nm above the sample. Topographic and MFM phase images obtained on an area covering 5×5 disc array is scanned. The sample is not subjected to magnetization. In figure 3.6, the phase contrast from the discs suggests that most CFO discs carry an out-of-plane spontaneous magnetization component, which is in accordance with the microstructural observation.

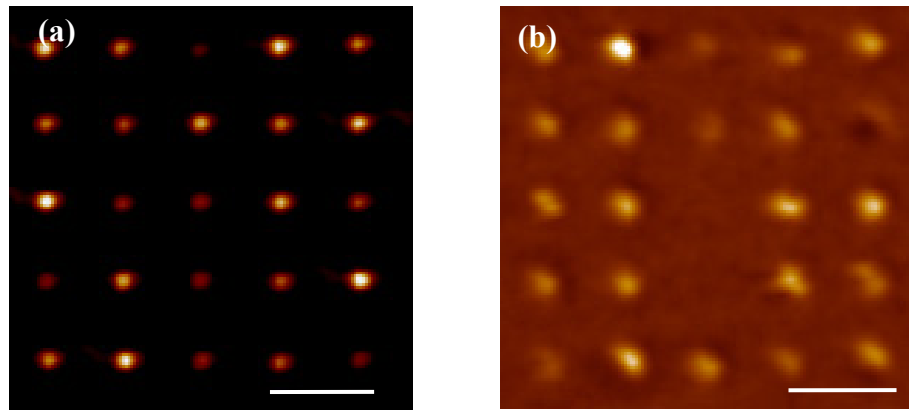


Figure 3.6: (a) Topographic image of a 5×5 array of CFO disc patterns; (b) MFM phase image on the same area without external magnetization. Scale bar = $1 \mu\text{m}$.

3.3.2 Equilibrium aspect ratio for “crack-free” patterns

Based on the observation on CFO disc arrays on STO substrate through SEM, AFM and TEM, their microstructural change with pattern dimension is described in table 3.2.

Table 3.2 Microstructural development of CFO disc patterns on STO with dimension

Diameter d (after annealing, nm)	500	200	100
Average height h (nm)	~80	80	84
Aspect ratio h/d	0.16	0.4	0.84
Microstructure	Cracked; polycrystalline	Dense; mostly single crystal; epitaxially grown on STO	

From table 3.2 it can be noticed that the pattern morphology appears to diverge at a critical diameter of around 200 nm, i.e., larger patterns tend to break into discontinuous crystallites, whereas smaller patterns develop into dense discs. Considering that the epitaxial nanodiscs, to an approximation, resemble strained epitaxial islands in typical semiconductor systems,¹⁶⁰⁻¹⁶² the morphology change may be qualitatively explained using the analytical results derived for the latter systems. By assuming the total free energy of the system to consist mainly of elastic strain energy and free surface energy of the islands, studies on the mechanics of epitaxial semiconductor islands^{160, 162} point out that: 1) the strain energy per unit volume stored in the island is a decreasing function of aspect ratio, whereas the normalized surface energy is an increasing function of aspect ratio, due to the fact that the ratio of its surface area to the amount of substrate surface covered is increasing. Consequently, for islands of larger volume for which elastic effects are more important than surface energy effects, the equilibrium aspect ratio is expected to be larger. This implies that for CFO patterns with large diameters (therefore larger volume and small aspect ratio), the strain energy can be so high that the patterns tend to crack to partly release the strain energy at the price of increasing the free surface energy; 2) an

equilibrium aspect ratio of the islands for fixed island volume at which the total free energy density is a local minimum can be determined, with a dimensionless parameter R for a fixed volume. R is defined by:

$$R \sim \frac{2\pi\gamma}{M\alpha^2 A^{1/2}} \quad (3.4)$$

where

γ = free surface energy of the island;

M = biaxial elastic modulus of the pattern, i.e., $M = 2\mu \frac{1+\nu}{1-\nu}$, where μ is the elastic shear modulus and ν is the Poisson's ratio;

α = lattice mismatch between the island and the substrate, with the same definition as in equations 3.2 and 3.3;

A = cross-sectional area of the island.

The parameter R here represents a measure of the relative importance of surface energy to strain energy in the system. The above argument assumes the islands take mesa morphology and are completely coherent with the substrate. Although the contributions to the free energy of a nanopattern from crystallographic shape and facets^{163, 164} and possible dislocations formed in the pattern^{160, 165} are not included, the model can still be used to give approximate estimation on the morphology of CFO patterns. For dense and epitaxial 200 nm-diameter CFO patterns on STO (001) substrate that exhibit faceted morphology, the system parameters have approximate values

of $\gamma = 1 \text{ J/m}^2$,¹⁶⁶ $M = 100 \text{ GPa}$,¹⁶⁷ $\alpha = -0.07$, and $A = 6000 \text{ nm}^2$ for which R is about 0.2. For this value of R , the minimization of the free energy density in the literature¹⁶⁰ implies an equilibrium aspect ratio larger than 0.4 (i.e., pattern height $\geq 80 \text{ nm}$), which corresponds to the observed dimension of the CFO patterns with the “critical” diameter of 200 nm.

It should be pointed out that the above theoretic model is based on a few assumptions on factors including the shape of the pattern and the interface energy for simplicity of calculation. Also, it considers the main contributions to the total free energy only from free surface energy and elastic strain energy due to lattice mismatch. Therefore it is more suitable to predict the equilibrium shape and size for self-assembled epitaxial systems such as semiconductors. The case for sol-derived nanopatterned system can be much more complicated because the contributions from phase transformation and intrinsic stresses induced by densification are not negligible. Because nucleation and grain growth are both diffusion-controlled, the pattern morphology development for sol-system must also be related to diffusion kinetics. Although detailed investigation on such correlation can be complicated, one may expect that it is more difficult for large patterns to develop into a single grain than for small ones because a significant amount of mass has to be transferred and re-arranged for this purpose.

Here we use the model of considering free energy as a balance of strain energy and surface energy to provide a lower bound of crack-free morphology development for a given nanopattern/substrate system. It can be expected that if substrate of smaller lattice mismatch with CFO is selected, crack-free and epitaxial patterns can be achieved for larger parameters. It reveals the potential of this approach for structural engineering via nanopatterning, i.e., to obtain

poly- or single-crystalline ceramic nanostructures through controlling the pattern size, and to achieve specific crystallographic orientation of the nanostructure by choosing proper substrates. This has led to the following experiments to prove the single crystal conversion strategy by patterning CFO or BTO nanodiscs with appropriate dimension on low-mismatch substrates.

3.4 SINGLE CRYSTAL CONVERSION STRATEGY AND ORIENTATION CONTROL

3.4.1 Example 1: CoFe_2O_4 disc patterns on (001) MgO substrate

Due to its very low lattice mismatch (0.39%), the CFO/MgO system serves a nice test system for comparison with the previously studied CFO/STO system. In fact, it is observed for CFO/MgO system that the disc patterns with diameter ranging from 100 nm to 500 nm can all develop into dense, crack-free structures after annealing (for the same 80 ~100 nm average height). The fact that crack-free morphology exhibit for larger diameters can be explained by the much less strain energy stored in the coherent CFO/MgO system and therefore a smaller critical aspect ratio required. Figure 3.7 shows a typical single crystal conversion result for such system. Figure 3.7(a) is a VP-SEM image of 200 nm-diameter CFO circular discs after development with about 130 nm average height (revealed by AFM). After annealing, all the circular discs develop into dense crystalline phase with a uniform square-bottom pyramid shape as shown in figure 3.7(b). The AFM image (figure 3.7(c)) confirms this shape development and reveals the sharp bottom edges and smooth side facets. Measurement of the angle between side facets and the bottom substrate surface gives a precise 57.4° angle, corresponding to that between $\{111\}$ and $\{100\}$. The $\langle 100 \rangle$ in-plane orientations for the single crystal MgO substrate are indicated with

white arrows on all images. Please note that the CFO bottom edge orientation is along $\langle 110 \rangle$. The schematic representation of the CFO pyramid-shape pattern is shown in the inset of figure 3.7(c). The well-defined faceted shape further proves the single-crystallinity of the CFO converted from as-deposited amorphous phase.

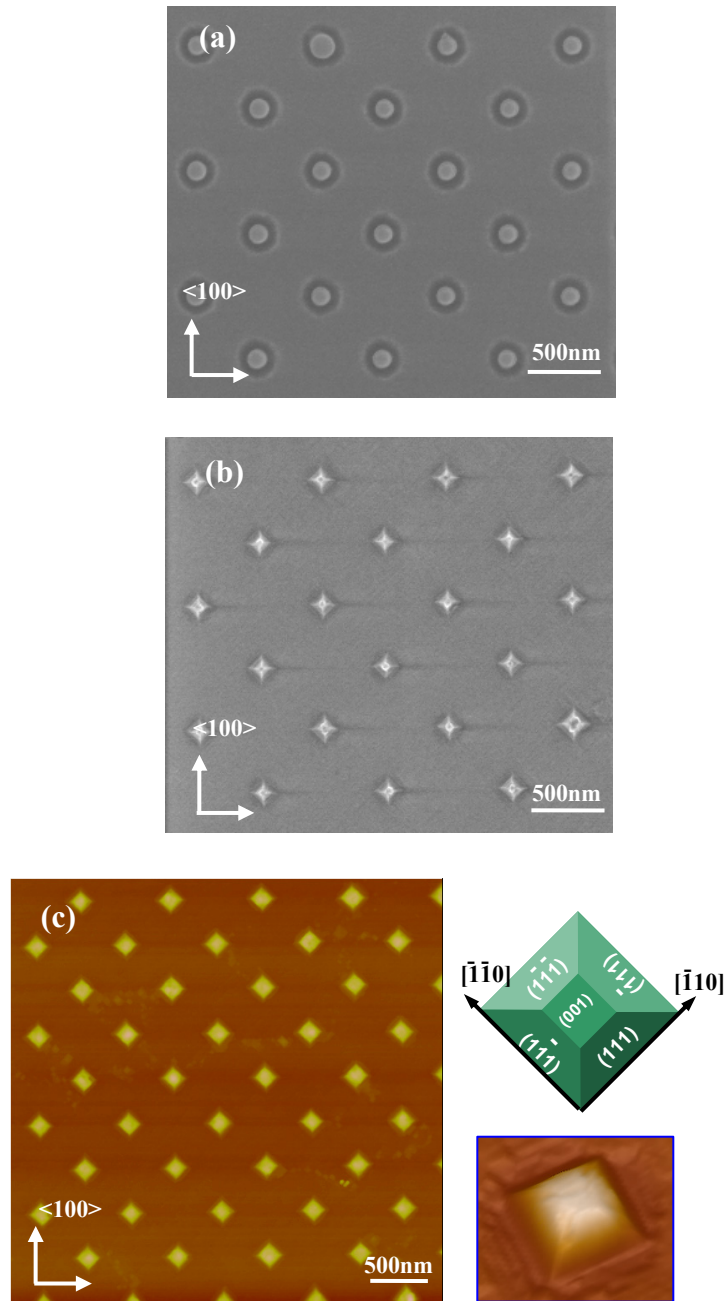


Figure 3.7: Single crystal conversion of CFO disc patterns on (100) MgO substrate. (a) VP-SEM image before annealing; (b) VP-SEM image after annealing in air at 1000 °C; (c) AFM image after annealing. Inset shows the schematic representation of the faceted shape (up) and a magnified three dimensional image of one CFO pattern (bottom). White arrows indicate the $\langle 100 \rangle$ directions of the MgO substrate.

As addressed before, the densification and phase transformation of sol-derived patterns are diffusion-controlled and should be related to annealing kinetics. In our study, the annealing time required for the single crystal conversion and the faceted shape development is studied. Particularly, four groups of patterned samples are annealed in air at 1000 °C for 30 min, 1 hr, 2 hr and 4 hr, respectively. These samples are patterned with same geometry of 200 nm-diameter circular disc arrays, under identical VP-eBL condition. The typical VP-SEM images of these annealed samples are shown in figure 3.8. Multiple small grains can be observed on top of the sample annealed for 30 min in figure 3.8(a). Annealing for 1 hr facilitates the development of the $\langle 110 \rangle$ edge directions and the square bottom (figure 3.8(b)). The structure is further densified, although sporadic small grains still exist on the top. This development has been advanced given longer annealing time and the single crystal conversion is achieved for patterns annealed for 4 hr. The single crystal conversion is accompanied by size shrinkage, particularly in the out-of-plane direction. AFM measurements (not shown here) have disclosed that the average height of the pattern changes from the original 130 nm to 75 nm during annealing. The observation that the square shape development initiates from the pattern bottom and advances towards the top suggests that the heterogeneous nucleation mechanism is dominated during sintering of sol-derived pattern.

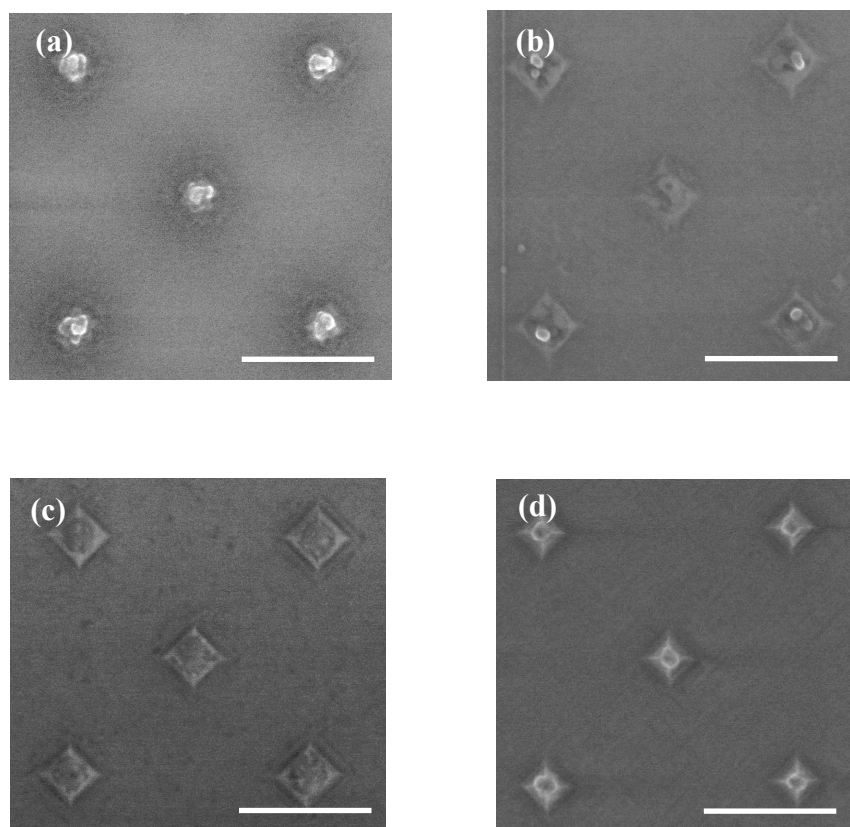


Figure 3.8: VP-SEM images of CFO disc patterns annealed at 1000 °C with increasing annealing time. (a) 30 min; (b) 1 hr; (c) 2 hr; (d) 4 hr. Scale bar = 500 nm.

3.4.2 Example 2: BaTiO₃ disc patterns on (001) SrRuO₃/SrTiO₃ substrate

The single crystal conversion of BTO has also been carried out on SRO, STO, DSO and GSO substrates. Among them, epitaxial thin film of SRO is particularly useful as electrodes for ferroelectric materials and junctions in microelectronic devices due to its structural compatibility with diverse perovskite ferroelectric oxides, electric conductivity, high resistance to chemical corrosion and outstanding thermal conductivity.¹⁶⁸⁻¹⁷⁰ Here we use the BTO/SRO system as an example to illustrate the efficacy of this single crystal conversion strategy.

In this study, ferroelectric BTO discs are patterned on SRO epilayer on STO substrate. The lattice mismatch between SRO and BTO is about -1.9%. Shown in figure 3.9 are SEM and AFM images of BTO disc patterns developed from the originally defined circular discs after annealing. The annealed BTO patterns exhibit truncated-pyramid shape and well-defined facets, with four bottom edges aligned along the <110> directions of the substrate, similar to what has been observed for CFO/MgO system. Given the similar structure and close lattice parameters of BTO and SRO, this morphology suggests that the BTO patterns are single crystalline, with cube-on-cube epitaxy with respect to the substrate.

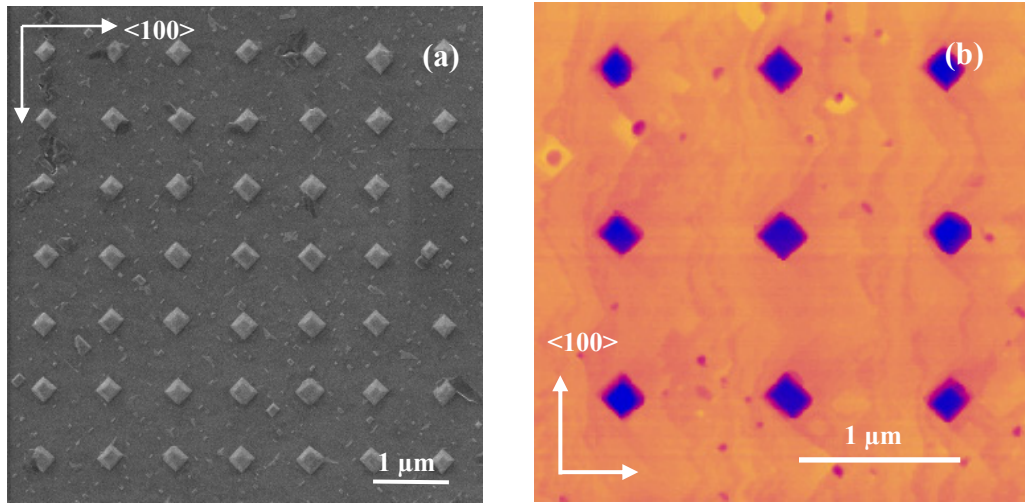


Figure 3.9: BTO single crystal patterns on SRO/STO substrate with faceted shape. (a) SEM image. (b) AFM image. Arrows indicate the $\langle 100 \rangle$ directions of the substrate.

The epitaxial relationship is further confirmed by TEM electron diffraction and high resolution imaging of the BTO/SRO interface. The cross-sectional TEM sample shown in figure 3.10(a) is prepared by using focused ion beam (FIB) lift-off method followed by cleaning in low angle ion milling (Fischione Instruments) to reduce FIB damage. The high resolution image at the BTO/SRO interface (figure 3.10(b)) reveals the heteroepitaxy between the pattern and the SRO film. This suggests a uniform ‘a’-domain or ‘c’-domain configuration of all BTO nanostructures, which is highly favorable to harness the ferroelectric properties of nanopatterns towards possible application such as high density memories. We notice that BTO patterns with less than 300 nm diameter on SRO substrate can all be readily converted into single crystal frustums with a typical height of about 50 nm (from AFM analysis, not shown) upon annealing.

Thus, this approach enables a reliable control over crystallinity, orientation and morphology of BTO patterns in sub-100 nm regime.

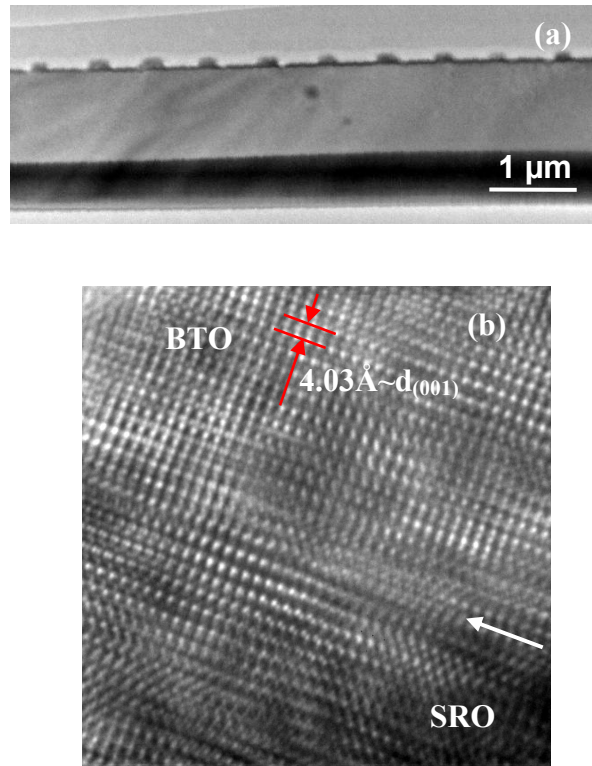


Figure 3.10: (a) TEM cross-sectional image of BTO/SRO/STO structures. Sample is cut along $\langle 110 \rangle$ direction of the substrate, through 10 nanopatterns. (b) TEM high resolution image at BTO/SRO interface showing the heteroepitaxy between the nanostructure and the substrate. Arrow indicates the interface position. The uneven background is due to the ion beam damage introduced during FIB lift-off procedure.

For BTO nanopatterns, it is essential to investigate the nature of the ferroelectric-electrode interface (i.e., BTO/SRO), which is expected to have a significant effect on interfacial strain and the ferroelectric properties in sub-100 nm thick structures.¹⁷¹ The chemical constituent

distribution of BTO pyramids at the interface is analyzed using electron energy loss spectroscopy (EELS) under the STEM mode. The spectra are collected at 9 nm interval across a $260 \times 300 \text{ nm}^2$ area (with a nominal electron probe size of $\sim 0.2 \text{ nm}$) that covers one BTO pattern and the underlying SRO/STO (cross-section sample). Figure 3.11 shows the elemental map constructed using EELS spectrum imaging with Ba ($M_{4,5}$), Ti ($L_{2,3}$) and C (K) edges. It clearly identifies the constituent elements of the nanostructure and does not imply any noticeable diffusion of Ba or Ti into SRO or STO, even after high temperature annealing.

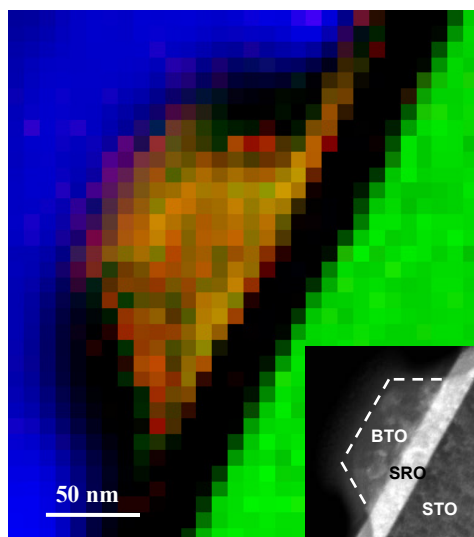


Figure 3.11: EELS map across one BTO pattern showing the chemical constituent distribution. The color scheme is set as: green=Ti ($L_{2,3}$ edges), red=Ba ($M_{4,5}$ edges), blue=C (K edge; carbon is introduced during TEM sample preparation), which brings a yellowish hue to the BTO pattern. The black layer under BTO pattern corresponds to the SRO film. Inset shows the corresponding dark field STEM image of the pattern. Pattern edge is indicated by the dash line.

Piezoelectric behavior of the BTO nanopatterns is confirmed with piezo-response force microscope (PFM) on a Nanoscope IV-Dimension 3100 AFM instrument. The AFM is equipped

with a signal access module and an external lock-in amplifier (Signal Recovery Model 5210). Pt/Ti coated conductive AFM probes (NSC 18, MickroMasch) with a nominal force constant of 3 N/m are used to apply dc or ac signal on and collect the piezo-response from the nanopatterns. Figure 3.12 is a phase-bias hysteresis loop obtained from one BTO disc pattern. The 180° phase change with *dc* bias changing from negative to positive clearly verifies the piezoelectric behavior. An overall shift of the hysteresis loop toward the positive bias is observed, which may be attributed to the polarization pinning due to either mechanical stress or trapped electronic charges near the interface. Such polarization pinning has been observed in thin film ferroelectrics and is still a subject of active study.^{71, 172, 173}

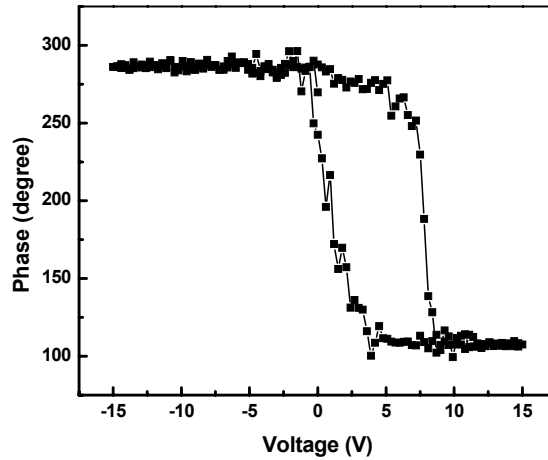


Figure 3.12: Bias-phase hysteresis loop obtained with PFM from one BTO disc pattern with 200 nm width on SRO/STO substrate.

As demonstrated above, the critical aspect ratio for different material/substrate systems can be estimated based on their lattice mismatches and mechanical parameters. The estimation can be then used as gauge to help design the pattern dimension in order to achieve epitaxy. Patterns

obtained this way not only possess very uniform shape and size, but a highly-aligned crystalline orientation dictated by the substrate. This is particularly important for materials with crystalline-anisotropic properties, of which CFO and BTO are good examples.

Epitaxial conversion from amorphous phase for functional oxide 0D structures by using appropriate heating condition has also been observed by Ma *et. al.*,²⁵ in their attempt of depositing BaTiO₃ and SrBi₂Ta₂O₉ using room temperature pulsed laser deposition (PLD) over self-organized latex spheres. However only hexagonal ordering can be achieved due to the nature of the sphere arrangement, and the pattern thickness is limited. Szafraniak *et. al.* have reported fabrication of Bi₂O₃ and PZT discrete nano-islands using the so-called “microstructural-instability” of ultra-thin film derived from liquid precursors.¹⁰⁵ The nanostructures obtained this way exhibit a random site distribution and significant shape variation.^{174, 175} It has been proposed that the registration and the shape of the islands can be tuned by engineering the strain fields in the substrates and adjusting the film deposition condition, separately. However these approaches may see practical challenges. These results project the great potential of using low temperature methods to deposit oxide materials followed by the microstructural engineering to achieve desired crystallinity. On the other hand, they underscore the necessity of acquiring a true patterning technique in order to guarantee the dimension uniformity. The e-beam lithography based strategy proposed in our work therefore may provide a practical solution to this dilemma.

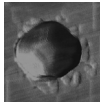
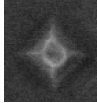
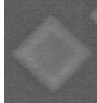
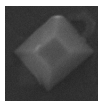
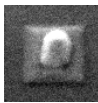
3.5 FACETED SHAPE DEVELOPMENT AND PATTERNING-CONTROLLED MORPHOLOGY

It is interesting to notice the well-defined truncated pyramid shape for CFO/MgO and BTO/SRO/STO systems. In this section, we discuss the possible reasons that account for this pyramid shape development, and propose that patterning-controlled morphology can be obtained for VP-soft-eBL obtained 0D and 1D nanostructures.

3.5.1 Faceted shape development for different material/substrate systems

During the single crystal conversion experiments, the out-of-plane orientations of the patterns are dictated by the underlying single crystal substrate if the lattice mismatch is moderate. Therefore most single crystal patterns exhibit $\{001\}$ top facets, given the (001) single crystal used in this study (the (110) GSO and DSO substrates can be considered as (001) orientation for a distorted perovskite). However, the side facets and the bottom edge orientations for different material/substrate systems may vary. This variation is summarized in table 3.3 from observations made on 200 nm-diameter disc patterns annealed under the same condition, i.e., 1000 °C for 4 hr. The side facets are determined by measuring the angle between the side and bottom in AFM.

Table 3.3 Morphology development for different material/substrate systems

System	CFO/STO	CFO/MgO	BTO/GSO	BTO/SRO/STO	BTO/STO
Lattice mismatch	-6.9%	0.39%	-0.68%	-1.9%	-2.3%
Side facets	Some with $\{111\}$ and $\{100\}$; others not defined	All $\{111\}$	$\{111\}$ dominates	$\{111\}$ dominates	Not defined ¹⁾
Bottom edge	Some $\langle 110 \rangle$	$\langle 110 \rangle$	$\langle 110 \rangle$	$\langle 110 \rangle$	$\langle 100 \rangle$
Typical image²⁾					

¹⁾ BTO/STO: the angle between the side facets and the bottom substrate varies between 40°~65°.

²⁾ All image frames are aligned with $\langle 100 \rangle$ directions of the substrates for comparison

The bottom edges of the crystallized patterns are essentially the intercepts of side facets and the bottom surface. We notice from table 3.3 that systems with low lattice mismatch (i.e., CFO/MgO, BTO/GSO and BTO/SRO/STO) seem to present consistent $\{111\}$ side surfaces and therefore $\langle 110 \rangle$ edges, probably due to the low free surface energy of $\{111\}$. However systems with larger lattice mismatches (CFO/STO and BTO/STO) show less defined side facets development. One can understand this difference by considering that the total amount of energy supply (by the heat treatment) for the sol-derived system is consumed in both directions: i.e., to achieve structural transformation (nucleation, grain growth and densification) and to achieve the free surface arrangement that is thermodynamically favored. Larger lattice mismatch implies

larger amount of energy has to be consumed in the structural change to accommodate this structural distinction. Therefore the shape development may deviate from the thermodynamically favored form given, the limited annealing time and temperature. The chemical stability of different lattice planes can also contribute to the complexity of the final faceted shape development.¹⁷⁶ The influence of the lattice mismatch on the development of side facets is also reflected in the difference between CFO/STO and CFO/MgO systems. Small $\{100\}$ facets at the four corners of CFO patterns are observed on STO substrate, probably functioning as to minimize the high interface energy between CFO/STO by decreasing the interfacial area. Similar phenomenon has been reported by Zheng *et. al.*¹⁷⁷ on CFO nanopillars self-assembled in BTO matrix during pulsed laser deposition and is explained as incomplete wetting of CFO on the STO substrate.

The morphology variations for different systems suggest that, by changing the material/substrate combination and therefore the misfit strain energy and interfacial energy between them, it is possible to tune the equilibrium shape of the nanopatterns accordingly. This can be readily investigated using VP-soft-eBL, given its high versatility in patterning on a very broad range of substrates.

3.5.2 Patterning controlled morphology of 0D and 1D nanostructures

As discussed above, the patterned system tends to minimize free surface energy by developing specific facets with low free surface energy. This has two interesting implications. First, providing enough BTO material at each patterned site, one may expect the ultimate shape of BTO pattern on SRO to be a pyramid with four $\{111\}$ side planes intersecting at the top corner,

in order to minimize the total surface energy. Given that a and c lattice constants for BTO are very close, patterns developed into pyramid geometry take an aspect ratio of height/width= $c/(\sqrt{2} a) \sim 1/\sqrt{2}$. That is, a pyramid with 200 nm bottom width should have a height of about 143 nm. This can be achieved by increasing the thickness of the eBL resist, which allows more sol precursor to be filled in each patterned trench. Second, the morphology control strategy to obtain 0D nanostructures with well-defined facets can be expanded to fabrication of 1D nanostructures for material systems with high surface energy anisotropy.

We now demonstrate the shape alterations based on the above argument. Shown in figures 3.13(a) and 3.13(b) are the development of a full pyramid versus a truncated pyramid shaped BTO nanostructures on SRO (both with 200 nm bottom width), obtained by patterning with 600 nm-thick and 300 nm-thick resist films, respectively. The AFM analysis (not shown) reveals a 50 nm height for the frustum and a 136 nm height for the pyramid, corresponding well to the estimated 143 nm. In order to verify the morphology development for 1D nanostructures, CFO lines are patterned on MgO substrate. CFO is an ideal example for this purpose, because spinel oxides normally show a strongly anisotropic surface energy due to the complexity in the arrangement of atoms.¹⁷⁸ In these materials the surface energy of $\{111\}$ planes is typically smaller than that for the $\{001\}$ planes by a factor of five, and smaller by a factor of ten than that for the $\{110\}$ planes.^{58, 179} Figures 3.13(c) through 3.13(f) are VP-SEM images of 4 μm -long CFO lines on (100) MgO substrate. When patterned along $\langle 100 \rangle_{\text{MgO}}$, the line develops into a saw-tooth-edged morphology, which can be considered as a group of aligned frustums. However, when patterned along $\langle 110 \rangle_{\text{MgO}}$, the CFO line shows very flat and smooth edges. The single crystallinity of the $\langle 110 \rangle$ lines can be confirmed with AFM phase image (not shown) where no

grain boundary contrast is observed. It has been reported in both micromagnetic simulations and experimental results that edge roughness of elongated magnetic nanostructures may contribute to increased coercivity due to the edge morphology induced spin-state distortions.^{143, 180} Thus, the control strategy of edge roughness and edge morphology for magnetic oxide introduced in this work may provide an interesting test-bed to study such phenomena. Another attribute of this approach is the simplicity of shape control, i.e., the dramatic morphology control of 0D or 1D functional oxide nanostructures is achieved by simply tuning the patterning parameters. This unique capability of soft-eBL to obtain “patterning-controlled morphology” implies a new degree of freedom for the design and fabrication of oxide nanostructures for functional devices.

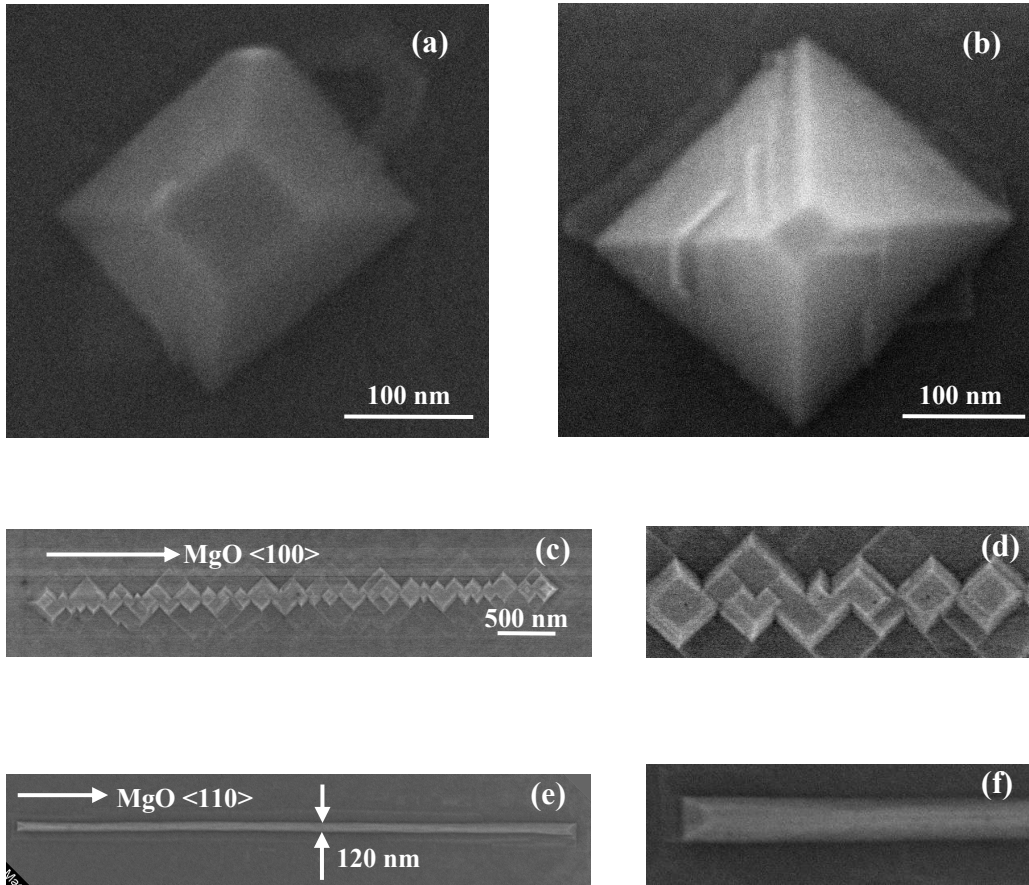


Figure 3.13: (a, b) BTO frustum and pyramid, obtained by patterning with different eBL resist thickness. (c) VP-SEM image of CFO line patterned along $\langle 100 \rangle_{\text{MgO}}$. (d) shows detail of the zig-zag edge. (e) VP-SEM image of CFO line patterned along $\langle 110 \rangle_{\text{MgO}}$. (f) Image of one end of the line showing the faceting detail.

3.6 SUMMARY

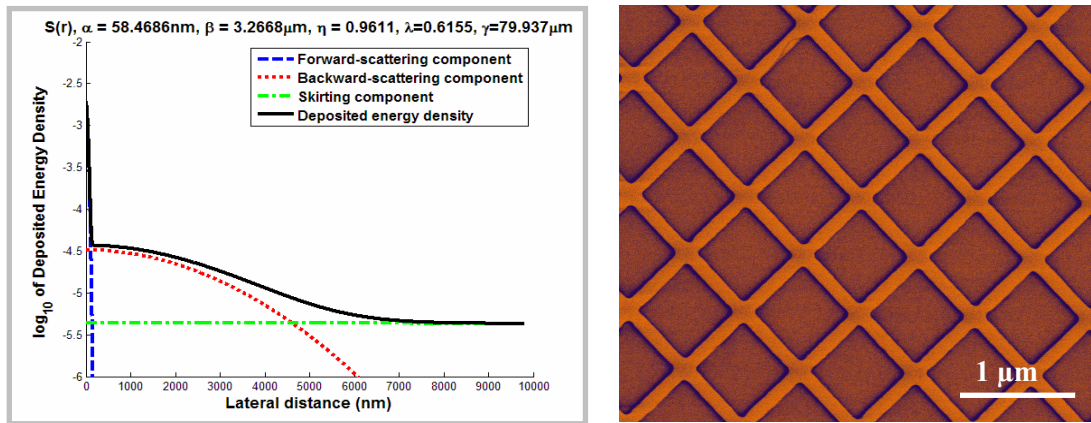
In summary, this chapter shows successful fabrication and site-specific characterization of 0D nanodisc patterns of CFO and BTO on diverse substrates with well-defined size and separation using the VP-soft-eBL approach. We demonstrate that below a certain pattern aspect ratio, the as-deposited amorphous nanodiscs can be readily converted into dense, single-crystal form that exhibit cube-on-cube heteroepitaxy with respect to the underlying single crystal substrate.

For systems with low or moderate lattice mismatch, single-crystal discs develop into truncated-pyramid morphology with defined side facets and edge direction. The mechanism of morphology development with the pattern size change is discussed. Patterning controlled morphology is demonstrated on 0D and 1D nanostructures by simply tuning the patterning parameters such as resist thickness and patterning directions with respect to underlying substrate orientation.

The structural, chemical nature and functional identity of the VP-soft-eBL fabricated nanostructures are probed with a complementary set of characterization tools. The flexibility of the approach described here allows patterning diverse oxides into nano-devices in order to explore their behavior at different length scales. In addition, given its material- and substrate-generalities, the proposed strategy to control the microstructure and morphology of nanostructures via patterning is expected to be applicable to a wide variety of materials systems. It opens up the possibility of fabricating all-oxide heterostructures with novel functionalities, and may pave the way for innovative applications which require nanopatterned architectures.

CHAPTER 4

DETERMINATION OF PROXIMITY FUNCTION IN VP-SOFT-EBL FOR FABRICATION OF 2D HIGH DENSITY FERROELECTRIC GRID



The aim of this chapter is to resolve the pressing challenges in patterning high density 2D nanostructures due to the enhanced proximity effect in VP-eBL. An analytical method is proposed to predict the distribution of the electron energy deposited by the beam skirt in the resist. This method allows estimation of multiple proximity parameters simultaneously based on VP-eBL exposure experiments with simple geometry design. Incorporation of these proximity effects in pattern design and dose compensation enables fabrication of high density 2D ferroelectric grid structures with precise dimension control.

The work demonstrated in this chapter will be presented on **2008 Microscopy and Microanalysis Meeting**.

4.1 VP-SOFT-EBL FOR 2D GRID PATTERNS

As discussed in chapter 1, geometric parameters (including shape, size and aspect ratio) of substrate-integrated patterns have vital influence on the constraint condition in the system, and consequently, its performance related to the stress or strain. Developing the multi-dimensional patterning capability of VP-soft-eBL will greatly enhance the versatility of this nanofabrication approach and help establish the preparation-structure-property relationship for a patterned system. Three typical nanopatterned geometries in different dimensionalities are illustrated in figure 4.1.

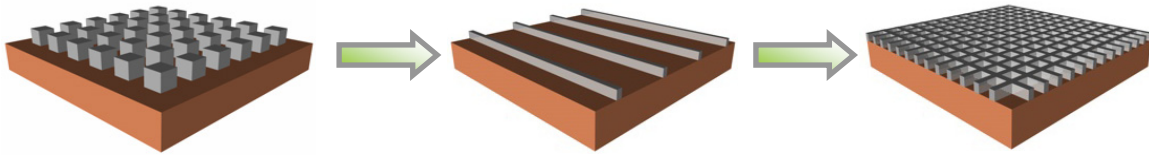


Figure 4.1: Schematic diagram of 0D, 1D and 2D nanopatterns

It is worth pointing out that the artificial-lattice-like 2D geometry shown in figure 4.1 is of particular interest to probe the accommodation of magnetic or electric moments in a geometrically frustrated system. “Geometrical frustration” refers to the phenomenon in accommodation of spins or dipoles on a geometric framework. When the intrinsic interaction between neighboring spins or dipoles is incompatible with the lattice symmetry, equal energy states exist in term of moments arrangement on the lattice topology. Geometrical frustration contributes to interesting intrinsic properties of many complex oxides, such as sensitivity of

electric properties to magnetic field. These oxides include perovskites RMnO_3 ,¹⁸¹ RMn_2O_5 (R: rare earths),¹⁸² $\text{Ni}_3\text{V}_2\text{O}_8$,¹⁸³ delafossite CuFeO_2 ,¹⁸⁴ Spinel CoCr_2O_4 ,¹⁸⁵ MnWO_4 ,¹⁸⁶ and hexagonal ferrite $(\text{Ba}, \text{Sr})_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$.¹⁸⁷ A practical way to directly probe such dipole-dipole or spin-spin interaction is to create an artificial lattice and find out how the spontaneous magnetization or polarization locally accommodates the geometric topology. Towards this end, previous workers have demonstrated recently that arranging magnetic permalloy nano-islands into an artificial lattice leads to certain spin arrangement distribution.^{188, 189} As an obvious extension to this effort, patterning of ferroelectric oxides into similar 2D grid structure may serve as a perfect analogy to study the dipole arrangement on such geometry.

To precisely mimic the dipole interaction on crystal lattice, an ideal ferroelectric 2D artificial lattice structure should satisfy the following: 1) uniform line width and thickness throughout the patterned area to eliminate any dimension-induced perturbation; 2) line width comparable to ferroelectric typical single domain size; 3) small periodicity to ensure the effective interaction between neighboring domains and to facilitate statistical observation on the order parameter arrangement; 4) controlled microstructure of the pattern. Particularly, in-plane polarization along the grid longitudinal direction is preferred. That is, the nanofabrication technique has to provide the capabilities of both high spatial resolution patterning and microstructural engineering. The 2D grid pattern therefore is an ideal application for VP-soft-eBL approach.

When attempting to apply VP-soft-eBL on the 2D high density grid, one may expect a major challenge from the proximity effect. It is known that dense pattern fabrication in eBL normally suffers from the electron proximity effect, as the incident electron beam is scattered by

the resist and the substrate. The scattering of electrons contributes to undesired exposure of a resist in regions adjacent to those actually addressed by the e-beam, causing lower dose contrast and wider feature size than designed.^{190, 191} Under VP-eBL conditions, the proximity effect is further complicated by the beam skirting phenomenon.¹²⁵ In order to pattern the high density 2D grid with precise control over dimension and shape, the exposure profile has to be modified through a quantitative understanding of the proximity effect in VP-eBL. In particular, the contribution of the beam skirt effect has to be characterized.

On the other hand, although VP-SEM has been widely used for imaging insulating samples since 1990s, the application of VP-SEM in eBL patterning has been a very recent endeavor. Investigation of the beam skirt influence on VP-eBL patterning has been particularly scarce. From this point of view, it is imperative to develop analytical method to characterize the VP-eBL process. The two-fold importance of obtaining quantitative understanding of the proximity effect in VP-eBL is the main motivation for the work reported in this chapter.

In the following sections, we present a facile approach for obtaining statistically averaged proximity parameters with good precision. Using Expectation-Maximization algorithm, quantitative understanding on the extent of proximity effect in high vacuum is obtained by fitting analytical equations related to the so-called “proximity function” to experimental results. The proximity function is then modified to include the contribution of beam skirt effect. The fitting results are then used to provide guidance for patterning the 2D high density structures successfully.

4.2 OBSERVATION OF PROXIMITY EFFECT IN PATTERNING HIGH DENSITY 2D GRIDS

A $100 \times 100 \mu\text{m}^2$ area of 2D grid with 100 nm line width and a periodicity of 700 nm has been proposed as the geometric design of the artificial lattice structures. The first attempt is made by patterning BaTiO_3 (BTO) into this geometry on single crystal (001) SrTiO_3 (STO) substrate. The eBL and development conditions are listed in table 4.1.

Table 4.1 Experimental conditions used for patterning the 2D grid shown in figure 4.2

Substrate	(001) STO, coated with 300 nm-thick 950 PMMA resist
Primary beam energy	30 keV
Water vapor pressure	1.5 Torr
Working distance	7 mm (also the beam-gas path length)
Area dose	$400 \mu\text{C}/\text{cm}^2$
Development	MIBK:IPA = 1:3 for 60 sec

This set of conditions has been used to fabricate isolated 0D and 1D nanopatterns on STO with precise size control, i.e., the pre-annealing in-plane dimension of the pattern is very close to the designed value. However, the high density 2D geometry patterned under the same conditions exhibits much larger line width (about 220 nm) than the designed value, as shown in figure 4.2. The expansion is more significant at the node area, causing the dimensional non-uniformity. It should be pointed out that the e-beam only exposes once at each spot inside the designed area. Therefore the expansion at the node is due to the higher aerial density there.

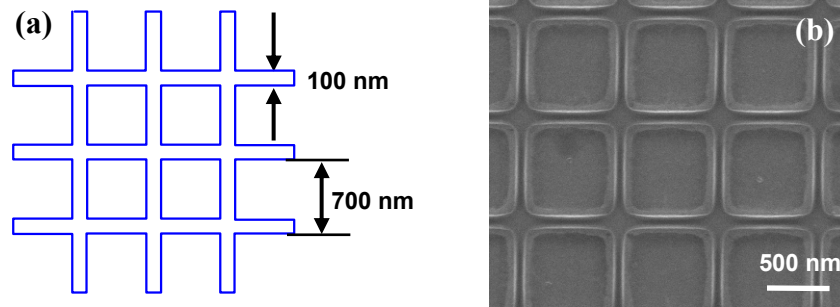


Figure 4.2: (a) A portion of the geometric design of the $100 \times 100 \mu\text{m}^2$ 2D grid. (b) VP-SEM image of BaTiO_3 grid pattern on SrTiO_3 substrate based on the design in (a). The pattern exhibit ~ 220 nm line width and overexposed node areas before annealing.

The wider line width and more severe expansion at the nodes are direct evidences of the “proximity effect” in eBL. In conventional (high vacuum) eBL processes, this effect is mainly induced by the electron forward scattering in the resist film and back-scattering by the substrate. It manifests up to a distance of several microns. In VP-eBL, however, the primary beam is also scattered by the gas molecules above the resist surface (i.e., the beam skirt effect). It can be expected that the proximity effect becomes more severe and the resultant feature widening may span much larger area in VP-eBL. Figure 4.3 illustrates the proximity effect under VP-eBL condition due to multiple contributions from the different scattering mechanisms. Obviously, the addition of the beam skirt significantly modifies the electron energy deposition profile at and near the spot of illumination. Achieving quantitative knowledge about the profile in VP-eBL is of primary concern in order to pattern the high density 2D structure with precision.

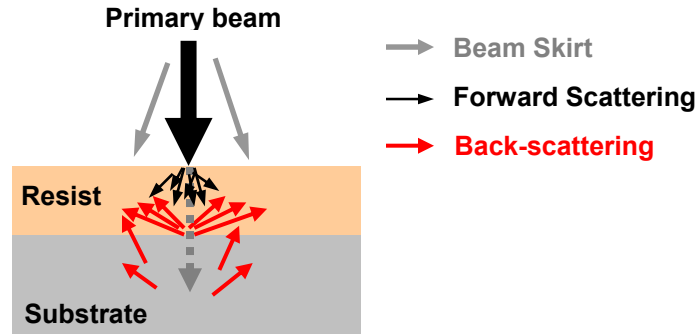


Figure 4.3: Proximity effect due to the primary beam scattering with resist film, substrate and the gas molecules in VP-eBL process.

4.3 PROXIMITY FUNCTION AND PROXIMITY PARAMETERS DETERMINATION

This section focuses on obtaining a quantitative understanding of the proximity effect in VP-eBL. Particularly, concepts of the proximity function in high vacuum eBL (hereafter HV-eBL for short) are briefly introduced in section 4.3.1. Modification of the proximity function in VP-eBL under low vacuum (hereafter LV-eBL for short) is then presented. Section 4.3.2 contains the fitting methodology, problem definition and the fitting results for HV-eBL. The fitting results for LV-eBL and the precise fabrication of 2D grid using the estimated dose are presented in section 4.3.3. Section 4.3.4 provides comments on the Expectation-Maximization algorithm and the implications of this analytical approach in understanding the VP-eBL mechanism.

4.3.1 Proximity function and proximity parameters

4.3.1.1 Proximity function in HV-eBL

In HV-eBL, a model function termed “proximity function” describing the electron scattering process is normally used. The general form of the proximity function is suggested by calculation of the energy deposition of electrons in the resist-substrate system. Theoretical calculations have shown that the proximity function can be approximated with fairly good accuracy by the combination of two components, i.e., the effect of forward scattering of the incident focused electron beam and the backscattering of electrons where the substrate serves as a source.¹⁹² The proximity function $f(r)$ can be written as the sum of two Gaussians in form of

$$f(r) = \frac{1}{(1+\eta)\pi} \left[\frac{1}{\alpha^2} \exp\left(-\frac{r^2}{\alpha^2}\right) + \frac{\eta}{\beta^2} \exp\left(-\frac{r^2}{\beta^2}\right) \right] \quad (4.1)$$

where $r = \sqrt{x^2 + y^2}$ is the lateral distance from point (x, y) to the incidence point of the e-beam in a Cartesian coordinate with the incident point as origin; α represents the characteristic width of forward scattering effect and β that of backward scattering effect; η is the ratio of total energy deposited by the backscattered electrons to that deposited by the forward scattered contribution. Variables α , β , and η are generally referred to as “proximity parameters” since they determine the energy (or electron dose) deposition distribution in the resist and subsequently the extent of the proximity effect for a given resist/substrate system under specific patterning conditions.

The absorbed effective dose Q at the position (x, y) is related to the designed exposure dose E through the convolution of E and $f(r)$ over the exposed area S :

$$Q(x, y) = \iint_S E(x', y') f(x - x', y - y') dx' dy' \quad (4.2)$$

with

$$f(x, y) = f(\sqrt{x^2 + y^2}) = f(r) \quad (4.3)$$

where x' and y' denotes the source point in S . Note the normalization condition

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(x, y) dx dy = 1 \quad (4.4)$$

is assumed in equation 4.1.

4.3.1.2 Modification of the proximity function in LV-eBL

Considering the skirted electrons around the focused probe, the proximity function with skirting effect is proposed to have the following form:

$$s(r) = (1 - \lambda)f(r) + \lambda g(r) \quad (4.5)$$

where λ is the proportion of electrons that are ‘skirted’ or dispersed out of the focused portion, and $g(r)$ corresponds to the impact of the beam skirting effect and has the following form:

$$g(r) = \frac{1}{\pi} \frac{1}{\gamma^2} \exp\left(-\frac{r^2}{\gamma^2}\right) \otimes f(r) \quad (4.6)$$

where $\frac{1}{\pi} \frac{1}{\gamma^2} \exp\left(-\frac{r^2}{\gamma^2}\right)$ is the Gaussian envelope of beam skirting, and γ is the characteristic width of the beam skirt. The impact of the beam skirting, $g(r)$, is the convolution of Gaussian

envelope of beam skirting $\frac{1}{\pi} \frac{1}{\gamma^2} \exp(-\frac{r^2}{\gamma^2})$ and the energy deposition function $f(r)$, since the electrons that are scattered by the gas molecules will also go through forward and backward scattering once hitting the resist and the substrate. The form of $s(r)$ is based on the following considerations: 1) due to the elastic nature of primary electrons scattering by gas molecules,^{193, 194} the kinetic energy loss of skirted electrons can be neglected; 2) the proximity parameters α , β , and η are mainly influenced by the primary energy and the resist/substrate system; 3) Q_c describes the sensitivity of resist to certain development condition. Therefore the value of these four parameters that are applicable to HV-eBL can remain unchanged for LV-eBL, if other processing conditions remain the same.

Typically, the Gaussian envelope of beam skirting is much wider than that of the scattering event with resist and the substrate, i.e., $\alpha \ll \gamma$, $\beta \ll \gamma$. Under this circumstance, the convolution of Gaussian envelope of beam skirting and the energy deposition function can be well approximated by the Gaussian envelope of beam skirting itself, that is:

$$g(r) = \frac{1}{\pi} \frac{1}{\gamma^2} \exp(-\frac{r^2}{\gamma^2}) \otimes f(r) \approx \frac{1}{\pi} \frac{1}{\gamma^2} \exp(-\frac{r^2}{\gamma^2}), \text{ when } \alpha \ll \gamma, \beta \ll \gamma \quad (4.7)$$

Putting equation 4.7 into 4.5, the proximity function with skirting effect can be expressed as:

$$s(r) \approx \frac{1-\lambda}{(1+\eta)\pi} \left[\frac{1}{\alpha^2} \exp(-\frac{r^2}{\alpha^2}) + \frac{\eta}{\beta^2} \exp(-\frac{r^2}{\beta^2}) \right] + \frac{\lambda}{\pi} \frac{1}{\gamma^2} \exp(-\frac{r^2}{\gamma^2}) \quad (4.8)$$

At this point, the task to determine the proper dose required for patternig high density 2d geometry boils down to two steps: first to estimate the proximity parameters α , β , η , γ and λ in

addition to the critical dose Q_c and determine the electron deposition profile $s(r)$ in LV-eBL; then to calculate the nominal dose desired for the specific geometry using the defined $s(r)$.

Theoretical calculations have helped to achieve tremendous understanding of the proximity effect in HV-eBL.¹⁹⁵⁻¹⁹⁷ Simulations based on Monte-Carlo method or Boltzmann transport equation were able to generalize proximity parameters so they could be applicable to a large set of resist and substrate materials. However, proximity parameters α , β , and η are functions not only of the primary beam energy, composition of the resist and substrate materials, but also of development processes which are unique in most applications. Also, the effect of electron beam spot size must be measured for the purpose of simulation. Discrepancy between the simulation result of proximity parameters and experimentally achieved values has been reported, due to empirical processes such as the inclusion of intermediate scattering and the developer effects.¹⁹⁸ This underscores the importance of empirical determination of proximity parameters for proximity effect correction and validation of the modeling results.

4.3.2 Determination of the proximity parameters in HV-eBL

4.3.2.1 Methodology

In principle, one can obtain the proximity parameters empirically following the scheme illustrated in figure 4.4 (using HV-eBL as an example). The key steps involve: (1) Prepare a series of patterns with different dimensions. Square shaped patterns are usually chosen to facilitate dimension measurement. (2) Expose these patterns with different doses. (3) Measure the dimension of the patterns after development. (4) Formulate a system of analytical equations corresponding to equation 4.2 for each pattern developed from the above procedure. To do this,

another variable is introduced as critical dose Q_c . The critical dose is the minimum dose required to develop a pattern and therefore corresponds to the absorbed dose at the edge of the observed pattern. With the knowledge of the designed exposure profile $E(x, y)$ and the edge positions x, y in the developed pattern, a series of equations corresponding to the convolution (equation 4.2) are formulated. Solving these equations provides the fitted value of proximity parameters α, β, η and the critical dose Q_c .

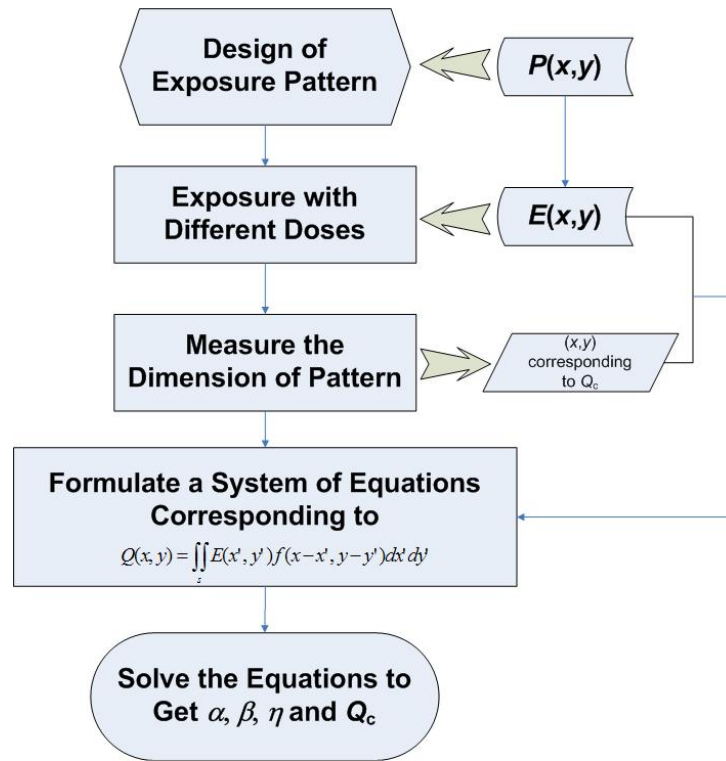


Figure 4.4: Procedure of determining proximity parameters from exposure experiments.
 $P(x,y)$ denotes the mathematic form of the pattern geometry.

The practical complication in this approach is: the analytical equations are highly nonlinear and involve information of all proximity parameters and Q_c simultaneously. Normally, non-

linear least-square fitting is used to estimate all proximity parameters from the equations at the same time.^{199, 200} This process may lead to inaccuracy of the estimation with multiple unknowns.¹⁹² To avoid these problems, effort has been spent on developing special pattern geometry. Examples include the “four-dot” technique²⁰¹ or line-density exposure wedge.¹⁹⁹ The idea is to derive approximate analytical expressions of proximity parameters by tuning the dimension and the exposure dose, so that each proximity parameter can be determined separately. However, obtaining approximation expressions of individual proximity parameter can be a lot more challenging when the number of unobserved data increases. Therefore this approach is not suitable for estimation of proximity effect in LV-eBL, where additional parameters describing beam skirt effect have to be added.

To solve these equations in an efficient manner, we apply an Expectation-Maximization (EM) algorithm for proximity parameters estimation. Particularly, experimental data are collected from exposures in both HV-eBL and LV-eBL at varied doses on two pattern designs, namely periodic line arrays and grid pattern. Using the data in HV-eBL, values of α , β , η and Q_c are first determined using alternating EM algorithms. These parameters are then applied in another EM algorithm to determine γ and λ and the modified proximity function for LV-eBL. Finally the desired nominal dose for specific geometry is estimated based on the fitting results of $f(r)$ and $s(r)$.

4.3.2.2 Pattern geometry and problem definition

The two sets of pattern geometries are designed as: (1) A series of parallel lines that are 100 nm wide, 6 μm long, and 5 μm separated from each other. This pattern is denoted as $P_{\underline{L}}$. (2) A

grid with perpendicular lines. Lines width is still 100 nm; periodicity of the grid is 700 nm. The grid spans across $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ area. This pattern is denoted as P_G . Figure 4.5 shows schematic drawings of the two patterns and the selection of the Cartesian coordinate.

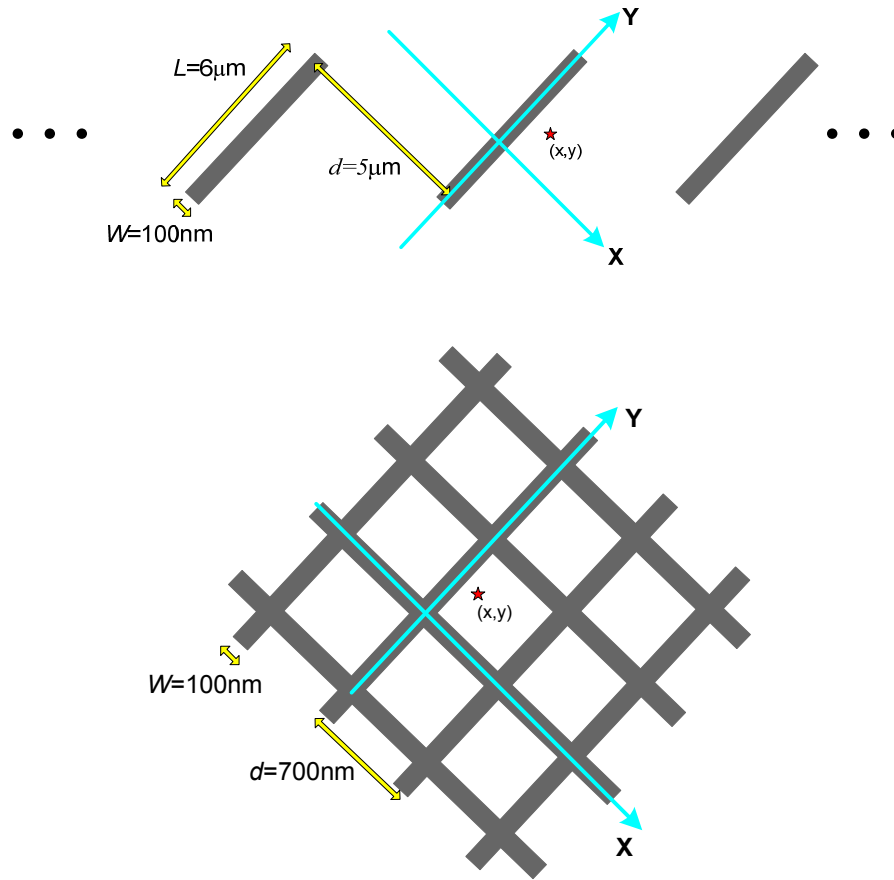


Figure 4.5: Schematic diagram of the two pattern designs.

Up: Pattern P_L ; Bottom: Pattern P_G .

The mathematical forms of the two patterns are as follows:

$$P_{-L} = \sum_{i=-K}^K U(x-i \cdot d, y), \text{ where } K \text{ is the number of lines to the left and right of origin, } d \text{ is}$$

the line spacing, and $U(x, y)$ is the functional form for one line, i.e.,

$$U(x, y) = \begin{cases} 1, & -\frac{W}{2} \leq x \leq \frac{W}{2}, -\frac{L}{2} \leq y \leq \frac{L}{2}, \\ 0, & \text{otherwise} \end{cases} \text{ where } W \text{ is line width and } L \text{ is line length.}$$

$$P_{-G} = \sum_{i=-K}^K U_x(x-i \cdot d, y) + \sum_{j=-N}^N U_y(x, y-j \cdot d), \text{ where } K \text{ is the number of lines to the left and}$$

right of origin in x direction and N for y direction, d is the line spacing. $U_x(x, y)$ is the functional form for one line in y direction and $U_y(x, y)$ is the functional form for one line in x direction:

$$U_x(x, y) = \begin{cases} 1, & -\frac{W}{2} \leq x \leq \frac{W}{2}, -\frac{L}{2} \leq y \leq \frac{L}{2}, \\ 0, & \text{otherwise} \end{cases}$$

$$U_y(x, y) = \begin{cases} 1, & -\frac{L}{2} \leq x \leq \frac{L}{2}, -\frac{W}{2} \leq y \leq \frac{W}{2} \\ 0, & \text{otherwise} \end{cases}$$

Both patterns are exposed in HV-eBL and LV-eBL respectively on Si substrate (coated with 300 nm thick PMMA resist). For each set of pattern, a series of exposure experiments with doses increasing from 300 to 600 $\mu\text{C}/\text{cm}^2$ with step size of 37.5 $\mu\text{C}/\text{cm}^2$ are carried out. The other instrumental parameters remain the same as described in table 4.1. Patterns are transferred to the substrate via lift-off processing (through deposition of a 20 nm-thick Au/Pd thin film). The line widths in both P_{-L} and P_{-G} patterns exposed under different designed doses are imaged and measured in SEM. The line width in the grid pattern is measured from the center position between two neighboring nodes so that the influence from the node geometry is minimized.

The mathematical description of this estimation process is as follows. For each pattern with a form $P(x, y)$ that is exposed under a series of area doses $\{Q_s, s = 1 \sim S\}$, the designed exposure profile is $E(x, y) = Q_s \cdot P(x, y)$. The developed lines expand beyond the targeted width of W (in both cases 100 nm) due to the proximity effect. Different beam dose leads to different degree of line expansion. The line expansions under different doses are denoted as $\{e_s, s = 1 \sim S\}$. Each e_s (in nm) represents the expansion on one side of a line under dose Q_s , hence the developed line width is $(W + 2e_s)$ nm. The problem is to estimate the proximity parameters and Q_c to form the proximity function from the designed experiments above.

4.3.2.3 Determination of α , β , η and Q_c with Expectation-Maximization algorithm

In this section, fitting approach for HV-eBL to obtain α , β , η and Q_c with alternating EM algorithm is demonstrated.

(1) Computation of the effective dose

For each point (x, y) in the defined coordinate system, effective dose $Q(x, y)$ is determined by the convolution of the pattern function P and the proximity function $f(r)$. For example, the convolution corresponding to the line pattern is shown below in equation 4.9 (detailed deduction of the final form of $Q(x, y)$ is included in appendix 4.1).

$$\begin{aligned}
Q(x, y) &= Q_s \int_u \int_v P_{-LHV}(x-u, y-v) f(u, v) du dv \\
&= Q_s \sum_{i=-K}^K \frac{1}{4(1+\eta)} \left[\left(\operatorname{erf}\left(\frac{x-id+W/2}{\alpha}\right) - \operatorname{erf}\left(\frac{x-id-W/2}{\alpha}\right) \right) * \left(\operatorname{erf}\left(\frac{y+L/2}{\alpha}\right) - \operatorname{erf}\left(\frac{y-L/2}{\alpha}\right) \right) \right. \\
&\quad \left. + \eta \left(\operatorname{erf}\left(\frac{x-id+W/2}{\beta}\right) - \operatorname{erf}\left(\frac{x-id-W/2}{\beta}\right) \right) * \left(\operatorname{erf}\left(\frac{y+L/2}{\beta}\right) - \operatorname{erf}\left(\frac{y-L/2}{\beta}\right) \right) \right] \quad (4.9)
\end{aligned}$$

where $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2) dt$ is the error function.

Similarly for the grid pattern, the effective dose $Q(x, y)$ is given by equation 4.10 (detailed deduction in appendix 4.1):

$$\begin{aligned}
Q(x, y) &= Q_s \int_u \int_v P_{-GHV}(x-u, y-v) f(u, v) du dv \\
&= \frac{Q_s}{4(1+\eta)} \left[\sum_{i=-K}^K \left\{ \left(\operatorname{erf}\left(\frac{x-id+W/2}{\alpha}\right) - \operatorname{erf}\left(\frac{x-id-W/2}{\alpha}\right) \right) * \left(\operatorname{erf}\left(\frac{y+L/2}{\alpha}\right) - \operatorname{erf}\left(\frac{y-L/2}{\alpha}\right) \right) \right. \right. \\
&\quad \left. \left. + \eta \left(\operatorname{erf}\left(\frac{x-id+W/2}{\beta}\right) - \operatorname{erf}\left(\frac{x-id-W/2}{\beta}\right) \right) * \left(\operatorname{erf}\left(\frac{y+L/2}{\beta}\right) - \operatorname{erf}\left(\frac{y-L/2}{\beta}\right) \right) \right\} \right. \\
&\quad \left. + \sum_{j=-N}^N \left\{ \left(\operatorname{erf}\left(\frac{x+L/2}{\alpha}\right) - \operatorname{erf}\left(\frac{x-L/2}{\alpha}\right) \right) * \left(\operatorname{erf}\left(\frac{y-jd+W/2}{\alpha}\right) - \operatorname{erf}\left(\frac{y-jd-W/2}{\alpha}\right) \right) \right. \right. \\
&\quad \left. \left. + \eta \left(\operatorname{erf}\left(\frac{x+L/2}{\beta}\right) - \operatorname{erf}\left(\frac{x-L/2}{\beta}\right) \right) * \left(\operatorname{erf}\left(\frac{y-jd+W/2}{\beta}\right) - \operatorname{erf}\left(\frac{y-jd-W/2}{\beta}\right) \right) \right\} \right] \quad (4.10)
\end{aligned}$$

(2) Expectation-Maximization algorithm

As stated previously, for each nominal dose Q_s , the developed pattern is expanded to a certain extent e_s . For a point $(\frac{W}{2} + e_s, \frac{d}{2})$ on the extended line boundary, the absorbed effective dose is $Q(\frac{W}{2} + e_s, \frac{d}{2})$. Solving the following non-linear least square problem gives the maximum-likelihood estimate of the parameters of $f(r)$, based on the series of experiments with increasing beam doses $\{Q_s, s = 1 \sim S\}$:

$$(\alpha, \beta, \eta) = \arg \min_{\alpha, \beta, \eta} \sum_{s=1}^S \left| Q\left(\frac{W}{2} + e_s, \frac{d}{2}\right) - Q_c \right|^2 \quad (4.11)$$

where each Q is given by equation 4.9 or 4.10 and Q_c is the critical dose.

In principal, either the line pattern or the grid pattern can be used in equation 4.11 to estimate the parameters. In practice, since the backscattering characteristic width is normally much larger than that of the forward scattering, we may anticipate more prominent backscattering effect for the high density grid pattern. Therefore it is expected that the fitting with data obtained from line pattern will give a better estimate of α , and that from the grid pattern will give a better estimate of β and η . However, all these parameters are involved simultaneously in the analytical equations. Therefore, when estimating α from the line pattern, β and η should be known beforehand and vice versa. This “chicken-and-egg” problem is solvable with an elegant Expectation-Maximization (EM) algorithm.

An EM algorithm is used in statistics for finding the maximum-likelihood estimates of parameters of an underlying distribution from a give data set, where the data is incomplete or partially observed. EM alternates between performing an expectation step (E-step), which computes an expectation of the likelihood by including the latent variables as if they were observed, and a maximization step (M-step), which computes the maximum likelihood estimates of the parameters by maximizing the expected likelihood found on the E-step. The parameters found on the M-step are then used to begin another E-step. The E-step and M-step are iterated as necessary, until convergence and a predefined maximum number of iteration is reached.

Mathematic specification of the EM procedure is introduced below.

Let X denote incomplete data consisting of values of observable variables. Let Y denote the missing data. X and Y together forms complete data $Z=(X, Y)$. Also assume Z takes the following joint distribution:

$$p(Z|\Theta) = p(X, Y|\Theta) = p(Y|X, \Theta)p(X|\Theta) \quad (4.12)$$

where Θ is the set of parameters of the distribution. The EM algorithm first finds the expected value of the complete-data log-likelihood $\log p(X, Y|\Theta)$ with respect to the missing data Y , given the observed data X and the current parameter estimates, *i.e.*, the following auxiliary function can be defined as

$$K(\Theta, \Theta^{i-1}) = E[\log p(X, Y|\Theta) | X, \Theta^{i-1}] = \int_{y \in Y} \log p(X, y|\Theta) p(y|X, \Theta^{i-1}) dy \quad (4.13)$$

where Θ^{i-1} is the parameter estimates of iteration $i-1$, and $p(y|X, \Theta^{i-1})$ is the marginal distribution of the missing data, given the observed data and the current parameter estimates.

The above procedure is the E-step of the EM algorithm. The second step, M-step, is to maximize the above expectation $K(\Theta, \Theta^{i-1})$, i.e., to find the optimal parameter estimates for iteration i as follows:

$$\Theta^i = \arg \max_{\Theta} K(\Theta, \Theta^{i-1}) \quad (4.14)$$

(3) Application of EM in proximity parameter determination in HV-eBL

To employ the E-M algorithm on our problem, two EM iterations are used: one EM estimates α and Q_c from the line pattern (P_L) with β and η as unobserved data, the other E-M estimates β and η from the grid pattern (P_G) with α and Q_c as unobserved. Using the first E-M as an example, here the incomplete data X is the set of line width expansion $\{e_s, s = 1 \sim S\}$ for P_{LHV} and the missing data are β and η , whereas $\Theta = \{\alpha, Q_c\}$. The marginal distribution $p(y|X, \Theta^{i-1})$ in equation 4.9 therefore is now $p(\beta, \eta | \{e_s\}, \alpha^{i-1}, Q_c^{i-1})$. Similarly for the second EM in which α and Q_c are the missing data, the marginal distribution is in form of $p(\alpha, Q_c | \{e_s\}, \beta^{i-1}, \eta^{i-1})$. For each of the two EMs, these marginal distributions can be assumed as Dirac distributions in practice for simplicity. A better estimate of these marginal Gaussian distributions will surely improve the accuracy of the estimates. In the M-step, assuming $p(X, y | \Theta)$ is a Gaussian, i.e., assuming the observed data is corrupted with independent white

noise, the M-step in equation 4.14 boils down to the non-linear least square form as in equation 4.11. The detailed derivation of EM is presented in appendix 4.2.

(4) Experimental data and EM fitting results

The change of average line width ($W+2e_s$) with increasing designed dose Q_s under HV-eBL condition is plotted in Figure 4.6. The red lines are the linear fitting of the trend. The line width expansion can be observed throughout the dose range for both P_L and P_G . The proximity effect manifests itself in the high density P_G by causing much larger expansion and the higher rate of width increase with Q_s . From the exposure experiments, $\{e_s, s = 1 \sim S\}$ values for both patterns are determined and used in the estimation.

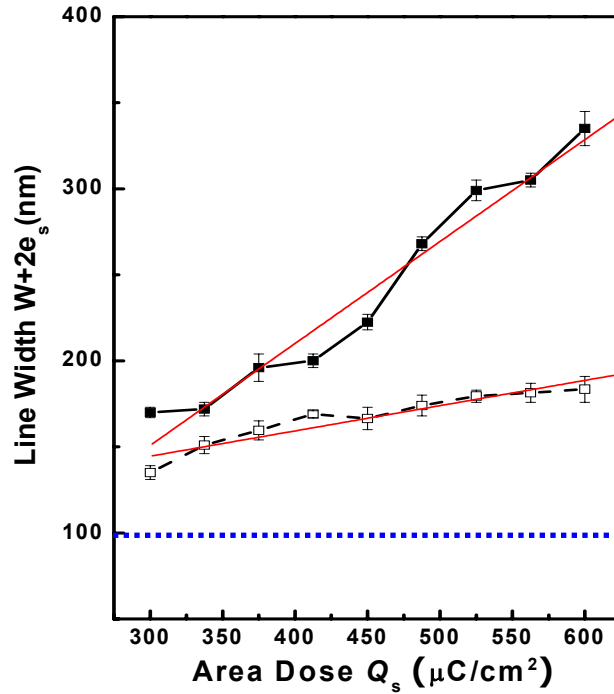


Figure 4.6: Line width expansion with increasing designed area dose for patterns P_L (open squares) and P_G (filled squares). Blue line indicates the designed width $W = 100$ nm.

With the two EMs alternating between the line pattern and grid pattern data with different incidence beam doses, the estimated parameters of the proximity function $f(r)$ are: $\alpha = 58.4686$ nm, $\beta = 3.2668$ μm , $\eta = 0.9611$. The estimated value of critical dose $Q_c = 65.7438$ $\mu\text{C}/\text{cm}^2$.

Our fitting results have been compared with reported values obtained using empirical methods. Table 4.2 summarizes data from patterning on Si wafer coated with PMMA resist of different thickness (t) and under different primary beam energy (kV). In all cases in table 4.2, the MIBK/IPA solution is used as developer. Since proximity parameters are highly dependent on the eBL operational conditions and the development procedure, it is hard to compare the specific values obtained from one's experiment with that of others directly. However, data shown in table 4.2 can provide a range in which the fitted values of proximity parameters are reasonable if the trends of these values changing with operational conditions are known. For example, α is found to increase with higher resist depth/thickness.¹⁹⁸ It has also been reported that α decreases for higher primary beam energy E following $\alpha = A \cdot E^B$ (A and B are functions of resist material and thickness).¹⁹⁷ Therefore, we may expect from table 4.2 that the value of α in our experiments ($t = 300$ nm; kV = 30) ranges between 50~70 nm. On the other hand, β is proportional to the incident electron energy to the 1.7 power but nearly independent of the resist depth, whereas η is not sensitive to the beam energy.²⁰² Therefore, β is likely to be between 2~4 μm , and η should be around 0.7~0.9. The above argument confirms that the fitting results from our two alternating EMs are reasonable.

Table 4.2 Reported values of α , β , η and Q_c from literature^{197, 199, 202, 203}

t (nm) kV	100	220	250	500	
	0.7 ~ 0.8	0.79	–	0.861	η
15	–	$\alpha = 270 \text{ nm}$ $\beta = 1.11 \mu\text{m}$ $Q_c = 60 \mu\text{C}/\text{cm}^2$	–	–	α, β, Q_c
20	$\beta \sim 2 \mu\text{m}$	–	–	$\alpha = 198 \text{ nm}$ $\beta = 2.15 \mu\text{m}$	
30	$\beta \sim 4 \mu\text{m}$	–	$\alpha \leq 50 \text{ nm}$	$\alpha = 60 \sim 70 \text{ nm}$	

The following figures plot the corresponding $f(r)$. The horizontal axes of figures 4.7(a) and (b) are the lateral distance r , and the vertical axes are the deposited energy density at r , shown in $\log_{10}$ scale. The whole two-dimensional energy deposition profile therefore can be obtained by 360° -rotation of $f(r)$ around vertical axis. As can be seen, forward-scattering contributes mainly to short-field proximity effect, while far-field proximity effect can be mainly attributed to the backward-scattering, with β around 56 times larger than α .

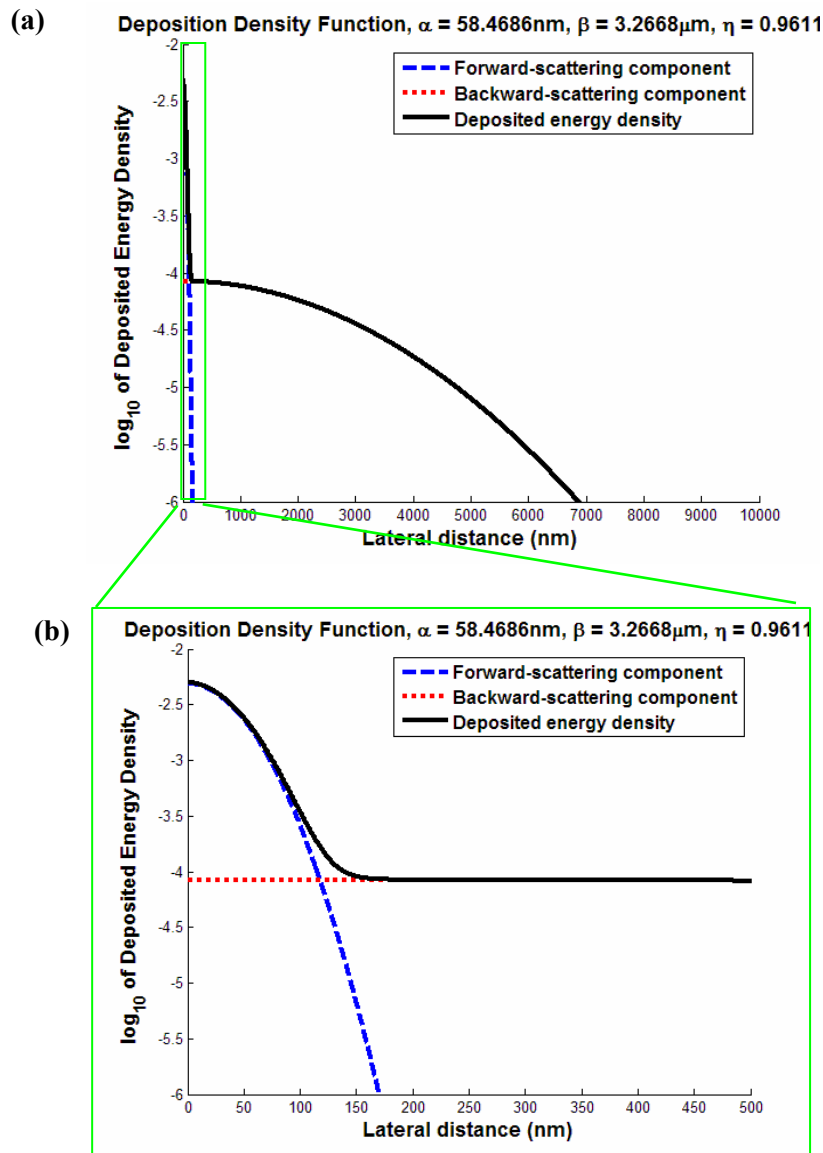


Figure 4.7: Energy deposition function $\log_{10}f(r)$ for the specific *e*BL patterning and development conditions used in the experiments, with $\alpha = 58.4686\text{ nm}$, $\beta = 3.2668\mu\text{m}$, and $\eta = 0.9611$. Figure 4.7(b) shows the magnified portion of (a) encircled by the green lines.

4.3.3 Estimation of the skirting effect in LV-eBL

In this section, experimental data and estimation result for deduction of proximity function in LV-eBL are demonstrated.

4.3.3.1 Experimental observation of patterning in LV-eBL

The line pattern and grid pattern described in figure 4.5 are patterned under LV-eBL using 1.5 Torr water vapor pressure. Change of average line width ($W+2e_s$) with increasing designed dose Q_s is measured. To demonstrate the effect of the low chamber pressure, the measured data are plotted together with the result from HV-eBL in figure 4.8. Here the line and grid patterns are referred to as P_{LHV} and P_{GHV} in HV mode, whereas P_{LLV} and P_{GLV} in LV mode, respectively. Two facts are observed for the low-vacuum experiments. First, the developed patterns are narrower than those developed under the same doses in the HV conditions, for both line and grid geometries. In fact, for nominal doses lower than $337.5 \mu\text{C}/\text{cm}^2$ in case of P_{GLV} and $450 \mu\text{C}/\text{cm}^2$ in case of P_{LLV} , pattern dimensions are smaller than 100 nm. This should be attributed to the attenuation of the received beam current at exposed area due to the beam skirt effect. Second, the value of $[e_s(P_{GLV}) - e_s(P_{LLV})]$ is larger than $[e_s(P_{GHV}) - e_s(P_{LHV})]$. This is considered to be the accumulating effect of the beam skirt. Although the applied dose is dispersed due to skirting, the skirted electrons are accumulated to a significant amount to make important contribution to the received energy in the resist for a dense pattern over a large area ($100 \times 100 \mu\text{m}^2$). From the above argument it can be noticed that the beam skirting effect has to be included in the proximity function for LV-eBL, in order to characterize the process precisely and fabricate nanostructures with high accuracy.

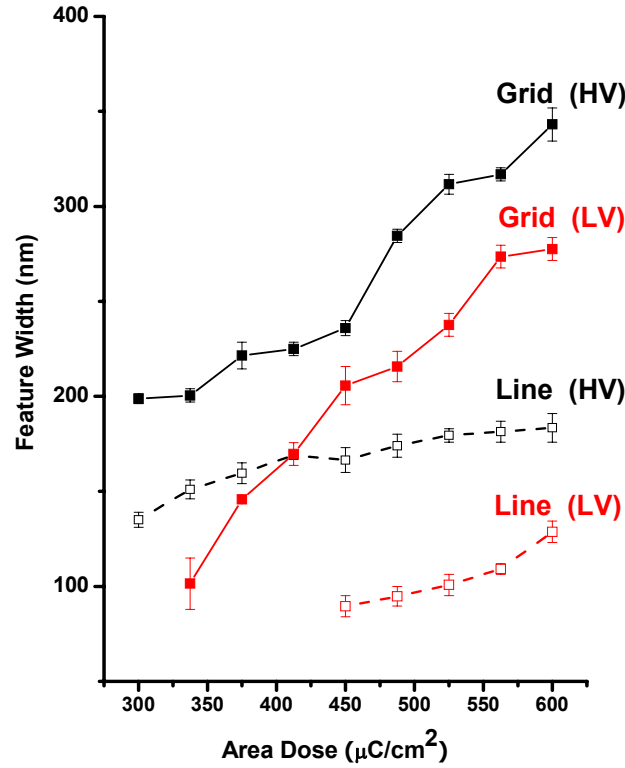


Figure 4.8: Comparison of line width change with area dose Q_s between high vacuum and low vacuum (1.5 Torr) conditions.

4.3.3.2 Determination of γ and λ with EM algorithm

The proximity function with skirting effect is proposed to have the form shown in equation 4.8, where λ is the proportion of electrons that are ‘skirted’, and γ is the characteristic width of the skirting effect. To estimate the values of γ and λ , the estimated parameters $\alpha = 58.4686$ nm, $\beta = 3.2668$ μm , $\eta = 0.9611$ and $Q_c = 65.7438$ $\mu\text{C}/\text{cm}^2$ are inserted in the expression of $s(r)$. The framework of two alternating EMs can be used again, with one EM aims at learning λ from the

line pattern in low-vacuum assuming γ is unobserved, while the other aims at learning γ from the grid pattern assuming λ is unobserved.

The fitting result gives $\lambda = 0.6155$, $\gamma = 79.937 \mu\text{m}$. That is, the low-vacuum environment generates a very broad beam skirt, with a characteristic width of nearly $80 \mu\text{m}$. Further, a more frequently used parameter that describes the significance of the electron-gas interaction, $r_{0.5}$, can be deduced. The parameter $r_{0.5}$, also referred to as the half width radius, is defined as the radius in the plane of the electron impact that contains 50% of the skirt electrons.^{127, 204} With the Gaussian envelop determined by the estimated value of γ , $r_{0.5}$ under our experimental conditions is calculated to be $66.5519 \mu\text{m}$. This value is consistent with the calculated results from Newbury's work,²⁰⁵ where a half width radius of $63.76 \mu\text{m}$ is deduced for conditions of 30 keV primary beam energy, 7 mm working distance, 200 Pa (~ 1.5 Torr) of water vapor and room temperature (300 K).

With the knowledge of all the proximity parameters, the corresponding energy density deposition function $s(r)$ is plotted in figure 4.9. Comparing with HV-eBL condition shown in figure 4.7, it can be clearly seen that energy deposited near the spot of illumination is lower in LV-eBL due to the scattering induced local dose attenuation, but at a larger scale, the beam skirt contributes to a very large and diffusive background extending far away from the spot of incidence. This corroborates the postulation proposed at the beginning of this chapter, that is, a significant amount of injected dose is dispersed out in the air and the skirting effect leads to deterioration of the developed patterns.

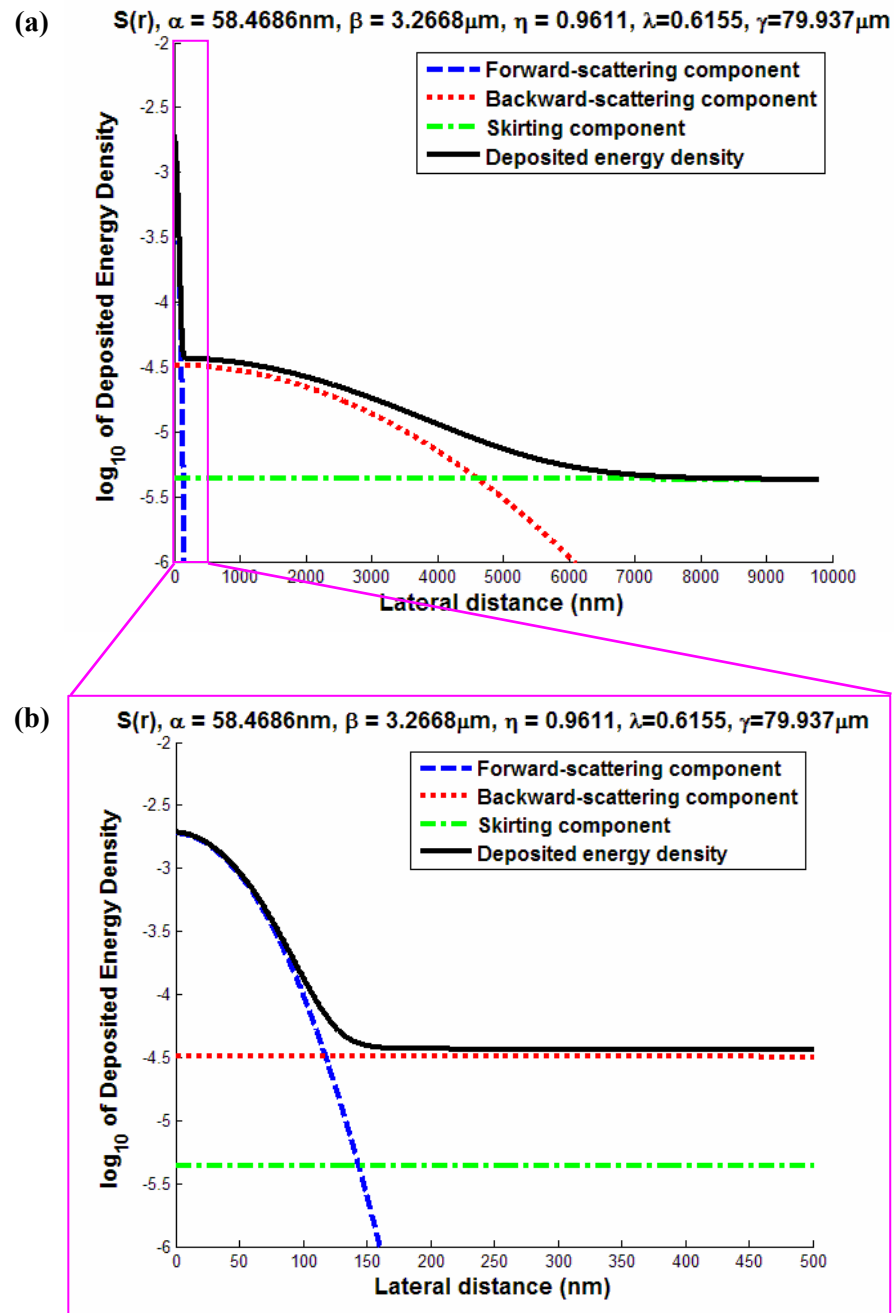


Figure 4.9: Energy deposition function $\log_{10} s(r)$ in LV-eBL for the specific patterning and development conditions used in the experiments. Figure 4.9(b) shows the magnified portion of (a) encircled by the pink lines.

4.3.4 Comments on the fitting approach using EM algorithm and the beam skirt effect

(1) The EM algorithm used in this project shows the following advantages in determination of the proximity parameters from experimental observations:

The approach of using two alternating EM iterations is more suitable for fitting with multiple unobserved parameters. This is a potentially significant improvement compared with non-linear least-square method. When the number of unknown parameters increases, the solution space of non-linear least-square fitting becomes much larger and non-linear least-square is more prone to being stuck in local minima instead of finding the global optimal solution, leading to inaccuracy of the estimation. In contrast, the number of unknown parameters is reduced in each of the two alternating EMs. On this smaller problem scale, the problem with non-linear optimization is mitigated. Due to this characteristic of EM, fewer exposure experiments may be required in order to resolve the problem in LV-eBL. For example, three alternating EMs can be used with each EM dedicated to a subset of parameters, i.e., one for fitting (α, Q_c) , one for (β, η) and one for (λ, γ) . All three EMs can be based on a single group of LV-eBL exposure experiments.

In general cases, $p(\beta, \eta | \{e_s\}, \alpha^{i-1}, Q_c^{i-1})$ and $p(\alpha, Q_c | \{e_s\}, \beta^{i-1}, \eta^{i-1})$ can assume, rather than Dirac distributions, more complicated distributions such as Gaussian or Wishart distribution which may give better approximation to the underlying true distributions; and $p(\{e_s\}, \beta^{i-1}, \eta^{i-1} | \alpha, Q_c)$ and $p(\{e_s\}, \alpha^{i-1}, Q_c^{i-1} | \beta, \eta)$ may take some form of distributions that better reflect the physical nature of data measurements. It is reasonable to expect that, with these

better distribution forms, the proposed EM algorithms can achieve better estimation of parameters of proximity effect.

Finally, although the above fitting results are obtained from specific exposure experiments, the EM approach can be easily adapted to different processing conditions. Actually the resist thickness, beam energy, working distance, gas pressure and development process in our experiments are fixed for reasons described previously. This further facilitates the fitting process since only limited number of parameters (e.g., β and η) may need to be modified from the results on Si wafer, due to selection of the substrate. Such an example is demonstrated in section 4.4, where proximity parameters can be fitted for patterning on STO substrate.

(2) The method presented here provides a means to estimate desired dose for certain pattern geometry. For example, in order to obtain 2D grid in PMMA resist with precisely 100 nm line width on Si wafer, the fitting results give that an area dose of $145.9920 \mu\text{C}/\text{cm}^2$ should be used in HV-eBL and $343.0071 \mu\text{C}/\text{cm}^2$ should be used in LV-eBL under the given instrumental conditions.

A more significant implication is that we can utilize this analytical method to explore the VP-eBL patterning capability and test its limits on fabricating high density patterns. One such limit is the loss of exposure contrast in resist due to proximity effect. The broad beam skirt adds a diffuse background to the designed exposure profile and may wash out the contrast between exposed and unexposed areas for a densely packed geometry, causing poor pattern definition during development. A simple way to validate this effect on the 2D grid geometry is to calculate the critical designed line width (i.e., the value of W) with which the received dose at the center of

grid reaches Q_c . For a given periodicity (700 nm) and fixed LV-eBL experimental conditions, any line width larger than this critical value will cause the whole patterned area ($100 \times 100 \mu\text{m}^2$) to be developed. Assuming $Q_s = 343.0071 \mu\text{C}/\text{cm}^2$ is used for patterning on Si substrate, the critical width is determined to be 241.1737 nm. It can be inferred from this result that, when attempting to prepare high density pattern in LV-eBL, one needs to be very careful choosing the proper combination of instrumental parameters and the designed pattern geometry. The analytical approach demonstrated here may save laborious and very time-consuming experimental efforts on patterning with various doses on multiple samples, before the proper geometry or patterning condition is determined.

(3) As observed from $s(r)$ plots, the scattering of electrons by the chamber gas molecules causes certain fraction of beam current transferred from the focused beam to the skirt. However due to the large range of the skirt, the electron current density (A/cm^2) at any point in the skirt is much lower than that of the focused beam. The above nature of the beam skirt has different degree of influences on all three attributes of VP-SEM, i.e., imaging, x-ray spectrometry and eBL patterning. The major influences for each application, along with operational strategies to correct or minimize these influences, are summarized in table 4.3.

Table 4.3 Influences of beam skirt effect on VP-SEM performance

	<i>Imaging</i>	<i>eBL</i>	<i>X-ray spectrometry</i>
Influence of Beam skirt	1. Adds a non-specific, steady state level to the measured signal 2. Increases the statistical noise and lower the signal/noise ratio	1. Causes lower localized dose received by the resist than the designed value 2. Adds a steady background across a large area 3. Deteriorates the proximity effect for high density, large area patterns	1. Remotely scattered electrons produces x-ray signals indistinguishable from that by the focused beam 2. Analytical performance of x-ray spectrometry is severely limited, particularly for minor or trace constituents' analysis; quantitative analysis at μm -scale; mapping, etc.
Operational Strategies	Increase the pixel dwell time	Methods for correcting proximity effect in HV mode (e.g., dose modulation and pattern biasing) can be applied, under the circumstances that the extent of the beam skirt contribution is known for the given geometry and patterning conditions	Select proper instrumental parameters to minimize gas scattering Pressure variation method ²⁰⁶ Intercepting the unscattered beam ²⁰⁷ Bremsstrahlung normalization method ²⁰⁸
Comments	The interaction of the beam skirt can be largely ignored ²⁰⁵	Investigation on the beam skirt influence over eBL has been scarce	Inevitable challenges in x-ray microanalysis performance Some degree of control over the beam skirt induced artifacts can be exerted, but depending on the exact situation

The importance of studying the beam skirt effect in VP-SEM can be noticed from table 4.3, particularly for x-ray microanalysis and LV-eBL patterning of high density, large area patterns. Quantitative investigation of beam skirt parameters is of great importance in order to apply the proximity correction methods properly in LV-eBL. In the correction methods developed for regular high vacuum eBL such as dose modulation, pattern biasing or GHOST, the electron energy deposition profile needs to be determined before dose or pattern geometry can be adjusted. However, this research area for LV-eBL is surprisingly underdeveloped. The value of direct-patterning on insulators in VP-SEM can be so great in existing and emerging technologies that it is worth the efforts to achieve better understanding of the VP-SEM mechanism, and to implement patterning protocols to get the best possible results within the limitations imposed by gas scattering. We believe the attempt presented in this chapter to estimate the beam skirt parameters from empirical data can not only be used as a guide for patterning the 2D grid, but also disclose site-specific information of electron-gas and electron-sample interactions in VP-SEM operation.

4.4 FABRICATION OF 2D HIGH DENSITY GRID WITH DOSE CONTROL AND MODIFIED GEOMETRY

The fitting results obtained for HV-eBL and LV-eBL can be employed to determine the proper dose profile for 2D high density grid under the same patterning conditions. Here the question has become determination of the Q_s value for a given e_s with the known energy deposition function.

A more complicated circumstance is encountered when we consider patterning 2D ferroelectric grid from sol-gel precursor on single crystal STO substrate. First, the patterns obtained from 0.1 M BTO sol regularly go through a volume shrinkage of 60~75%, depending on the annealing condition. If we roughly assume the same linear shrinkage along in-plane as well as out-of-plane directions, the trench width in PMMA after development should be between 135.72 nm and 158.74 nm in order to achieve a final BTO line width of ~100 nm. These values correspond to $e_s \in (17.86 \text{ nm}, 29.37 \text{ nm})$. Second, the electron backscattered coefficient of STO is 0.2795, much higher than that of Si (0.1644). This means the contributions of β and η to the proximity function are different for STO. Further, the Gaussian form for description of the backscattered electron contribution may need to be altered. The cosine angular distribution of the backscattered electrons²⁰⁹ suggests that the maximum number of backscattered electrons is emitted along the surface normal in case of a normal beam incidence. For Si wafer and other substrates with low backscattered coefficient, a Gaussian form with a relatively small standard deviation β is sufficient to simulate this distribution. However for substrates with high backscattered coefficient such as STO, the Gaussian form with a large β may not precisely portrait the high yield near the spot of illumination. To resolve this, another term can be added to the form of the energy deposition function.^{210, 211} We modify the energy deposition function as the following:

$$s(r) = \frac{1-\lambda}{(1+\eta+\mu)\pi} \left[\frac{1}{\alpha^2} \exp\left(-\frac{r^2}{\alpha^2}\right) + \frac{\eta}{\beta^2} \exp\left(-\frac{r^2}{\beta^2}\right) + \frac{\mu}{\tau^2} \exp\left(-\frac{r^2}{\tau^2}\right) \right] + \frac{\lambda}{\pi} \frac{1}{r^2} \exp\left(-\frac{r^2}{\gamma^2}\right) \quad (4.15)$$

The extra term $\frac{\mu}{\tau^2} \exp(-\frac{r^2}{\tau^2})$ is to better describe the electron energy density deposition for a heavier substrate.

Assume that α , γ , λ and Q_c remain the same for STO (considering same resist thickness and instrumental conditions), we employ the line width expansion obtained on grid patterns in LV-eBL (shown in table 4.4) to fit the values of β , η , τ , and μ . The E-M fitting estimates $\beta = 7.9998$ μm , $\eta = 0.7940$, $\tau = 204.9849$ nm, $\mu = 1.1040$. The required dose to achieve ~ 100 nm line width after annealing, i.e., $e_s \in (17.86 \text{ nm}, 29.37 \text{ nm})$, therefore is determined for the modified $s(r)$ to be $Q_s \in (281.5204 \text{ } \mu\text{C}/\text{cm}^2, 315.6106 \text{ } \mu\text{C}/\text{cm}^2)$. This range of Q_s can be used as a guidance to control line width of the annealed grid pattern.

Table 4.4 Change of average line width for P_{GLV} with exposure dose on STO substrate

Q_s ($\mu\text{C}/\text{cm}^2$)	300	337.5	375	412.5	450	487.5	525	562.5	600
$W + 2e_s$ (nm)	146	187	209	261	267	318	432	503	555

Adjusting dose alone will not fully prevent the overexposure at the node areas using the original perfect grid design, since the aerial density at the node area is naturally higher. A simple yet effective method to solve this problem is to modify the design geometry as shown in figure 4.10(a). That is, patterning an array of repeating “L” shape features with 10 nm edge-to-edge gap between neighboring “L”s. Here the proximity effect at the node areas is utilized, other than avoided, to expose the gaps and obtain an interconnected grid pattern with precise dimension all over the patterned area. Figure 4.10(b) shows a successful example of BTO grid with 118 nm

line width after annealing on STO substrate, where the expansion at the nodes is eliminated effectively. This pattern is prepared using the modified geometry and an area dose of $280 \mu\text{C}/\text{cm}^2$ determined by the fitting results. The line width is still larger than the expected 100 nm, probably because the in-plane shrinkage of the pattern is less than that of out-of-plane during annealing, leading to a higher estimated exposure dose. Such a structure has also been replicated on Nb:STO and GdScO_3 substrates. The preliminary work on piezoelectric property characterization of this 2D structure and its potential application in studying the geometrical frustration will be demonstrated in chapter 7.

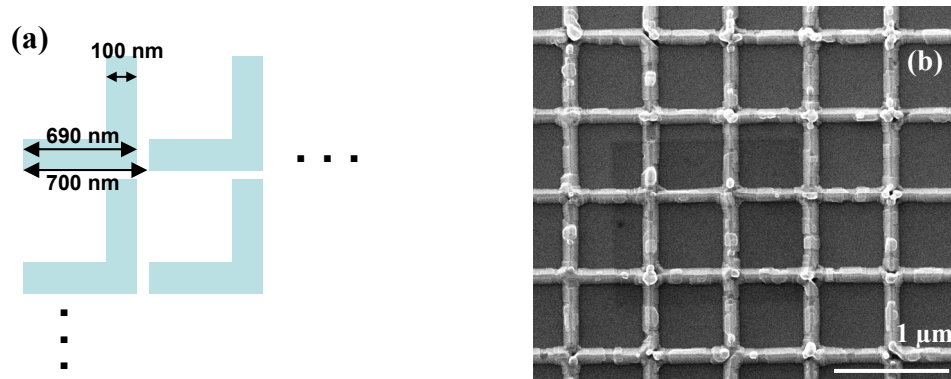


Figure 4.10: (a) Geometric design to avoid overexposure at the nodes. (b) BTO grid on STO substrate (after annealing) patterned using the modified geometry in (a) with $280 \mu\text{C}/\text{cm}^2$ area dose.

4.5 SUMMARY

This chapter aims at patterning high density 2D grid structures with precise control over dimension and shape, as a complimentary expansion of the VP-soft-eBL portfolio. Proximity effect in eBL is found to be a major issue that causes significant line width expansion and hinders the precise fabrication of the ideal geometry. In particular, this phenomenon exacerbates under VP-eBL mode due to the scattering of the electron beam by the chamber gas molecules. On one hand, the scattering leads to a lower energy density deposition at the incident position; on the other hand, it adds a broad background within the range of the beam skirt which may contribute to the overexposure for large area patterns.

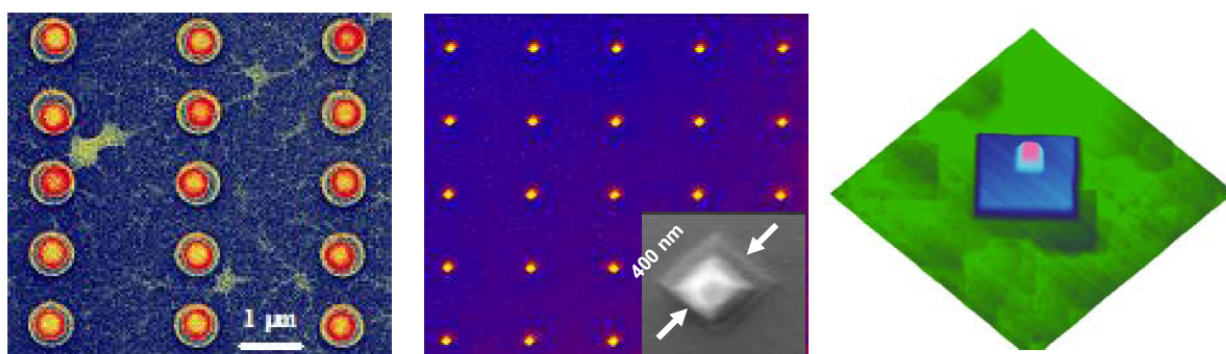
We present a facile approach for obtaining statistically averaged proximity parameters at regular eBL mode as well as variable pressure eBL mode with good precision. This approach utilizes experimental observation on the pattern dimension development of two special design geometries. Alternating Expectation-Maximization algorithm is employed to estimate the proximity parameters from fitting with experimental results. For the first time, the proximity function is modified and expanded to describe the electron energy density deposition in low vacuum eBL. Based on the modified proximity function, area dose required for patterning 2D grid on STO substrate is determined. With modified geometric design and the predetermined dose, a high density 2D ferroelectric grid structure is fabricated with high precision on insulating STO substrate.

The advantages of the analytical approach presented here are three-fold: (1) It has been used to determine the proper exposure dose in order to achieve the designed high density grid

structure; (2) It can serve as a versatile framework that easily adapts to estimating the proximity effect for systems with different pattern geometries and on diverse substrates; (3) The performance of VP-SEM in terms of eBL patterning can be evaluated using the postulated LV-eBL proximity function model. We hope this study can provide site-specific information and add to the understanding of electron-gas and electron-sample interactions in VP-SEM operation.

CHAPTER 5

FABRICATION OF THREE-DIMENSIONAL (3D) HETEROSTRUCTURE PATTERNS



This chapter pursues extending the VP-soft-eBL scope into the capability of three-dimensional stacking of heterostructures. The goal is approached from two directions, i.e., vertical stacking through double-step VP-soft-eBL with strict alignment procedures, and formation of radially stacked heterostructure through controlled substrate hydrophobicity.

The work described in this chapter was published in **Small**, 2, 274 (2006) and presented on the **2005 American Ceramic Society Meeting** (student poster).

The recent decade has witnessed emergence of diverse techniques for patterning wide variety of molecular and “soft” nanostructures within two-dimensional regime.²¹²⁻²¹⁵ However, as the nanostructure paradigm shifts from monolithic single-phase materials and planar geometry to complex compounds and stacked 3D architecture, there is continuing need for advancing non-planar stacking of solid-state structures, especially for multifunctional materials, in a patterned geometry. Heterostructures composed of multifunctional oxides (e.g., multilayer structures) exhibit fascinating breadth of properties for applications such as microelectromechanics,²¹⁶ optoelectronics,^{217, 218} microwave devices,²¹⁹ and data storage,²²⁰ among many others, based on the interaction between different phases when stimulated by external fields. Recently, vertically aligned heterostructures (such as nano-pillars of one phase embedded in the matrix of another)^{51, 55} have attracted considerable attention as these nanostructures significantly enhance such interactions. While these vertical heterostructures are fabricated using phase separation based self-assembly approach, a patterning technique that affords controlled dimension and separation of such miniature structures is highly favorable.

Current “top-down” patterning techniques are well suited for fabrication of single component planar structures. There are considerable challenges in fabricating non-planar ceramic heterostructure nanopatterns. The key bottleneck is the stringent requirement on feature realignment between multiple patterning steps^{215, 221-223} required in order to form non-planar patterns composed of more than two materials. Such constraint is particularly critical for nanometer sized structures as it would mandate alignment precision at a relatively small scale. Methods such as polymer phase separation,²²⁴ templated growth,²²⁵ interference lithography²²⁶ and nanotransfer printing²¹⁵ have been developed for fabricating non-planar nanostructures

without the need for high precision feature-alignment. However they are demonstrated mainly for metals and polymers, and are not well suited for ceramics. Direct deposition methods such as robotic deposition²²⁷ enable fabrication of intricate ceramic structures, yet there are restrictions on the deposition environment and the smallest feature size attainable.

We have pursued the fabrication capability of oxide 3D hybrid architectures using VP-soft-eBL. Examples of our endeavor include: (1) two-step patterning of vertically stacked bi-layer heterostructure patterns by utilizing the excellent registry capability of eBL, and (2) fabrication of radially stacked structures without feature realignment based on a modified soft-eBL procedure. Both two approaches will be demonstrated in this chapter.

5.1 TWO-STEP PATTERNING OF VERTICALLY STACKED HETEROSTRUCTURE PATTERNS

Vertically stacked bi-layer heterostructures are fabricated by virtue of properly designed alignment markers and exquisite stage movement control. Stacking of two different materials is done in a straightforward manner, as illustrated in figure 5.1.

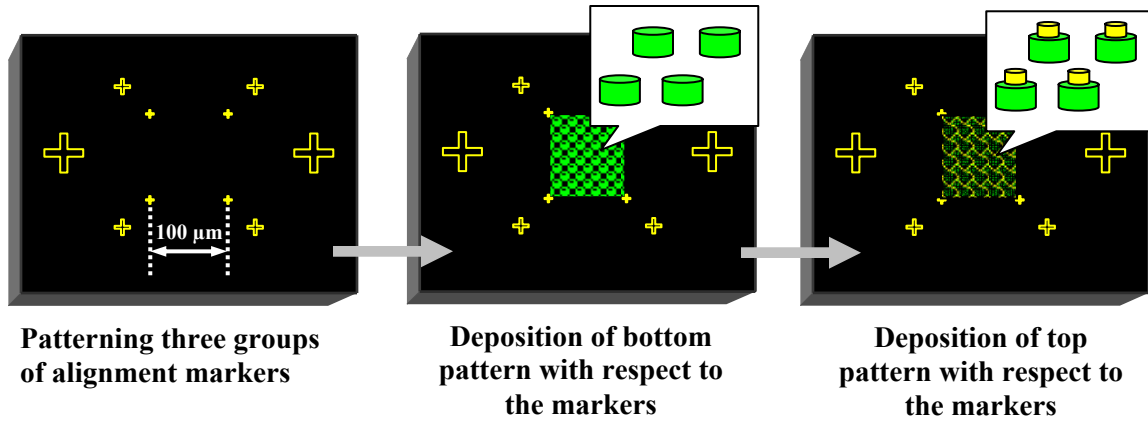


Figure 5.1: Fabrication procedures for vertically-aligned patterns

In an attempt of patterning $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$ heterostructures, three groups of Au/Pd alignment markers in cross shape are first prepared on the substrate. The arm widths of these markers are 5 μm, 1 μm and 50 nm, respectively. The four smallest markers are positioned at four corners of a $100 \times 100 \mu\text{m}^2$ square area inside which the patterning of oxides are conducted. The substrate is then coated with 300 nm thick PMMA resist. The bottom BaTiO_3 layer is patterned by exposing 500 nm-diameter disc arrays covering $100 \times 100 \mu\text{m}^2$ area, through aligning the three groups of markers from the largest to the smallest, and positioning the center of disc array with respect to the smallest markers. After drying of the BaTiO_3 pattern and lift-off, the sample is coated with resist again and subject to VP-soft-eBL patterning of CoFe_2O_4 using the same alignment approach. The CoFe_2O_4 patterns are designed to be 200 nm-diameter disc arrays with the same periodicity and same area coverage as the previous BaTiO_3 discs. Smaller diameter for CoFe_2O_4 patterns is designed so that the efficacy of vertical stacking can be directly observed using planview SEM. Figure 5.2 shows the SEM and AFM images of such heterostructure patterns. The ability of positioning one material with respect to the other, with

sub-100 nm precision over $100 \times 100 \mu\text{m}^2$ area has clearly demonstrated the great potential of the site-specificity of the VP-soft-eBL.

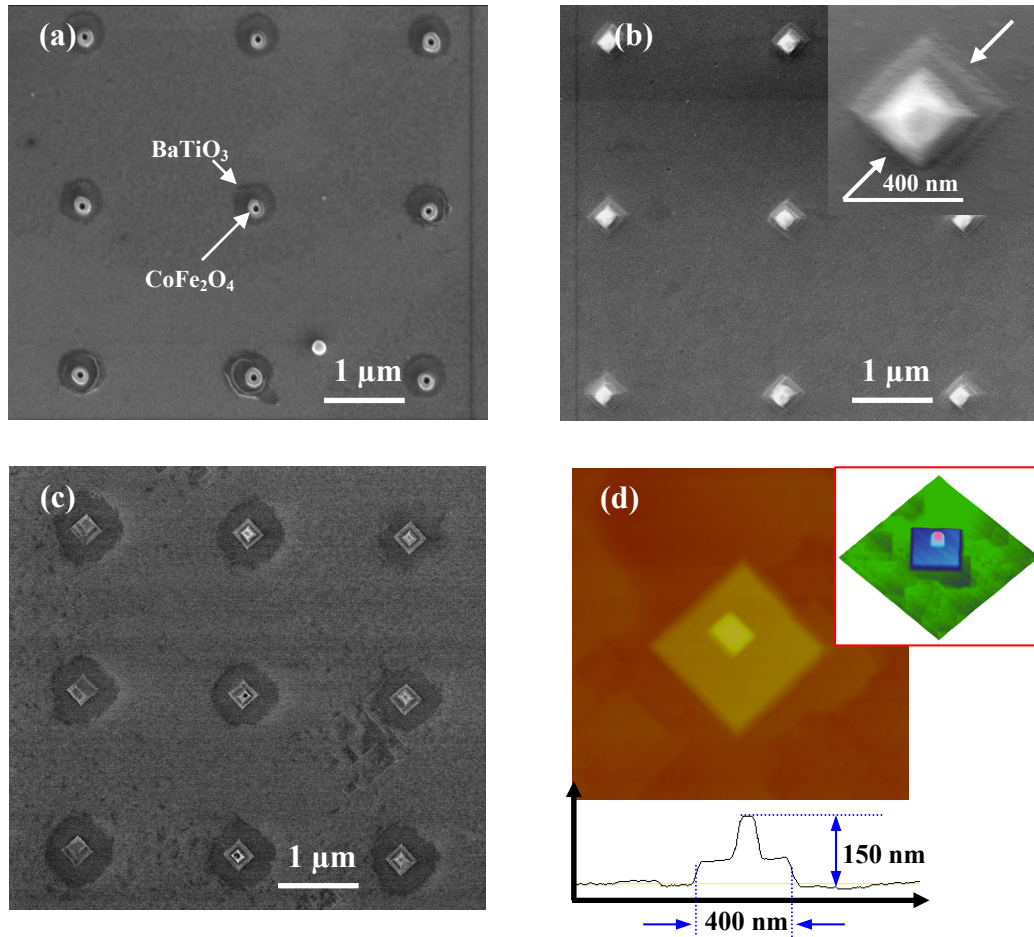


Figure 5.2: CoFe₂O₄/BaTiO₃ heterostructure patterns fabricated through double-alignment procedure in VP-soft-eBL. (a) SEM image of BaTiO₃ (bottom)/CoFe₂O₄ (top) on Si wafer, before annealing. (b) SEM image of BaTiO₃ (bottom)/CoFe₂O₄ (top) on SRO/STO, annealed at 900 °C. Inset shows the detail of one such heterostructure, the top white contrast corresponds to the CoFe₂O₄ layer due to the higher thickness. (c) VP-SEM image of CoFe₂O₄ (bottom)/ BaTiO₃ (top) on MgO substrate, annealed at 900 °C. (d) AFM topographic image and cross section analysis of CoFe₂O₄ (bottom)/ BaTiO₃ (top) on MgO substrate. Inset shows the three-dimensional profile for one pattern.

5.2 FABRICATION OF RADIALY STACKED HETEROSTRUCTURES

The direct stacking of the bi-layer structures involves two-step patterning procedure. This method, albeit effective, requires preparation of markers before hand and double eBL exposure steps. Also, the alignment precision is strongly dependent on the operational proficiency of the experimentalist. In the following section, we present an alternative of patterning hybrid structures without the need for feature-alignment or etching.

5.2.1 Barrel-shape pattern development

VP-soft-eBL is characterized by spinning liquid precursors on patterned eBL resist films. Normally the shape and size of the as-developed pattern is determined by that of the trench in the resist. However, it has been noticed in certain cases that the shape of the sol pattern can be deviated from the design in resist. We report below one such example where a “barrel” shape oxide pattern is developed from a disc-shaped trench in eBL resist.

In a typical run, platinized silicon wafer (Pt/Si) is spin-coated with a bi-layer resist (copolymer at the bottom and PMMA on the top). The resist coated substrates are patterned with array of circular (1 μ m diameter) or square discs (1 $\times$ 1 μ m). After development, the patterned substrates are treated with oxygen plasma and spun with Pb(Zr_{0.3}Ti_{0.7})O₃ (PZT) sol (0.1 M concentration). The samples after drying and lift-off are shown in figure 5.3. The AFM topographic images and the cross-sectional profile in figure 5.3(a) and 5.3(b) indicate that the square patterns have in fact developed into barrel shapes. Each barrel has about 90 nm wall thickness and 150 nm height as analyzed by AFM profiles. SEM images of the pattern before annealing and after annealing at 600 °C for 1 hr are shown in figures 5.3(c) and 5.3(d). Please

note the thin layer of PZT at the bottom of the barrels and that the substrate surface is not completely free of the patterned material. After annealing, the wall thickness reduced by nearly 30% to about 60 nm and the bottom layer becomes thinner. The underlying Pt substrate can be observed in figure 5.3(d) inside as well as outside of the pattern.

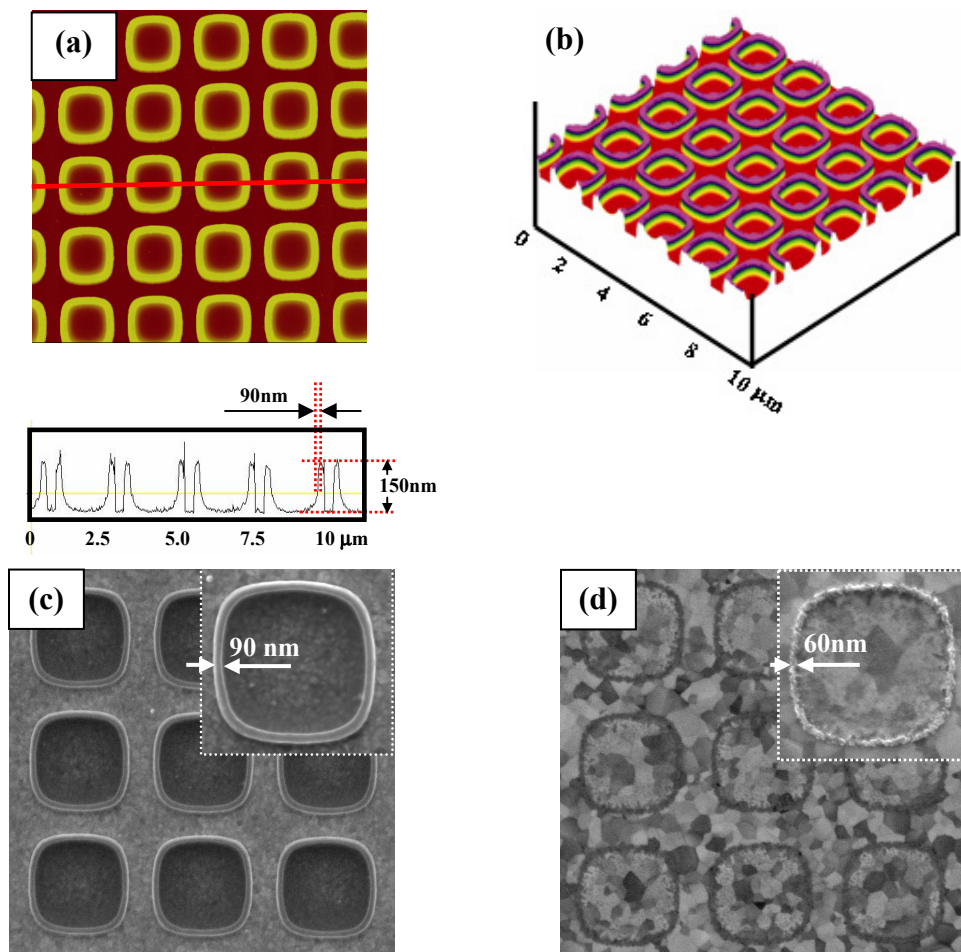


Figure 5.3: PZT barrels developed from square ring patterns on platinized silicon substrate. (a) AFM topographic image and cross sectional analysis of PZT barrels before annealing. (b) AFM 3-D construction of the barrels. (c) SEM image of PZT barrels before annealing. (d) SEM BSE image of PZT barrels annealed at 600 °C for 1hr. Insets in (c) and (d) shows image of one pattern.

We attribute the barrel shape formation out of a disc trench to a combined effect of both high spinning speed and the capillary force. That is, certain amount of the sol material is expelled out of the air holes due to high centrifugal force. The remainder sol preferentially accumulates towards the walls of the discs upon drying with the contact line pinned by the wall. The latter effect is illustrated in figure 5.4. When a sessile drop of solution dries on a surface, the behavior of the contact line of the drop determines the thickness profile of the dried film. A contact line should move toward the center of the droplet to keep the liquid/substrate contact angle constant during the process of solvent evaporation. However, if the contact line is pinned near the initial position, a radial capillary flow takes place to compensate for the differences in volume change and evaporation rate across the droplet, carrying solute to the contact line. This results in a ridge structure at the edge, also known as “coffee-stain” effect discussed first by Deegan *et. al.*^{228, 229} In practice, a thin wetting layer is often present in the central areas of the droplet during evaporation because the viscosity of the solution increases and therefore hinders the flow. This explains why the majority of gelled mass in our pattern agglomerates at the edges and forms barrel shape geometry.

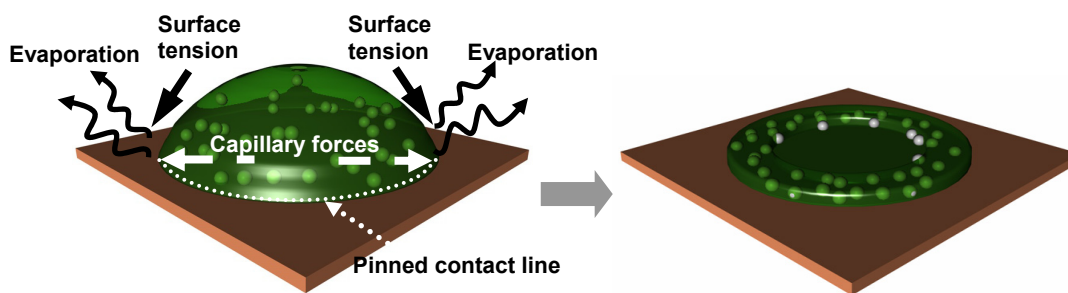


Figure 5.4: Evaporation of a sessile droplet on the substrate with pinned contact line and formation of barrel-shape geometry after drying.

The mechanism of rings (or barrels) formation has been explained in terms of correlation between surface tension, liquid-substrate wetting properties, and evaporation-driven convective flows.^{230, 231} Particularly, the evaporation flux $J(r)$ at position r is found to be strongly dependent on the liquid/substrate contact angle θ_c following the equation:²²⁹

$$J(r) \propto (R-r)^{\frac{\pi-2\theta_c}{2\pi-2\theta_c}} \quad (5.1)$$

where R is the radius of the droplet-substrate contact area. Higher contact angle implies higher value of $J(r)$ and therefore more effective mass transfer from the central area to the edge. By adjusting the wetting behavior of certain liquid/substrate system (i.e. θ_c), the shape and thickness of the contact-line deposition can be controlled. This method has been utilized in assembly of nanoparticles or nanoaggregates from their liquid suspensions.^{232, 233}

The above argument implies the possibility to control the shape of the sol-derived ceramic patterns by varying the surface property of the exposed substrate area. Further, building radially stacked heterostructure patterns would be possible if the bottom center of the patterns are made free of spin-coated material to attain pure (bottom-less) ring geometry. By simply filling the rings with another functional oxide sol, columnar “core-shell” architecture can be fabricated without requiring painstaking realignment and multi-step patterning. In the following section, we describe our effort in achieving pattern shape control by tuning the substrate hydrophobicity using chemical modification such as self-assembled monolayers.

5.2.2 Surface modification and fabrication of ring reservoirs

5.2.2.1 Surface Modification using Self-Assembled Monolayers (SAMs)

One way to keep the substrate surface inside of the ring free of sol material is to increase the contact angle of the sol with the substrate, which can be achieved through chemical modification using SAMs.²³⁴⁻²³⁷ For example, 1-octadecanethiol (ODT) and octadecanetrichlorosilane (OTS) can effectively increase the contact angle of water or alcohol on noble metal and silicon oxide surface, separately.^{236, 237} The result of the contact angle increase is summarized in table 5.1. Further, the SAMs modification procedure is compatible with the VP-soft-eBL approach. Therefore, SAMs are utilized after developing the patterns in e-beam resist and oxygen plasma treatment to render a hydrophobic substrate surface.

Table 5.1 Contact angle change of water and ethylene glycol on substrates functionalized with ODT and OTS SAMs²³⁸

Solid Surface		Contact Angle θ_c (°)	
Substrate	SAM	Water	Ethylene Glycol
Au	-----	65.9	53.1
Au	ODT	110.0	83.3
SiO ₂	-----	9.8	2.3
SiO ₂	OTS	110.4	78.9

Particularly, Si substrates (with 60 nm thermal oxide) are functionalized with OTS, while Au substrates (30 nm thick Au sputter-coated Si wafer with 5 nm Ti adhesion layer) are functionalized with ODT. SAM modification of the patterned substrates is conducted by

immersing the Au substrates in 3 mM ODT-isopropanol solution for 3 hr and the bare Si substrates in 5 mM OTS-anhydrous hexane solution for 20 hr. The substrates are then thoroughly rinsed with corresponding solvents, blown dry with nitrogen. The treated substrates are immediately used for spin-coating PZT sol. Subsequent steps are same as outlined earlier. Sol patterning is done on the same substrate but without SAM treatment for control experiments.

The AFM topographic images and cross-sectional profiles of PZT structures on unmodified and ODT modified Au/Ti/SiO_x/Si substrates are shown in figure 5.5(a) and 5.5(b), respectively. From cross-sectional profiles it can be noted that on unmodified substrate PZT structures form as barrels with nearly 50 nm thick film at the center of each barrel. In contrast, ODT modified surface generates a pure ring structure with the same height inside as well as outside of each ring. Chemical maps are obtained using secondary ion mass spectroscopy (SIMS, PHI TRIFT III, Physical Electronics, USA)) to further confirm the absence of PZT at the bottom of the rings. The Ti⁺ ion map of the pattern in figure 5.5(c) clearly shows that the interior of each ring is devoid of any PZT material, and therefore validates the AFM results.

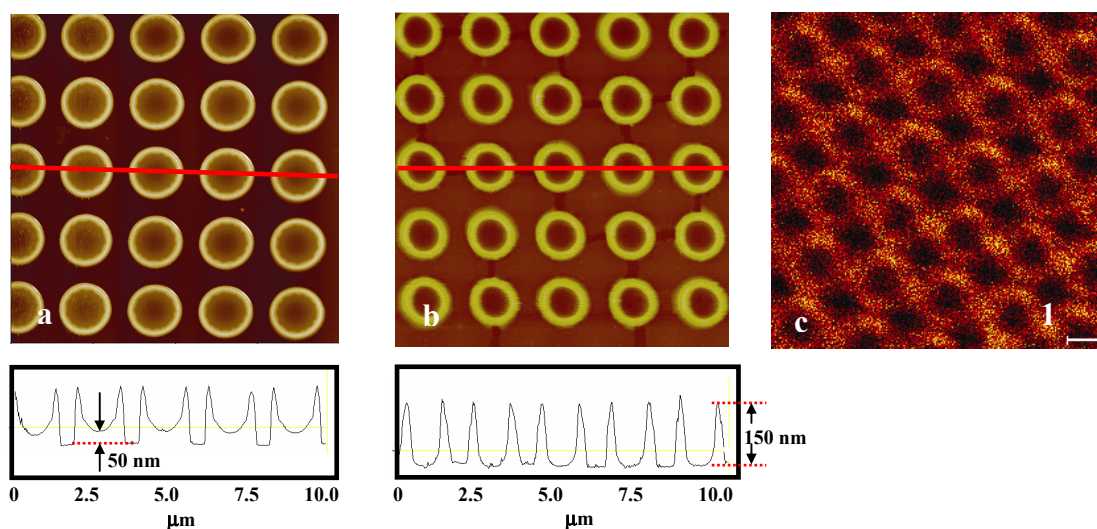


Figure 5.5: The effect of Au surface functionalization using ODT SAM on PZT ring formation (a) AFM image of PZT patterns on bare Au. The patterns developed into barrel shape after drying, leaving 50nm thick PZT at the center of the bottom. (b) AFM image of PZT rings formed on ODT modified Au surface. (c) SIMS Ti^+ map further confirms the pure ring structure formation. The rings appear to be connected due to the shadowing effect from the restriction of the incident angle and the probe size of the ion beam.

Similar results have been observed on OTS modified Si wafer as shown in figure 5.6(a) and 5.6(b), where both AFM and SIMS images offer clear evidence for the PZT ring formation. Besides the modification on noble metal and Si substrates, we have also extended this approach to complex oxide substrates such as SrTiO_3 (STO) single crystals. Such perovskite structured substrates have excellent structural compatibility with PZT and may provide control over PZT crystallography (e.g., high texture or epitaxy).²³⁹⁻²⁴² It should be noted that SAM formation on complex oxides is scarcely reported, probably due to the bonding difficulty between the organic molecule's head groups and the complex oxide surfaces. Nonetheless, we have attempted to increase the hydrophobicity of STO single crystal using the same SAM treatment as for Si substrates, considering that a layer of $-\text{OH}$ group readily forms on STO surfaces may facilitate SAM formation through the reaction with trichlorosilane.²⁴³ Furthermore, the oxygen plasma treatment utilized prior to SAM modification may help increase the density of hydroxyl groups on oxide surface^{243, 244} and even facilitate the $-\text{OH}$ group to be preferentially oriented,²⁴⁵ both of which can boost the silane-hydroxyl reaction. Although the bonding density may be lower than that for the silane/Si case, they may still be effective in changing the surface energy even if partial monolayer is formed. Figure 5.6(c) shows the SEM images of a PZT ring on OTS treated STO crystal substrate demonstrating the effectiveness of OTS treatment on the ring structure formation. We have also succeeded in patterning PZT rings on SiN_x surface using this approach. These collective results demonstrate the effectiveness and broad applicability of substrate functionalization with SAMs as an approach to realize oxide pure rings with nanoscale width on variety of substrates, starting from micrometer sized prior patterns. Our experiments have shown that the process is highly reproducible and can be readily used to pattern areas as large as 1 mm^2 .

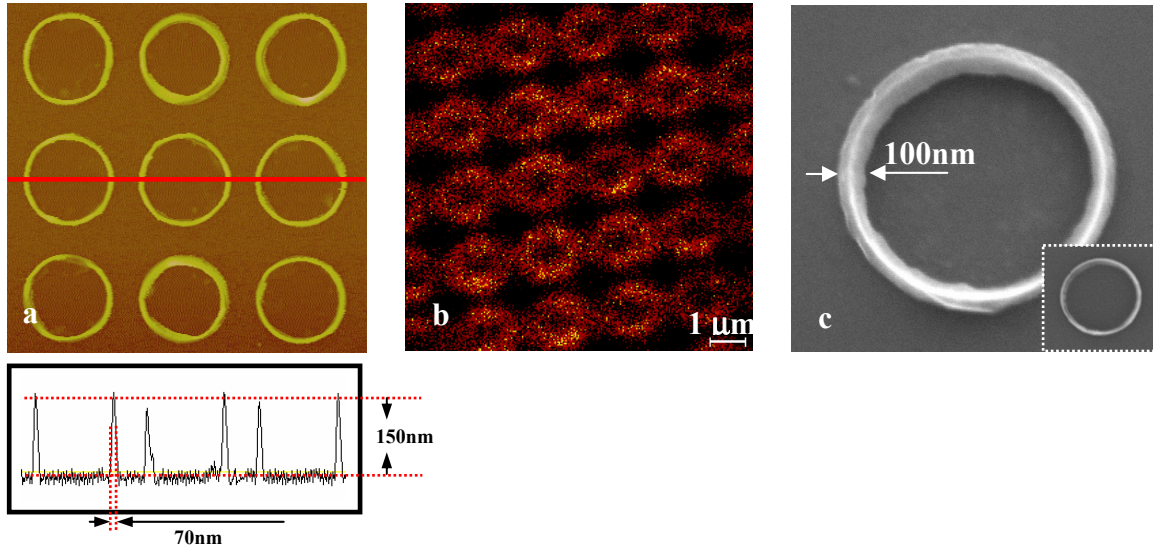


Figure 5.6: PZT rings on Si substrate and SrTiO₃ substrate modified by OTS SAM. (a) AFM topographic image and cross sectional profile of PZT rings formed on OTS modified Si wafer. (b) SIMS Ti^+ map further confirms the pure ring structure formation. (c) VP-SEM image of PZT ring structure on OTS modified single crystal SrTiO₃ substrate. Inset shows backscattered electron image.

5.2.2.2 Influence of resist undercut geometry

Besides the surface modification through SAM treatment, the eBL undercut also plays an important role in defining the geometry of the ring structure. The undercut profile is created due to the higher e-beam sensitivity of the bottom copolymer layer compared to the top PMMA layer. Figure 5.7 shows the cross-sectional SEM image of the bi-layer resist after eBL patterning and development. The undercut length, defined as the length of PMMA layer overhanging the copolymer layer, is about 100 nm which is close to the width of PZT rings shown in figure 5.3, 5.5 and 5.6. In addition, the thickness of PMMA and copolymer is about 150 nm each, which is

remarkably close to the height of PZT rings. This suggests the following explanation for the formation of ring structures.

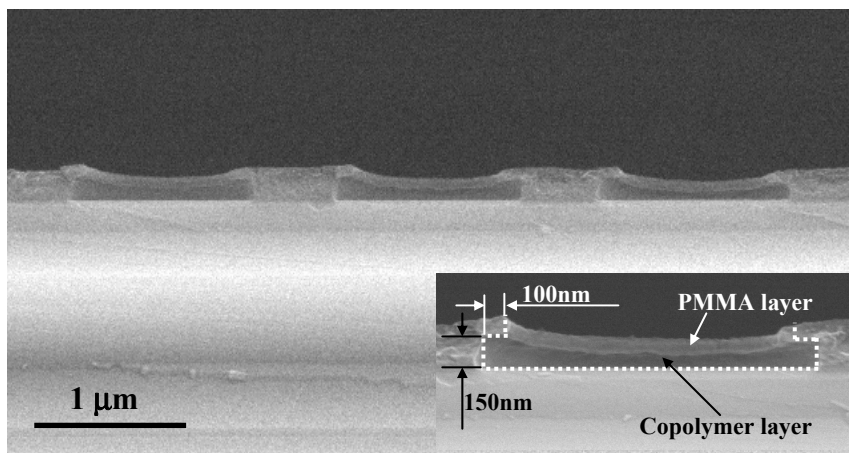


Figure 5.7: eBL undercut profile in bi-layer resist. White dotted line in inset schematically shows the edge of the profile. The thickness of the copolymer layer is 150nm and the undercut length is 100nm.

The undercut profile functions in a way analogous to an aperture on top of a barrel. It allows part of the sol to be expelled under high rotational speeds, yet retains the remaining sol which is pushed to the perimeter of each disc and preferentially accumulates there due to the solvophobicity of the bottom surface to form the ring structures after drying. Thus, the PZT ring height is determined by the thickness of the copolymer layer and the width is defined by the undercut length. We have further confirmed the above model through control experiments. When a 300 nm thick PMMA single layer was used instead of a bi-layer of same thickness and patterned SAM-treated substrates, nearly 90% of the patterned area was devoid of ring structures. Moreover, the height and thickness distributions of the rings in the rest area were nonuniform

(image not shown). The low yield and poor geometric uniformity therefore underscore the significance of the undercut.

5.2.3 Fabrication of radially stacked heterostructures

Based on the controlled formation of the nanoscale rings, radially stacked vertical heterostructure patterns are developed by simply spinning the sol of a second material to fill the rings and form the “core”, and this process can be repeated for additional radial stacking. We choose CoFe_2O_4 (CFO) as the “core” material due to its high magnetostrictivity and relatively high Néel Temperature.²⁴⁶ Also, CFO and PZT have commensurate lattice parameters ($a_{\text{CFO}} \approx 2a_{\text{PZT}}$).⁶⁰ This innate structural compatibility between the two phases with large magnetostriction or electrostriction (i.e., piezoelectricity) can enhance magneto-electric coupling effect when made into appropriately aligned heterostructures,^{53, 247, 248} particularly for “vertically aligned” geometry.^{55, 249} The patterning scheme of the heterostructures is illustrated in figure 5.8. PZT is first spun at 6000 rpm on SAM treated substrates and heated at 150 °C for 5 min to generate PZT rings. This is immediately followed by cooling the substrate and spinning CoFe_2O_4 sol at 5000 rpm to fill the PZT rings. The lower spinning speed for the core material is used to achieve larger bottom thickness of the barrels after drying. The substrates are then heated at 150 °C again and soaked in acetone to lift-off material outside patterned areas.

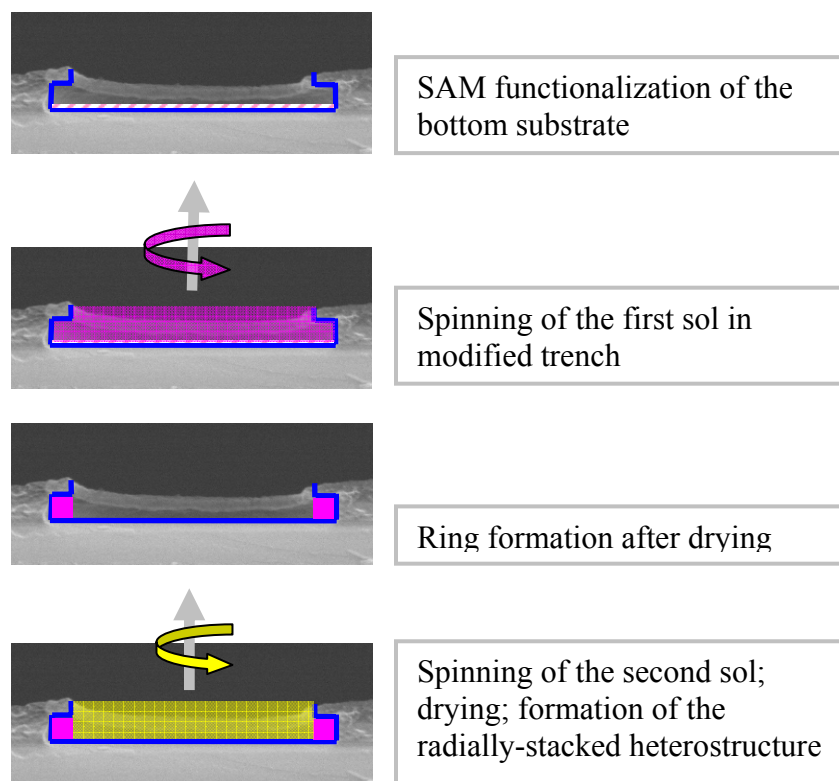


Figure 5.8: Scheme of patterning radially stacked heterostructures without feature re-alignment.

Figure 5.9(a) shows an SEM image of the columnar core-shell heterostructures (on Pt/SiO_x/Si substrate, annealed at 700 °C for 1 hr). The inset BSE image shows the average atomic number contrast between the “core” and the “shell” materials. Similar heterostructures have been fabricated on SiN_x surfaces treated by OTS. The TEM images, before (figure 5.9(b)) and after annealing (figure 5.9(c)) at 750°C in air for 1.5 hr, further corroborate the “core-shell” geometry. Electron diffraction pattern taken from one of the heterostructure patterns (figure 5.9(c) inset) shows polycrystalline rings, and the diffraction rings correspond well to PZT (tetragonal phase) and CFO. This indicates that both the core and the shell materials have crystallized after

annealing, and thus demonstrate the feasibility of this approach in preparing solid heterostructures with appropriate ceramic phases. There is no hint of third phase in the diffraction profile, suggesting the phase purity of the heterostructures. Since the interface between the piezoelectric and the magnetic materials play vital roles in the their interaction in order for such heterostructures patterns to function, more detailed studies on the microstructure of each phase and the inter-diffusion between the core and the shell materials are required and are in progress.

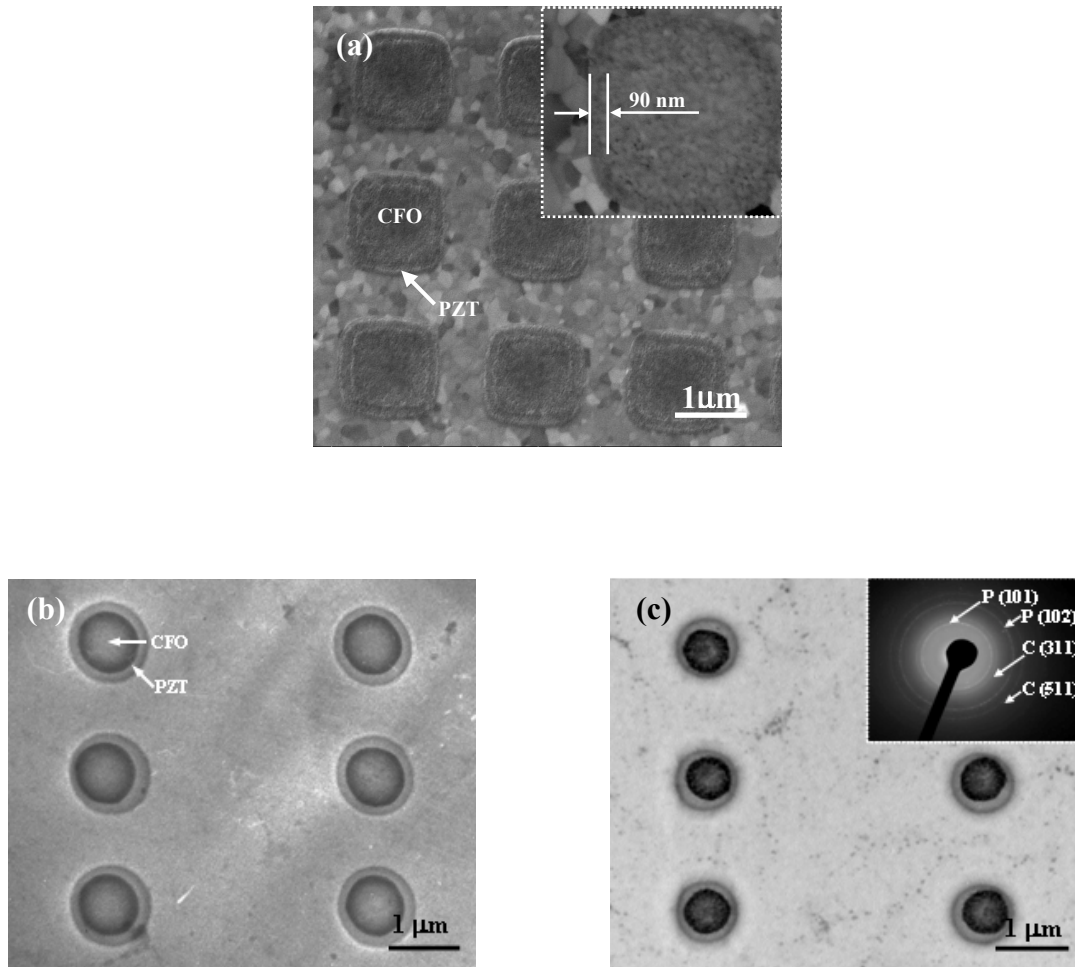


Figure 5.9: Radially stacked PZT/CFO heterostructure patterns fabricated using the PZT rings as building block “containers”. (a) SEM image of PZT shell/CFO core on Pt, after annealing. Inset is the BSE image showing contrast between the core and shell materials with white lines indicating the edge of the PZT shell. (b, c) TEM images of PZT shell/CFO core heterostructures on amorphous SiN_x membrane, before (b) and after annealing (c). Inset shows the electron diffraction pattern taken from one core-shell pattern, where “P” stands for PZT (tetragonal phase) and “C” for CFO.

These collective results reveal a facile and general route to fabricate oxide heterostructure patterns with excellent control over pattern dimensions from both “bottom-up” and “top-down” directions: SAM treatment determines the pattern shape (i.e., ring or barrel), while the high resolution eBL and the undercut profile simultaneously provide more rigorous control over the dimensions of the structure (i.e., thickness and height of the shell, diameter of the core, etc.). It does not require painstaking feature re-alignment between steps to generate the “shell” and placing the “core” inside the sub-100 nm-thick shell, and the simple spin-coating exploited eliminates the need for subsequent etching. This basic approach can be further extended to fabricate other radially stacked structures (e.g., concentric multi-ring patterns) if appropriate spinning speed with substrate surface property control can be utilized. The different schemes to achieve barrel (or disc) shape, pure ring shape and radially stacked heterostructures are summarized in figure 5.10 for comparison. On the other hand, in addition to patterning on different substrates, we also have patterned heterostructures of different oxide systems such as ZnO/PZT and BaTiO₃/CFO. This approach should be broadly applicable to patterning solid-state structures from any appropriate solution (e.g., sols, liquid phase polymer precursors and colloid particle suspensions^{250, 251}) that is compatible with e-beam resists.

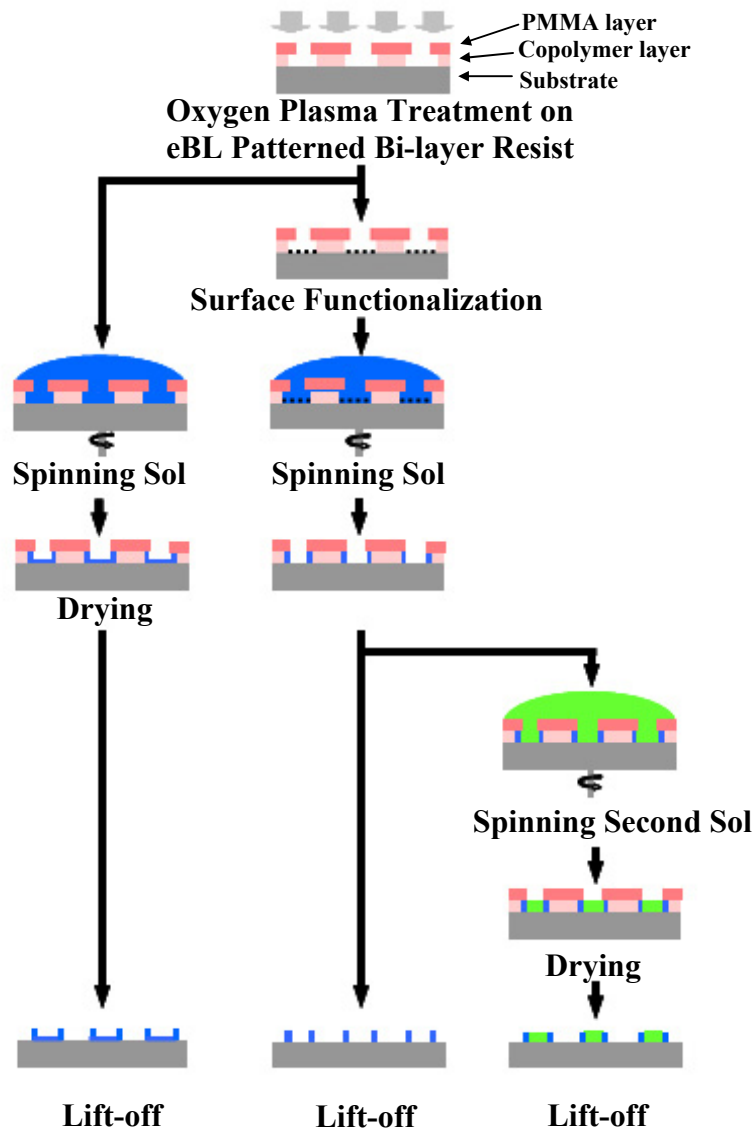


Figure 5.10: VP-Soft-eBL process for pattern shape control from disc-shape trenches in e-beam resist. Scheme I: For barrel structure development; Scheme II: For nanoring structure development; Scheme III: For radially stacked heterostructures development.

5.3 SUMMARY

The content of this chapter can be summarized as the following:

(1) Direct fabrication of vertically stacked hybrid nanopatterns has been demonstrated by double-step alignment and eBL exposure. Using the current alignment marker design, ~ 100 nm alignment precision can be obtained over $100 \times 100 \mu\text{m}^2$.

(2) Barrel-shape development of VP-soft-eBL prepared oxide patterns from disc trenches has been observed. It is argued that such as shape development is a joint effect of fast spinning speed, capillary flow of the sol with pinned liquid contact line during solvent evaporation and the undercut geometry of the eBL-defined trench in bi-layer resist.

(3) By carefully controlling the surface solvophobicity with appropriate self-assembled monolayers, pure ring structure with sub-100 nm thickness can be generated from the micron-sized patterns determined in the e-beam resist.

(4) The nanorings can be utilized as building block “containers” by filling them with a second sol to form radially stacked “core-shell” heterostructure patterns. This directed patterning of oxide heterostructures is successfully achieved on diverse substrates with control over their dimensions, and it avoids painstaking feature-alignment procedure between patterning of the first and second materials. This contribution demonstrates the efficacy and feasibility of fabricating radially stacked “core-shell” heterostructures via VP-soft-eBL.

Through chapters 3 to 5, the multi-dimensional patterning capability of VP-soft-eBL has been successfully demonstrated with examples spanning 0D disc array, 1D nanolines, 2D high

density grids and 3D heterostructure patterns. The wide versatilities of this patterning scheme in material/system selection, pattern geometry control and patterning site control are highlighted through these examples. VP-soft-eBL therefore presents itself as an enabling tool and an excellent platform, on which the substrate confinement on functional oxide nanostructures at diverse dimensionalities can be compared and investigated systematically.

CHAPTER 6

PROBING EPITAXIAL 1D NANOPATTERNED SYSTEM USING X-RAY MICRODIFFRACTION: A PRELIMINARY STUDY

Motivated by the novel properties and the increasing technological interest based on the confinement effect of oxides (note for instance, the crucial advances in high- T_c superconductors, ferroelectrics and colossal magnetoresistors), extensive scientific attention has been paid to the new emerging oxide-based nanotechnology, as discussed in detail in chapter 1. Patterning substrate-integrated oxide architectures is the prerequisite of exploration of this rich field and realization of novel functional miniature devices. Patterning, as a critical means of material processing, also has a profound bearing on the way functional materials interact with the underlying substrate and/or surrounding capping layers. For semiconductor systems, for instance, vast literature has reported experimentally or predicted theoretically that nanopatterning significantly changes the strain field in a heteroepitaxial architecture compared with in a blanket thin film.²⁵²⁻²⁵⁵ The same trend is also expected in the functional oxide regime. Although far from being a mature field, investigation of stress and strain distribution in spatially-confined structures is now turning into one of the frontier subjects in the field of functional oxide nanotechnology. It is particularly important for ferroelectrics and ferrimagnetics, given the high sensitivity of their operational characteristics to the stress field.²⁵⁶⁻²⁵⁸

The capability to site-specifically measure the strain field in and around a confined oxide nanostructure will fill in the gap between analytical or simulation result on mechanical behaviors

and experimental observation of material functionality change. To achieve this capability, developing and advancing suitable characterization techniques are of great importance and research value. We have attempted to approach this goal by applying x-ray microdiffraction technique on our VP-soft-eBL patterned 1D nanostructure. In this chapter, we describe our preliminary effort in this direction.

6.1 STRESSES EVOLUTION IN SOL-GEL DERIVED THIN FILMS

We first review the possible sources of stress in a soft-eBL patterned system. Soft-eBL approach is characterized by the employment of sol precursor and heat treatment after deposition for crystallization of the pattern. In this context, it is similar to preparation of sol-gel-based oxide thin film. It is well known that significant residual stresses develop in sol-gel processing of thin films during the transformation of metalorganic gel to oxide upon annealing.^{155, 259, 260} This transition is embodied in several stages: i) drying of solvent and pyrolysis of organics; ii) structural rearrangement and densification; iii) crystallization and grain growth; iv) cooling. The total residual stress in the final polycrystalline film consists of intrinsic and extrinsic contributions. The intrinsic stress (or growth stress) is induced by shrinkage and constrained densification during drying and firing, and formation of intergranular stresses as anisotropic grains grow. For ferroelectric materials such as PZT, intrinsic stresses can also be induced upon cooling through the Curie temperature.²⁵⁹ Intrinsic stresses as high as 200 MPa to 500 MPa have been reported for various sol-gel-derived thin film.²⁶⁰ Intrinsic stresses depend on the relative rates of evaporation, viscous deformation and flow of liquid through the pores of the gel. These

parameters are extremely sensitive to the sol chemistry (i.e., concentration, precursor, solvent, etc.) and the heating condition (i.e., pyrolysis temperature, heating rate, etc.). Therefore, it is very hard to estimate the amount of intrinsic stress for a given sol-derived thin film. Extrinsic stresses for a polycrystalline gel film are mainly induced upon cooling due to the thermal mismatch between the film and the substrate. The thermal stress σ_{th} in the film can be described as the following:

$$\sigma_{th} = E_f (\alpha_f - \alpha_s) \Delta T \quad (6.1)$$

where E_f is the elastic modulus of the film, α_s and α_f are thermal expansion coefficients of the substrate and the film, separately, and ΔT is the temperature range of cooling. The stress evolution in polycrystalline gel films or patterns during heating and cooling is schematically shown in figure 6.1.

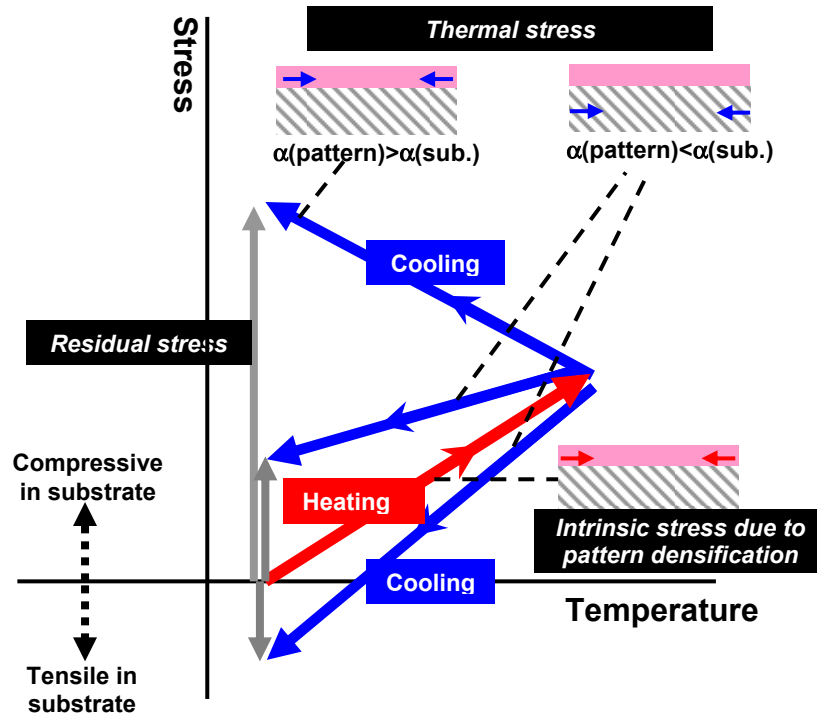


Figure 6.1: Stress evolution in gel patterns during heating and cooling

For epitaxial thin films, extrinsic stress also originates from the lattice mismatch between the film and the substrate, which can be described as:

$$\sigma_{epi} = \frac{E}{1-\nu} \epsilon = \frac{E}{1-\nu} \cdot \frac{a_s - a_f}{a_s} \quad (6.2)$$

where E and ν are the elastic modulus and poisson's ratio of the film, a_f and a_s are lattice parameters of film and substrate, separately. From equations 6.1 and 6.2, the thermal stress and the epitaxial stress in a large-area, epitaxial CFO film on MgO single crystal substrate can be roughly calculated based on their mechanical properties and lattice parameters listed in table 6.1.

Given the annealing temperature used in our experiments (between 850 ~ 1000 °C), the largest cooling range $\Delta T = 1000 - 25 = 975$ °C. The thermal stress $\sigma_{th} = -546$ MPa (the negative sign means the stress in film is compressive), and the $\sigma_{epi} = 983$ MPa. Therefore, the amount of intrinsic stress (200 MPa to 500 MPa) in a sol-gel-derived thin film system can be quite comparable to that of the extrinsic stress. This is a very different scenario from thin films deposited via metalorganic chemical vapor deposition (MOCVD), in which case the extrinsic contribution dominates the residual stress in the thin films.

Table 6.1 Mechanical properties of CoFe₂O₄ and MgO

	Elastic Modulus (GPa)	Poisson's ratio	Thermal expansion coefficient (10 ⁻⁶ /°C)	Lattice Parameter (nm)
CoFe ₂ O ₄ ⁴	173.4 (polycrystalline)	0.33	8	0.4196 (1/2 a _{CFO})
MgO ⁵	294.7	0.186	11.23	0.4212

6.2 “EDGE-EFFECT” IN NANOPATTERNED SYSTEMS

The above stress-evolution mechanisms also apply for a micro- or nano-patterned system derived from sol-gel approach. However, unlike a continuous film which is fully “clamped” by the underlying substrate, the patterns carry a great number of free edges and free side-wall surfaces. It has been extensively predicted by theoretic analysis that, at the neighborhoods of discontinuities in thin film, the edge of the film has a large effect on the stress field in both the film and the substrate.^{261, 262} This phenomenon is usually referred to as “edge-effect”. Particularly, stresses in the film material are relaxed near the free edges. Therefore the amount of stress near the edge of the discontinuity is always smaller than the stress in the middle of a

blanket film (given by equations 6.1 and 6.2). Figure 6.2 below schematically illustrates three possible mechanisms of edge-induced stress relaxation that have been discussed in theoretical analysis of epitaxial islands/substrate systems.²⁶³

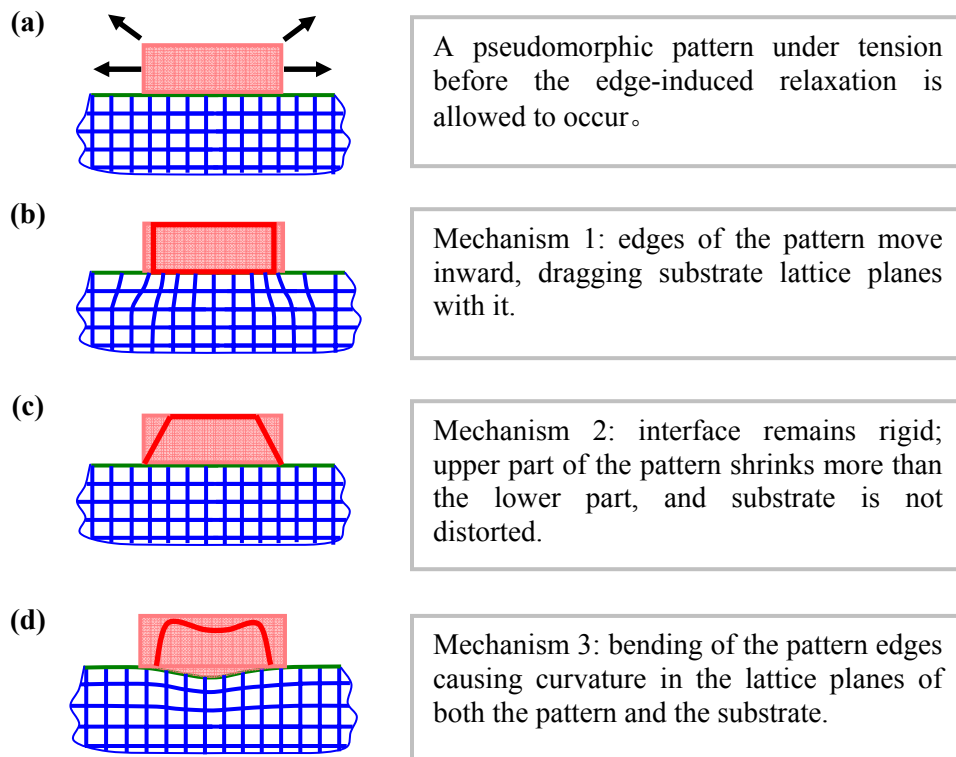


Figure 6.2: Schematic illustration of different mechanisms for edge-induced stress relaxation in a patterned system (assuming tensile stress in the initial pseudomorphic pattern before relaxation).

Free edges also modify the strain field in the substrate. In a blanket film under a uniform biaxial tensile strain on a rigid substrate, the stress field in the middle of the film does not strain the substrate (except for a small strain caused by the curvature) because the thickness of the substrate is considerably larger than that of the film. In contrast, near the film discontinuities or pattern free edges, the lattice of the substrate can be distorted. For convenience we assume that a stretched discrete pattern tends to shrink. In doing so, a compressive stress is caused in the surface layer of the substrate under the pattern, and a tensile stress in the exposed part of the substrate. The signs of the stresses induced in the substrate by the pattern edges are therefore reversed at the pattern edge. The stresses in the exposed part of the substrate will show sharply peaked maximum values close to the edges of the film and then decay to zero as distance from the edges increases. Figure 6.3 shows the simulation result done by Jain *et. al.*²⁶⁴ of normal and shear stresses distribution in the Si substrate induced by the edges of $\text{Ge}_{0.5}\text{Si}_{0.5}$ stripe pattern (note in this case the patterned material is under compression initially).

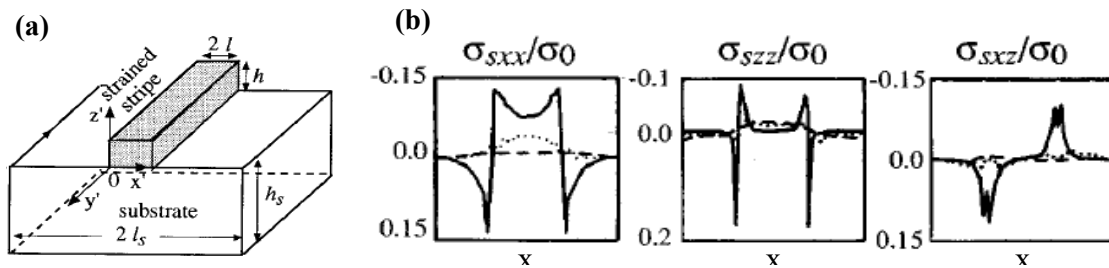


Figure 6.3: Simulation result of stress in the substrate of a patterned sample adapted from literature.²⁶³ (a) Schematic diagram of the strip heterostructure with width = $2l$ and thickness = h . (b) Calculated stresses in the substrate of a patterned sample with $(l, h) = (20, 1)$. Substrate thickness $h_s = 50$ units. Solid line: at a depth of $h_s/50$ from the interface; dotted line: at a depth of $h_s/5$ from the interface; and dashed line: at a depth of $h_s/2$ from the interface. σ_0 represents the biaxial mismatch stress value in an infinitely-large film of the same material system. The range of x -axis is $(0, 100)$.

When the size of the deposited materials decreases (as in the case of nanopatterning), the number of edges and interfaces increases and they come close together. Therefore, nanopatterning significantly modifies the stress field in both the patterned material and the substrate, which may further change the material's behavior related to the stress. For example, it has been demonstrated experimentally that patterning ferroelectric thin film into discrete islands greatly enhanced the piezoresponse (the nominal d_{33} value).^{44, 45} Finite element analysis by Roytburd *et. al.*²⁶⁵ on patterned piezoelectric systems further reveals that the strain induced by the substrate local deformation should also contribute to the measured piezoelectric coefficient of the pattern, besides the intrinsic piezo-strain in the pattern. Obviously, the phenomena related with the stress or strain will become more significant as well as complicated as the size of the features decreases and as more complex structures are designed and fabricated. It is also worth noticing that the edge-induced stress in the substrate is highly localized, i.e., the stresses decay rapidly along in-plane directions and along the depth direction. Further, the distribution of the stress field is very sensitive to the geometry of the pattern, including width, length, thickness, and the aspect ratio. In order to better understand the contribution of a patterned architecture to the modified stress, it is critical to be able to visualize the “edge effect” and the localized stress or strain distribution in the substrate near the pattern for a given geometry.

For micro- or nano-patterned semiconductor systems such as Ge or GeSi patterns on Si wafer, extensive theoretical studies have been conducted since 1990s.²⁶⁶⁻²⁶⁸ Experimental observation of stresses in substrates of such systems were made mainly using Raman scattering spectroscopy.^{252, 269, 270} Practically, this is done by either collecting Raman shift signals from a large number of patterns as statistical results, or by using micro-Raman technique to obtain

spatially resolved information from patterns at least a few micrometer in size. As a sharp contrast, edge-effect in oxide-on-oxide patterned systems has remained significantly under-explored, both theoretically and experimentally. Besides the difficulties in achieving uniformly patterned epitaxial oxide nanostructures, a few major reasons for this underdevelopment are: 1) the intrinsic stresses induced during deposition of oxide thin film or nanopatterns are non-negligible and hard to estimate theoretically, particularly for sol-gel-derived systems; 2) experimental investigation is challenged by the oxide materials property and the high spatial resolution required. For example, the well-developed micro-Raman spectroscopy technique for semiconductors is not very well suited for oxide-on-oxide systems. Most ferroic oxides are wide-band-gap materials. Conventional visible Raman spectroscopy works poorly for these materials because the visible photon energy is much smaller than their band gap.²⁷¹ UV-Raman can provide the proper photon energy, but it usually suffers from lower throughput efficiency, and high stray light level.²⁷² Furthermore, stress measurements using Raman techniques require knowledge of the relation between the observed shift in the spectrum frequency and the elastic response of the oxide material. On the other hand, conventional x-ray stress measurements performed with the use of a relatively large beam ($\sim$ mm) have been used to assess the volume-averaged stress within arrays of features, such as patterned Al lines on Si.²⁷³ However, much higher resolution is required in order to differentiate the stress at the edge of the pattern versus outside of the pattern, when the typical feature size is less than 500 nm. The above reasons have underscored the significance of both developing a versatile oxide patterning approach and employing a high resolution, high precision experimental technique to characterize the “edge effect” on the as-prepared patterned system.

As shown in the previous chapters of this dissertation, the VP-soft-eBL approach has been developed into an enabling tool to fabricate diverse oxide-on-oxide nanopatterned systems with precise size, shape and structural control. It is a tantalizing task to employ the nanopattern fabricated with VP-soft-eBL as test-bed structures and investigate the distribution of strain or stress in a given structure using a characterization technique suitable for non-destructive, high resolution analysis.

6.3 X-RAY MICRODIFFRACTION TECHNIQUE

We attempted to employ the x-ray microdiffraction technique to probe the VP-soft-eBL patterns. Unlike the conventional in-house x-ray sources, the introduction of synchrotron x-ray microbeam techniques allows for a localized examination of the strain within crystalline thin-film features.²⁷⁴ In particular, the ability to resolve lattice spacing as a function of position within the feature at a submicron resolution provides us with a method to map elastic deformation due to the presence of free edges. Equipped with these capabilities, we aim at obtaining direct observation of the edge-modified strain field in the patterned system for a given pattern geometry, and revealing the type of deformation induced in the substrate and its extent.

6.3.1 Experimental set-up

Measurements are conducted at station 2-ID-D of the Advanced Photon Source (APS) at Argonne National Laboratory. The hard x-ray microprobe uses the radiation generated by an APS undulator. The first main optical component located 29.5 m from the source (centre of the undulator) is a water-cooled, grazing-incidence, horizontal-deflection mirror designed to

preserve source brilliance and beam coherence and to suppress high order harmonics of the undulator radiation. A double-crystal Si(111) monochromator located 62 m away from the source is used to select a beam energy of 10.08 keV, corresponding to a wavelength of 1.230 Å. A hard x-ray phase zone plate located 71 m from the source is employed to achieve high focusing power. In this experimental set-up, a focused beam with 200 nm diameter is produced with a divergence smaller than 0.01° (the footprint of the beam on the sample surface is usually larger than the beam diameter depending on the incident angle). An order-sorting aperture (OSA) of 20 μm is used to select the first-order focusing beam, and a gold beam stop (30 μm in diameter and 40 μm thick) is used to reduce the zero-order beam through the OSA. A photon flux of 10^{10} photons s^{-1} can be achieved at the focal spot. The focal point of the x-ray beam is aligned with the center of an x-ray diffractometer to allow precise diffraction measurements. Diffracted x-rays are collected with a charge-coupled device (CCD) camera that allowed measurements of the angular position, angular width, and intensity of x-ray reflections. An x-ray fluorescence (XRF) detector is equipped so that diffraction and fluorescence can be simultaneously measured. By monitoring the fluorescence signals, the beam location with respect to the micro- or nanopatterns can be determined at all times. The sample stage can be moved in-plane at less than 100 nm step size, which allows line scan or mapping of the scattering or XRF signal. Figure 6.4 shows a schematic diagram of the zone-plate optical system.

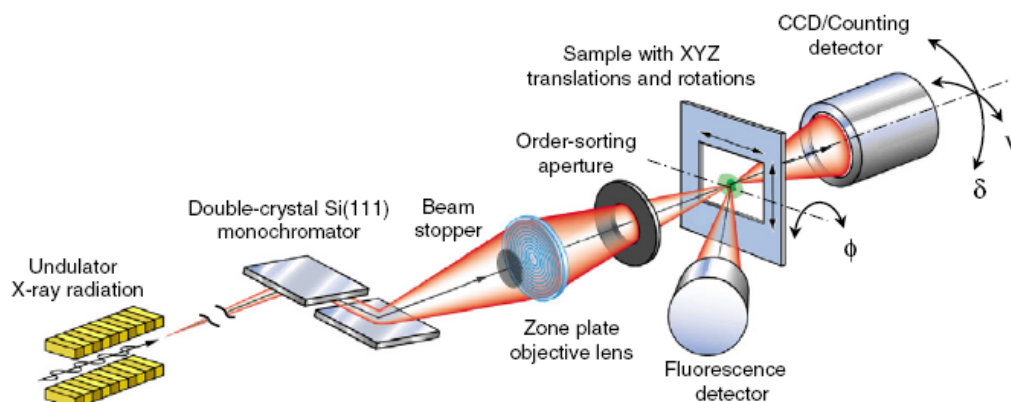


Figure 6.4: Schematic diagram of the x-ray microprobe set-up at the 2-ID-D station of the APS. All of the slits and the mirror are omitted. ²⁷⁵

6.3.2 Sample preparation

Single crystal (001) MgO substrate patterned with CFO line nanostructures is used in the diffraction experiment, for a few reasons. First, although the line width is comparable to beam size, the length of the lines is in the range of a few micrometers, much larger than the beam footprint. Therefore the spatial resolution of the scattering signal should be high enough to resolve the change along the line, if not inside each line. From this point of view, the line pattern is a better test structure for x-ray microdiffraction than the 0D nanodiscs. Second, due to the high aspect ratio of length/width for line patterns, the stress distribution along the line is expected to be different from that across the line from theoretical calculations.⁴⁶ It is of great interest to investigate this effect experimentally.

Specifically, CFO lines with a nominal width of 200 ~ 500 nm and length of 6 μm are patterned on (001) single crystal MgO substrate. The line direction is along $\langle 100 \rangle$ direction of the substrate, therefore the lines exhibit zig-zag edged morphology. The line thickness is around 20 to 50 nm, determined by AFM measurement. Center-to-center separation between neighboring lines is 6 μm . After annealing the CFO lines, the sample is patterned with Au/Pd cross marker at the center of CFO line groups as shown in figure 6.5. The Au/Pd cross is 5 μm wide, 50 μm long, and 50 nm thick. The cross can be easily located using XRF due to the strong fluorescence signal produced by Au/Pd and the large dimension of the cross. By recording the relative position of the CFO lines with respect to the center of the cross using SEM beforehand, the line patterns can be conveniently located by offsetting the sample stage from the center of the marker in both “x” and “z” directions.

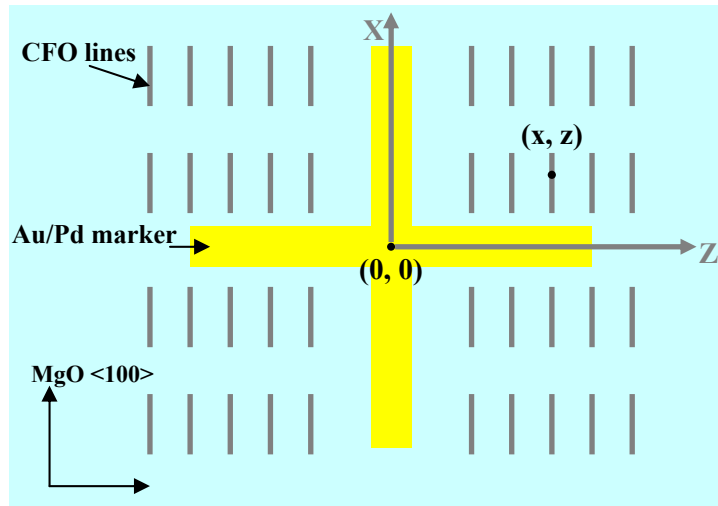


Figure 6.5: Schematic illustration of the sample with CFO line patterns and Au/Pd marker on (001) MgO substrate.

Figure 6.6 shows a simplified illustration of geometry for detection of the diffraction and XRF signal from the nanopatterns. The angle between the diffracted beam and the incident crystal plane (indicated by the green plane) is χ . Using the CCD detector allows recording of the diffracted beam intensity in association with 2θ and χ angles.

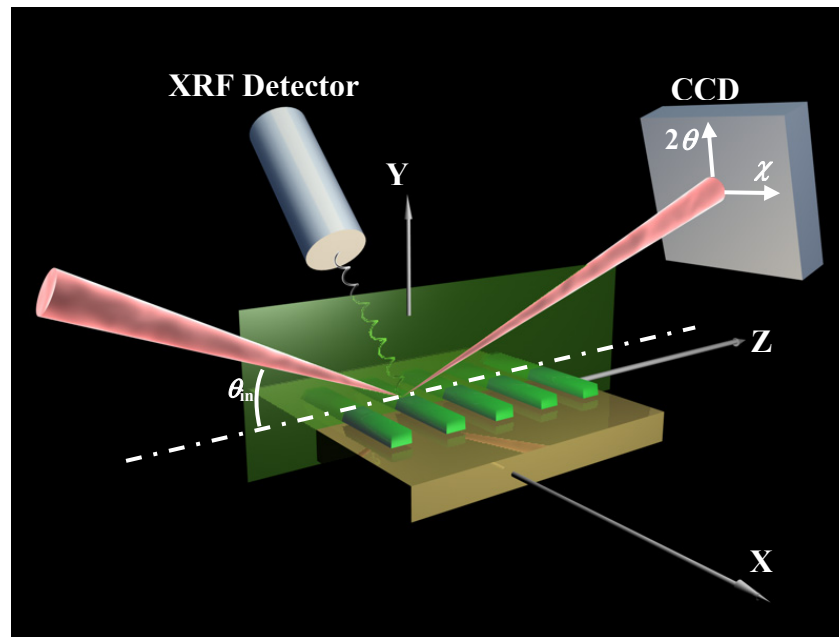


Figure 6.6: A simplified illustration of geometry for detection of the diffraction and XRF signal from the nanopatterns.

6.3.3 Experimental procedure

6.3.3.1 Methodology and determination of Bragg angle

In principle, diffraction signal from either the epilayer or the substrate can be used to determine the strain field in a patterned epitaxial architecture. Using x-ray microbeam technique, both have been pioneered at station 2-ID-D of APS on semiconductor systems. For instance,

SiGe stripe (20 μm wide, 240 nm thick) on Si substrate has been investigated by Murray *et. al.*²² using the SiGe (008) diffraction peak intensity change across the line. In another experiment by the same group, diffraction intensities of the (004) and (333) diffraction peaks of the Si substrate were collected from samples patterned with a few micron wide SiGe stripes and 190 μm Ni dots, respectively.²⁷⁶ In these examples, the moderate lattice mismatch between the pattern and the substrate as well as the large pattern dimension ensure either a distinguishable diffraction signal from the pattern itself or a noticeable diffractive intensity change of the out-of-plane substrate lattice due to the pattern. However, this may not be the case for the CFO/MgO system. The small feature size of the CFO lines and the lattice mismatch between CFO and MgO as low as 0.4%, (almost 10 times smaller than the SiGe/Si) make it difficult to directly observe the Bragg diffraction intensity of CFO (00 l) plane. This is because the diffraction pattern collected by the CCD at the corresponding Bragg angle will be presumably dominated by the strong intensity from the single crystal bulk MgO substrate, and very short exposure time has to be used to prevent CCD from saturation. Selection of CFO (311) plane diffraction may resolve this problem since MgO does not have the corresponding lattice plane at similar Bragg angle. However, this operation is not allowed by our set-up geometry. Therefore, we select using the diffraction signal from the MgO substrate at or around the Bragg angle of the (004) plane.

The Bragg angle of (004) plane of MgO (001) single crystal substrate is determined by the Bragg's Law, i.e.,

$$2d \cdot \sin \theta_B = \lambda \quad (6.3)$$

Input $\lambda = 1.230 \text{ \AA}$ and $d_{(400)} = 1.052 \text{ \AA}$, the Bragg angle $\theta_B(004) = 35.724^\circ$. This is practically done by first aligning the sample into the geometry shown in figure 6.6., and then collecting the diffracted beam intensity in a θ - 2θ scan at an area free of CFO pattern on the substrate. A typical θ - 2θ scan profile is shown in figure 6.7. After this, the peak position to set to be 35.724° .

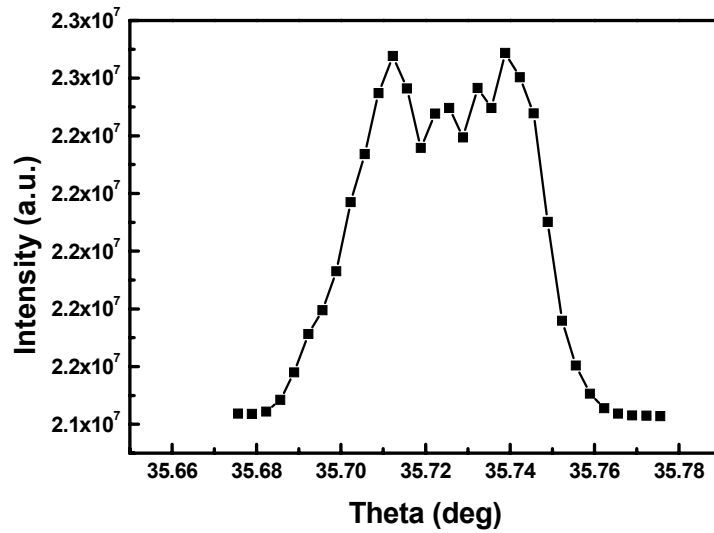


Figure 6.7: Theta-2theta scan about $\theta_B(400) = 35.724^\circ$. The intensity drop at the center is due to the beam stop used to reduce the zero-order beam and prevent the saturation of CCD.

6.3.3.2 X-ray scattering from MgO substrate

Signal is first obtained from an area free of CFO pattern on the MgO substrate, and the diffracted beam intensity (I_D) within a certain range of 2θ and χ is collected by the CCD detector. It is observed that two subspots with high intensity consistently appear on CCD pattern when the incident angle is slightly off the Bragg angle of (004) MgO, as shown in figure 6.8. Figure 6.8 is taken at $\theta_{in} = \theta_B + 0.2^\circ = 35.924^\circ$. White dotted line indicates the two subspots as two areas

of interest (ROI), ROI-1 and ROI-2, respectively. The sharp, bright ROI-1 subspot is centered at $(2\theta = 71.85^\circ, \chi = 0.81^\circ)$, whereas the relatively diffuse ROI-2 subspot is centered at $(2\theta = 71.62^\circ, \chi = 0.81^\circ)$ (ROI-2). The center splitting of the two subspots along 2θ -direction is about 0.23 degrees, whereas the splitting along χ -direction is negligible. On the other hand, the diffuse subspot itself shows a fairly broad intensity distribution within a certain range of 2θ as well as χ . The two subspots are consistently observed for $\theta_{in} = \theta_B \pm \Delta$, where Δ ranges from 0.05° to 0.4° .

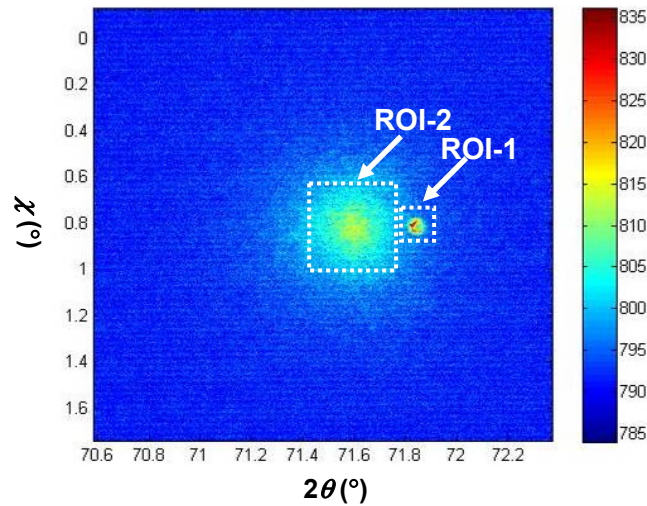


Figure 6.8: 2θ - χ frame collected by exposure on an area of MgO substrate free of CFO pattern, $\theta_{in} = \theta_B + 0.2^\circ = 35.924^\circ$.

The 2θ angle positions of ROI-1 and ROI-2 intensity change differently with the incident angle, as measured from the CCD detector. Table 6.2 summarizes this change and the outgoing angle θ_{out} (i.e., the angle between the outgoing beam and the substrate surface in the goniometer plane) for ROI-1 and ROI-2 at different incident angles (all angles are in degree unit).

Table 6.2 Change of ROI 2θ angle and outgoing angle with incident angle

$\theta_{in} = \theta_B + \Delta$	$\theta_{in} < \theta_B$		$\theta_{in} > \theta_B$	
	35.524	35.624	35.824	35.924
$2 \times \theta_{in}$	71.048	71.248	71.648	71.848
$(2\theta)_{ROI1}$	71.05	71.25	71.65	71.85
$\theta_{out} (ROI1) = (2\theta)_{ROI1} - \theta_{in}$	35.526	35.626	35.826	35.926
$(2\theta)_{ROI2}$	71.32	71.38	71.49	71.62
$\theta_{out} (ROI2) = (2\theta)_{ROI2} - \theta_{in}$	35.796	35.756	35.666	35.696
$\theta_B - \theta_{out} (ROI2)$	-0.072	-0.032	0.058	0.028

The narrow intensity distribution inside ROI-1 subspot and the intensity drop at the center position (due to the beam stop) suggest that the origin of ROI-1 intensity is the specular reflection from the MgO substrate surface. This is further corroborated by the fact that the 2θ position of ROI-1 remains precisely two times that of the incident angle, as listed in table 6.2. That is, the outgoing angle corresponding to the ROI-1 intensity equals to the exact incident angle. Comparatively, the 2θ positions of ROI-2 satisfy $(2\theta)_{ROI2} > (2\theta)_{ROI1}$ when $\theta_{in} < \theta_B$, and $(2\theta)_{ROI2} < (2\theta)_{ROI1}$ when $\theta_{in} > \theta_B$. The outgoing angle corresponding to ROI-2 subspot is very close to the Bragg angle, with a maximum offset of 0.07° . Therefore the origin of ROI-2 is considered to be diffuse scattering, as illustrated in figure 6.9.

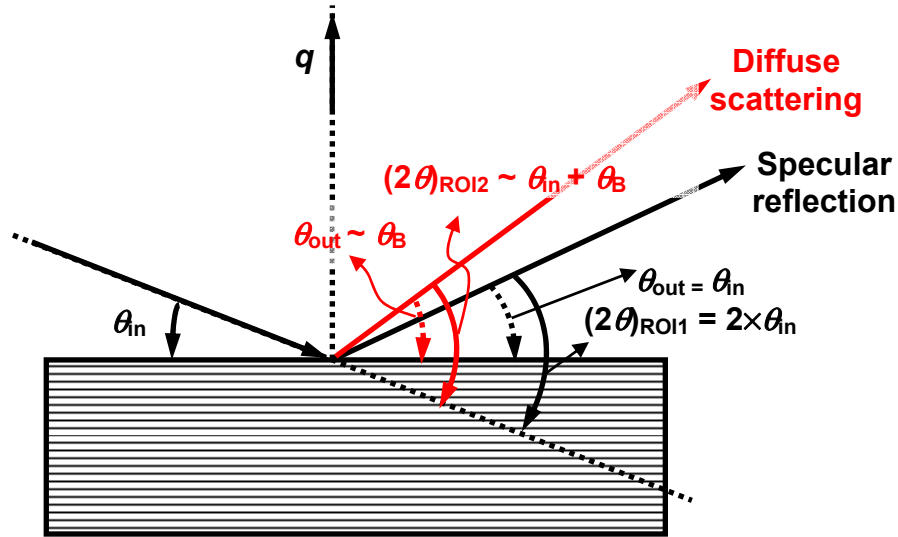


Figure 6.9: Schematic illustration of specular reflection and diffuse scattering from a single crystal substrate (with zero-miscut in the goniometer plane).

As compared with specular diffraction which provides information about the average crystal structure, x-ray diffuse scattering contains information about the deviations from the average over a range of 10 to 1000 Å.²⁷⁷ In case of small-angle Bragg reflections, diffuse scattering is mainly caused by electron-density fluctuations at surfaces (e.g., surface roughness). In contrast to that, in case of lattice Bragg diffractions, diffuse scattering is also caused by variations in lattice strain. It has been well-known that the final stage of single crystal substrates fabrication usually requires substantial cutting, shaping and polishing, all of which may introduce residual strain and defects in terms of roughness and crystallographic misorientation.²⁷⁸ Besides, many oxide single crystal substrates such as SrTiO₃ and MgO show structural rearrangements involving several atomic layers upon thermal treatment.^{279, 280} All these structural deviations from a perfect crystal

can contribute to the diffuse scattering intensity collected. In fact, we have conducted similar off-Bragg angle scattering on a (001) SrTiO₃ single crystal substrate annealed in O₂ flow at 1000°C. Similar intensity distribution with two subspots is observed for an incident angle that is 0.1° away from the Bragg angle of STO (004) plane. The 2θ positions of the two subspots follow the same trend as stated earlier.

X-ray diffuse scattering provides a useful tool for surface/interfacial roughness and strain field studies in thin films,²⁸¹ superlattices²⁸² as well as mesoscopic heterostructures.²⁸³ Since the existence of the CFO 1D epitaxial lines may cause non-uniform strain field in the substrate area in close proximity of the patterns (e.g., lattice bending or disorientation in MgO), it will then be interesting to detect the diffuse scattering intensity change of the substrate site-specifically around the nanostructure. This is done practically by moving the sample in small step size in x-z-plane so that the x-ray beam scans across the CFO line or a two-dimensional area containing CFO lines, and collecting the integrated intensity of ROI-2 as described in the section below. It is worth pointing out that diffuse scattering is normally several orders of magnitude weaker than the Bragg scattering. In order to observe it, either a very long exposure time or very intense incident radiation is required. In our experiments, synchrotron x-ray source has greatly facilitated the observation of diffuse scattering in our experiment. On the other hand, Bragg scattering is diminished by incidence at deviation angles $\theta_m = \theta_B \pm \Delta$, which helps to follow the diffuse scattering intensity on the Bragg peak tail.

6.3.3.3 Variation of diffuse scattering intensity across CFO line

(1) Z-scan across one CFO line

The integrated intensity of ROI-1 and ROI-2 are first plotted as a function of the beam position perpendicularly across an individual CFO line over 6 μm length. The ROI-1 and ROI-2 ranges in terms of $(2\theta, \chi)$ are carefully selected and kept constant so that the intensity value from each point of the plot can be compared. The step size used for z-scan is 200 nm. The exposure time for CCD detector is 2 sec, and the XRF collection time is 1 sec. To ensure the generality of the observation, the z-scan experiment is repeated many times on different areas of the sample after careful beam alignment at each area. The incident angles for these scans are set to be within 0.2° range of offset from θ_B .

A typical result of the z-scan at $\theta_{\text{in}} = 35.824^\circ$ is shown in figure 6.10. Figure 6.10(a) is a schematic illustration of the sample cross-section. Figures 6.10(b) to 6.10(d) are the XRF signal of Co $K\alpha$ intensity, the integrated intensity of ROI-1, and the integrated intensity of ROI-2, separately. Figures 6.10(a) through 6.10(d) are labeled with yellow, green and grey colors to indicate the substrate surface area near the edges of the pattern, just below the pattern, and far away from the pattern, respectively. Inset of figure 6.10(a) is a VP-SEM image of part of a CFO line from the area investigated. The full-width-half-maximum (FWHM) of XRF peak is about 2 μm , much larger than the pattern width observed with SEM. This is due to the large beam footprint on the sample at $\theta_{\text{in}} = 35.824^\circ$ and the resultant beam interaction with CFO even when the beam center is certain distance away from the edge of the pattern (see appendix 6.1 for schematic explanation). Figure 6.10(c) shows a valley at around $z = 3 \mu\text{m}$, corresponding to the ROI-1 intensity drop with a magnitude of about 3000 counts. This drop is about 21% of the reference integrated intensity measured from the areas far away from the pattern (14300 counts on average). The offset between the XRF peak position and the center position of the ROI-1

valley is due to the asymmetric XRF signal yield from the left and right sides of pattern induced by the scanning direction, as detailed in appendix 6.1. From figure 6.10(d) it is interesting to notice two sharp peaks centered at $z = 2 \mu\text{m}$ and $z = 4 \mu\text{m}$ positions. The relative intensity increase at the peak is about 17% of the reference intensity. At the center position of the pattern, the ROI-2 intensity drops down to a value slightly (about 6%) higher than the reference intensity. The significant difference of the integrated ROI intensities from substrate areas under the line (green region), near the edge of the line (yellow region), and far away from the line (grey region) indicates a non-uniform strain distribution in the MgO substrate around the patterned area.

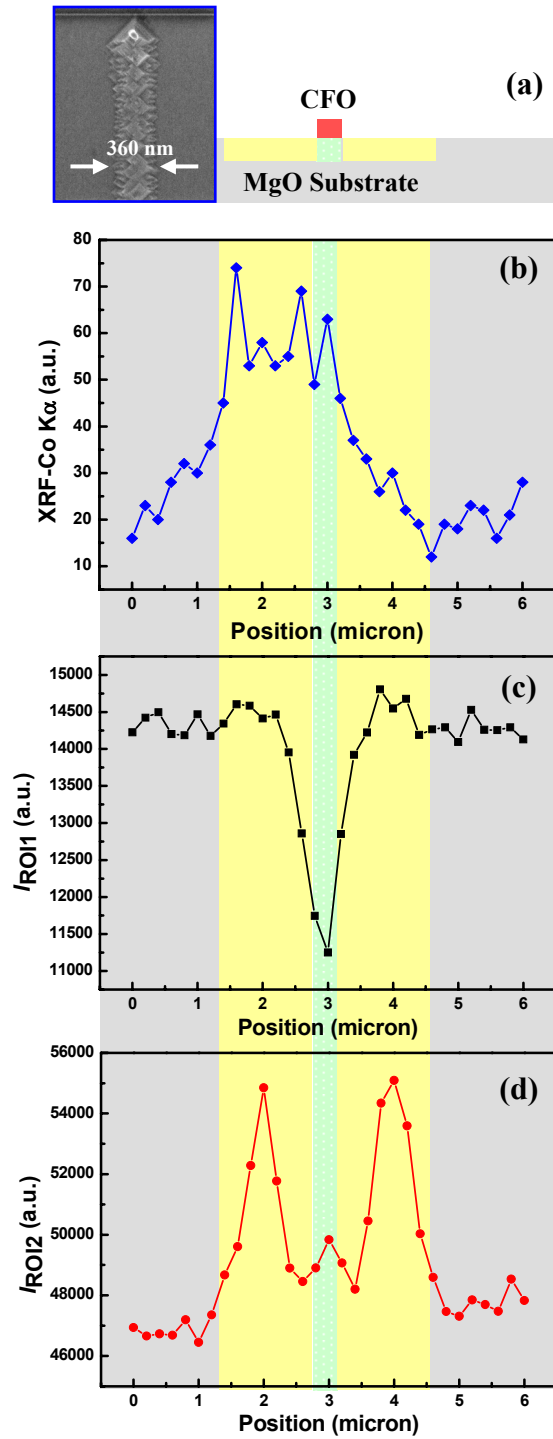


Figure 6.10: Diffraction result from scanning across one CFO line. (a) Schematic illustration of the sample cross-section. Inset shows the VP-SEM image of the line at the illuminated area. (b) XRF signal; (b) Integrated intensity of ROI-1 across the line; (c) Integrated intensity of ROI-2 across the line.

In the following paragraphs, we discuss the possible mechanism for the formation of multiple maxima and minima in ROI-1 and ROI-2 plots. We consider two factors that may contribute to a decreased intensity of the substrate specular reflection (ROI-1) from the patterned area, i.e., x-ray absorption of CFO pattern and the destructive interference of the beams reflected at different surfaces and interface of the heterostructure. The relative intensity decrease caused by the absorption due to a 50 nm-thick CFO stripe at $\theta_{in} = 35.824^\circ$ is only 1.16%, much smaller than the 21% drop observed from figure 6.9. The detailed calculation is shown in appendix 6.2. Therefore the major contribution to the intensity decrease can be ascribed to the destructive interference of the x-ray beams reflected at different interfaces and surfaces due to the existence of the epitaxial layer of CFO. Such interference has been widely reported in x-ray reflectivity experiments on superlattices and epitaxial thin films.^{284, 285} The interference in principle may cause either increase or decrease of the reflection intensity, depending on parameters such as the thickness and electron density of the film and the incident angle. When condition applies, the drop in reflectivity intensity may reach up to a few tens of percentage. Estimation of the exact amount of intensity drop due to the destructive interference is under exploration in our laboratory and is beyond the scope of this dissertation. Considering the nature of the ROI-1 intensity as the specular reflection, its valley position may represent the position of the CFO line more precisely than the XRF signal peak position.

The origin of the two sharp peaks in ROI-2 plot is of great interest to us. The peaks are observed consistently on different patterns and with different incident angles (both $\theta_{in} < \theta_B$ and $\theta_{in} > \theta_B$). The peak positions are about 700 nm away from the physical line edges suggested by the ROI-1 intensity plot and the SEM image. The intensity variation of the diffuse scattering for

an epitaxial nanopatterned system may include the following contributions: (i) lattice perturbation in the substrate a few nanometers or tens of nanometers deep from the top surface, caused by the local strain gradients due to the pattern edge-effect. We refer to this effect as the structural factor; (ii) roughness variation of the substrate surface. This includes the true roughness change across the nanostructure due to the patterning process (if any) and the abrupt edges of the pattern that can be considered as nominal height variation of the surface. Both are referred to below as the morphological factor. Considering the patterning procedure involves mainly gentle e-beam lithography and sintering of sol-gel precursor, it is reasonable to assume that the true morphological roughness change raised by the patterning process can be neglected. On the other hand, the nominal height variation due to the existence of the CFO line is highly localized within the nanostructure, as can be seen from the inset of figure 6.9(a). This minimizes the possibility of diffuse scattering change due to the influence of morphological factor. Given the near-Bragg scattering condition (i.e., the incident and diffracted angles are both close to Bragg angle), the pattern-modified inhomogeneous strain field that causes deviations from perfect lattice periodicity may carry significant weight in the diffuse scattering intensity variation.

(2) Two-dimensional high resolution mapping of diffuse scattering intensity

To confirm the observation from figure 6.10 and demonstrate the ROI intensity change in a more illustrative way, z-x-mapping has been conducted on an area that covers a few CFO lines. The mapping is done by sample translation along x and z directions, equivalent to scanning the x-ray beam across the sample at fixed incident angle. The area under investigation is a 12×4

μm^2 square containing portions of 3 CFO lines. The sample moving step size is 200 nm along x-direction, and 100 nm along z-direction. X-ray scattering data are acquired at $\theta_{\text{in}} = \theta_{\text{B}} + 0.1^\circ = 35.824^\circ$. The exposure time is fixed at 4 sec at each spot. The integrated intensity changes of ROI-1 and ROI-2 with position are collected, as shown in figure 6.11. Figure 6.11(a) is a schematic illustration of the exposed sample area that includes half the length and one end of the CFO lines. Figures 6.11(b) to 6.11(d) are the XRF signal of Co $K\alpha$ intensity, the integrated intensity of ROI-1, and the integrated intensity of ROI-2, respectively. The bending of the line profile in these plots is due to the sample drifting during the long time scan (the total collecting time of this scan is about 10 hrs). The uneven background contrast in figures 6.11(c) and 6.11(d) is caused by the slight offset of the incident beam angle away from the ideal 35.824° along at different regions of this $12 \times 4 \mu\text{m}^2$ area. This is due to a minor sample tilting about z-axis, which can be hard to correct by system alignment since sample stage rotation about z-axis is not allowed.

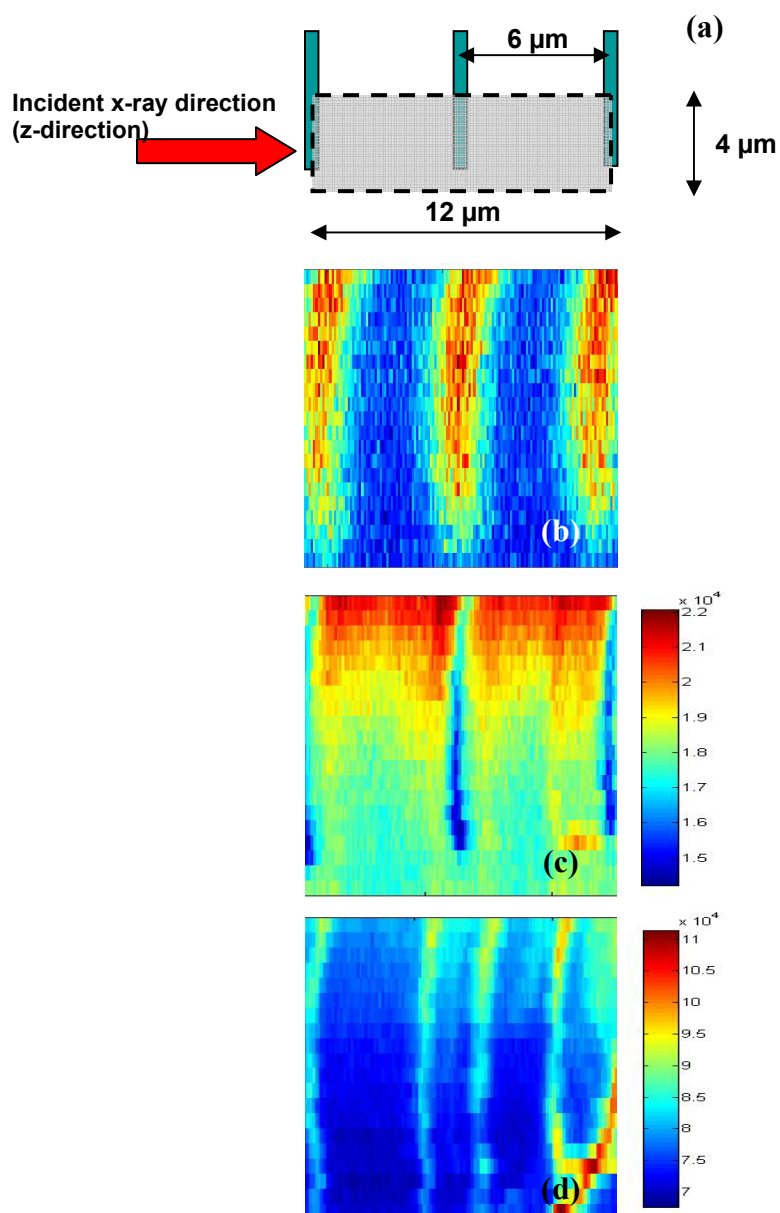


Figure 6.11: (a) Schematic illustration of the sample area; (b) XRF signal; (b) Variation of the integrated specular reflection intensity (ROI-1) across this area; (c) Variation of the integrated diffuse scattering intensity (ROI-2) across this area. The high contrast at bottom-right is probably due to a random substrate defect (i.e., a scratch).

By comparing the XRF signal and the intensity variation of ROI-1 and ROI-2, there is clearly a tendency of consistent intensity change in diffuse scattering signal at both sides of each line along the length direction. The absolute intensities at these peak positions in figure 6.11(d) range between 78000 to 82000 counts, whereas intensities further away from the edges are below ~68000 counts. The continuity of the intensity profile suggests that the CFO lines are fully mechanically “clamped” along the length direction by the substrate.

We notice from figures 6.10 and 6.11 that the peak positions of the diffuse scattering intensity do not correspond exactly to the edge positions of the CFO lines. Rather, they seem to show up repeatedly at a few hundred nanometers away from the physical line edges indicated by SEM image. Further investigation is to take place to explain why the diffuse scattering intensity reaches extrema at such positions. At this stage, however, we should point out that the diffraction geometry at 35.824° incidence and the size of the beam footprint (about 340 nm) may both contribute to this phenomenon. Particularly, we should consider the effect of x-ray interaction with sample along the depth direction. Because the three-dimensional strain field distribution in MgO substrate near nanolines and the variation of the lattice deformation along the depth direction below the pattern, the correspondence between the ROI-2 intensity variation and the highest extent of lattice perturbation can be rather complicated.²⁸⁶ However, the characteristic profile exhibited by the diffuse scattering intensity is indicative of the deformation induced by an edge force due to the nanopatterned geometry.

Another interesting feature observed from the intensity maps is: the intensity contour near the edges seem to extend further along the longitudinal direction (i.e., x-direction) than the position of the line end observed from both figure 6.11(c) and 6.11(d). This has suggested that

the lattice perturbation (i.e., strain) other than the morphological factor may be the major contribution to the diffused scattering increase at the CFO edge position. It further implies that the lattice perturbation induced in the substrate may extend further than the length of the pattern, probably due to the high length/width aspect ratio of the CFO lines. It is known that the edge-effect is strongly related to the geometry of the pattern. For example, finite element analysis has shown a more prominent increase of stress in the substrate at pattern edge for patterns with higher width/height ratio.²⁶³ In our experiment, the CFO lines have length/width aspect ratio as high as about 10 ~ 20, which can potentially result in a different strain field distribution in MgO at the tails of lines as compared with at near the side edges. To confirm this, multiple z-scans are conducted under identical conditions with the exception of the illuminated position with respect to the end of one CFO line. Figure 6.12(a) shows four typical scan results from (i) in the middle of the line; (ii) at the end of the line; (iii) about 800 nm away from the line end; and (iv) about 2.6 μm away from the line end. Figure 6.12(b) is a schematic illustration showing the relative positions where each scan is performed. It can be inferred from the plot that the intensity contour from both sides of the line meets and closes at the end of the line. It further extends a certain length along the line direction. This extension length is more than 1/3 of the line length. This clearly suggests that a non-zero strain field still exists in the substrate even at a certain distance away from the end of the line along the longitudinal direction and gradually dissipates along this direction. Similar epilayer strip structures have been extensively studied theoretically using FEA method.^{263, 287} Further, the longitudinal component of stress in the substrate is expected to be the highest due to the large constraint along the line direction.⁴⁶ Therefore, the extension of the intensity contour may be the result of the non-zero longitudinal stress dissipation

along the line direction. To our knowledge this is the first time the existence of a substantial deformation in a substrate area outside of the patterned region induced by the pattern/substrate constraint is experimentally observed.

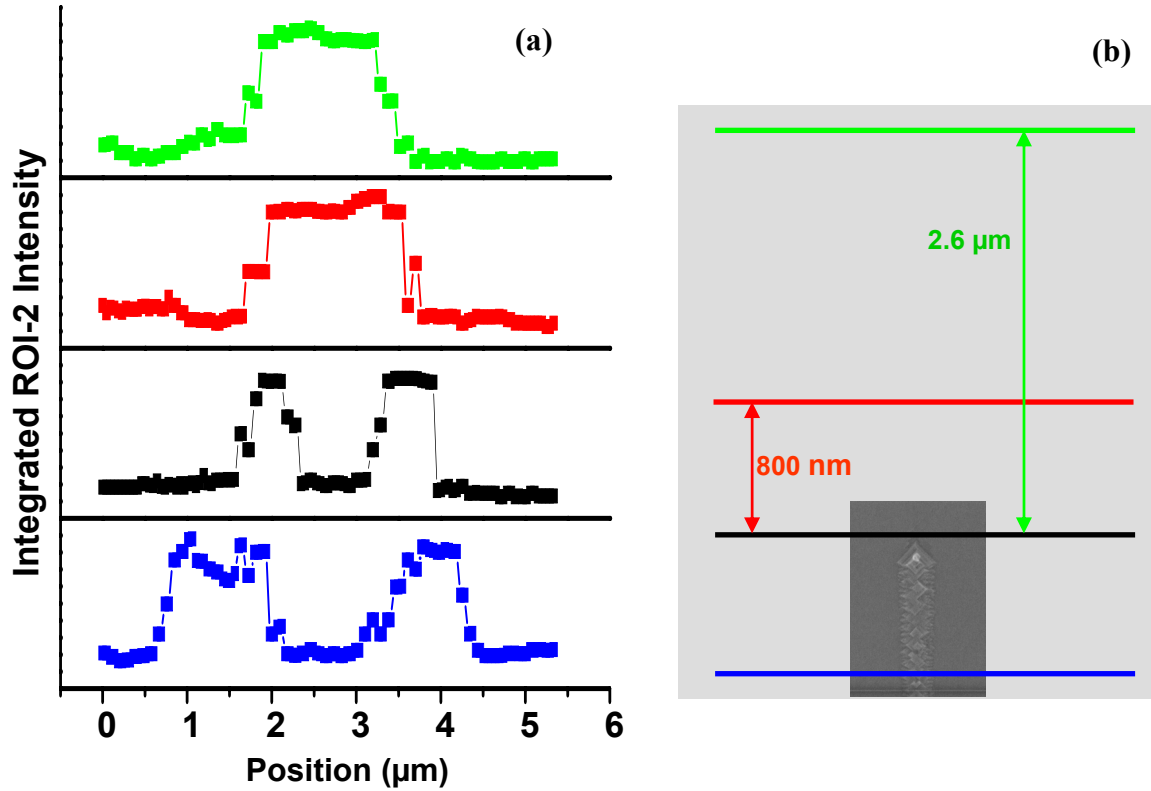


Figure 6.12: (a) Plots of integrated ROI-2 intensity at different longitudinal positions. From top to bottom: scan results at x-positions corresponding to the middle of the CFO line, at the end of the line, 800 nm away from the line end and 2.6 μm away from the line end. All line scans are plotted within the same vertical scale. (b) Schematic illustration of the relative positions where the scans are performed.

6.3.4 Comments on the microdiffraction method employed in this work

Diffuse x-ray scattering has emerged over the past two decades as a powerful way to analyze the correlation of interfacial roughness between successive layers,²⁸⁸⁻²⁹⁰ as well as determination of shape, size, strain profile and positional correlation of mesoscopic and nanoscale semiconductor structures.²⁹¹⁻²⁹³ In most cases, diffuse scattering measurements are made at small angles of incidence or grazing incidence. Grazing-incidence x-rays penetrate only several hundred angstroms into the sample and therefore may be limited for probing structures at larger depths. In our exploratory work, diffuse scattering intensity at near-Bragg incident angles on a synchrotron x-ray microbeam set-up is measured and plotted as a function of the position with respect to the epilayer pattern edge. For systems with discrete nanopatterns and a low lattice mismatch between substrate and patterned material, this approach is potentially a suitable alternative of conventional x-ray diffraction. For such systems, the low diffraction intensity from individual pattern or the small intensity variation due to strain induced in the weakly deformed substrate can add formidable difficulties in data collection with conventional diffraction methods. Although interpretation of the experimental data are still at developmental stage, nevertheless the initial results offer points of interests in understanding the influence of the pattern geometry on the spatial constraint related phenomena. Theoretical modeling of various possible contributions to the diffuse scattering amplitude is indispensable in order to disentangle the strain field information. This is further discussed as future work in chapter 7.

6.4 SUMMARY

This chapter describes our exploratory work on site-specific probing of the dimensional constraint effect in a nanopatterned system using synchrotron x-ray microbeam technique. X-ray microdiffraction method has been employed on single crystal (001) MgO substrate patterned with epitaxial CFO nanolines, aiming at investigation of the localized strain field variation in the substrate in vicinity of the pattern free edges. Specular reflection and diffuse scattering intensities from the MgO substrate are collected at near-Bragg incident angles. The diffuse scattering intensity has shown consistent peak value near the line edge positions. Further, the higher intensity extends more than 2 μm away from the line tail along the longitudinal direction. Lattice perturbation caused by the edge-induced strain field in the substrate is considered to be a major reason for this intensity variation. Better understanding of the experimental results and theoretical modeling are required to achieve quantitative understanding of the patterning-modified stress distribution in a sol-gel derived nano-constrained system.

CHAPTER 7

SUMMARY AND FUTURE WORK

7.1 SUMMARY OF THE DISSERTATION

In this dissertation, we report the development of VP-soft-eBL approach, a facile and versatile patterning scheme for fabrication and microstructural engineering of spatially and dimensionally constrained functional oxide nanostructures. Combining the advantages of the electron beam lithography and wet chemistry synergistically, VP-soft-eBL resolves challenges in nanofabrication of refractory and chemically inert ceramics from either pure “top-down” or pure “bottom-up” methods. We have demonstrated that the VP-soft-eBL approach possesses four major attributes pertinent to patterning of oxide ceramics: etch-free, high spatial resolution, registry and material/substrate generality.

Based on its remarkable versatility, the scope of VP-soft-eBL has been greatly expanded not only as a nanofabrication technique for spatially constrained oxide nanostructures at diverse dimensionalities, but also as an enabler for exquisite control over morphology, shape evolution, and crystalline orientation of these nanostructures. Our effort span fabrication and structural engineering of zero-dimensional to three-dimensional nanostructures, and understanding of fundamentals in the VP-eBL process. Embedded are varied site-specific characterizations of the nanopatterns, using scanning probe microscopy, electron microscopy and synchrotron x-ray probe. Particularly:

(1) Zero-dimensional CoFe_2O_4 and BaTiO_3 nanodisc arrays are fabricated with preferred crystallinity and orientation on diverse substrates. We show that below a certain pattern aspect ratio, the as-deposited amorphous nanodiscs can be readily converted into epitaxial, single-crystal form. The mechanism of microstructure development with the pattern size change is discussed. Patterning controlled morphology is demonstrated on zero-dimensional and one-dimensional nanostructures by simply tuning the VP-soft-eBL patterning parameters. The structure, chemical nature and functionality identity of the VP-soft-eBL fabricated nanostructures are probed with a complementary set of characterization tools.

(2) The enhancement of proximity effects due to the beam skirt in VP-eBL process is of primary concern when fabricating dense two-dimensional grid patterns over large areas. We have developed an analytical method to predict the distribution of the energy deposited by the beam skirt, using a modified form of the proximity function suitable for VP-eBL condition. This analytical method allows for dose compensation during VP-eBL patterning and serves as a platform to analyze the general distribution of electrons in the beam skirt. Incorporating these proximity effects in pattern design, two-dimensional, high-pattern-density BaTiO_3 grids are fabricated with precise size control.

(3) Patterning of vertically-stacked and radially-stacked heterostructures have been demonstrated for VP-soft-eBL. Particularly, modification of the substrate hydrophobicity with self-assembled monolayers allows for formation of nanoring “reservoirs”, which can be filled with a different sol to form “core-shell” heterostructure patterns. This directed patterning of oxide heterostructures avoids painstaking feature-alignment procedure between fabrication of the

first and second materials. This contribution demonstrates the efficacy and feasibility of fabricating hybrid oxide nanostructures via VP-soft-eBL.

The dissertation also incorporates the exploratory work performed in our laboratory on site-specific probing of the dimensional constraint effect in a nanopatterned system using synchrotron x-ray microbeam technique. This work utilizes 1D epitaxial patterns fabricated via VP-soft-eBL as test-structures, and employs diffuse scattering intensity from the substrate as a gauge to provide indicative information of lattice perturbation caused by the edge-induced strain field. This work, albeit still in developmental stage, may prove an interesting approach to investigate the VP-soft-eBL patterned oxides under diverse dimensional confinement conditions.

The reported approach to the formation of oxide nanopatterns with controlled microstructure, as well as the site-specific characterization strategy, is highly general. Our effort described in this dissertation lays the groundwork for in-depth exploration in the rich phenomena related to the spatial and dimensional confinement for functional ceramics. Combined with further refinement, it may open up wide possibilities of achieving novel functionalities and applications that require miniaturized functional oxide building blocks.

7.2 SUGGESTIONS ON FUTURE WORK

Based on the VP-soft-eBL platform, further work on dimensionally constrained oxide nanopatterns can be focused on obtaining site-specific microstructural and functional information from the nanostructures. Specifically, the following research directions can be explored.

I. Development and advancing of innovative characterization methodologies applicable to nanopatterned systems

(1) Continuing efforts on advancing high resolution x-ray diffraction technique

In this area, applying the x-ray microdiffraction technique to investigate the influence of pattern geometry for the epitaxial nanopattern/susbstrate system can be an exciting subject. Analytical work has shown the normalized stresses in both semiconductor or metal epilayers and the underlying substrate are significantly modified by the aspect ratio of the pattern.^{154, 263, 267, 294} Experimental observation of the aspect ratio effect for sol-derived oxide nanopatterns will help establish such relationship for oxide-on-oxide systems. The same strategy can be also applied to investigate the ferroelectric nanostructures, aiming to set up the correlation of strain-microstructure-ferroelectric performance.

On the other hand, it is necessary to achieve quantitative analysis on the x-ray microdiffraction data. Knowledge obtained from our experiments can be incorporated with TEM analysis and/or simulation results to relate the amount of stress or strain in the nanopattern (or in the substrate) with lattice distortion or interfacial defects. *In-situ* monitoring the diffraction intensity change under heating or external magnetic field can be also carried out to probe the

intrinsic strain field development and the strain field change related to magnetocrystalline anisotropy of the patterned materials.

(2) Direct observation of the strain distribution in a nanopatterned system using Electron Backscatter Diffraction (EBSD)

EBSD is a technique which allows crystallographic information to be obtained from samples in the SEM, by striking a stationary electron beam on a tilted sample and obtaining the diffracted electrons pattern on a fluorescent screen. The diffraction pattern can be used to measure the crystal orientation, measure grain boundary misorientations, discriminate between different materials, and provide information about local crystalline imperfection. EBSD method has been utilized to measure elastic strain and small lattice rotations on epitaxial semiconductor films including SiGe/Si, AlGaAs/GaAs and GaN/sapphire systems.²⁹⁵⁻²⁹⁹ Compared with other characterization techniques, EBSD enjoys the following unique advantages:

- Lateral resolution down to some ten nm
- Information depth between 50 to 100 nm
- Strain sensitivity up to $\pm 2 \times 10^{-4}$
- Short acquisition time of 10 to 100 points/sec

Although precedents of EBSD study on substrate-integrated oxide nanopatterns have not been widely reported, it is highly possible that this technique can be very useful for the VP-soft-

eBL fabricated systems given the high crystalline quality and the surface smoothness that can be achieved.

(3) Investigation of microstructural evolution during sintering of sol-derived nanopatterns using grazing-incidence small-angle x-ray scattering (GISAXS).

We have noticed that the size constraint may result in different microstructural development kinetics for nanostructures compared with thin films or bulk materials derived from sol-gel systems.¹³³ It is imperative to study the constrained sintering effect especially in the early stage of nucleation, which is normally very challenging to detect due to the very small size of the nuclei and/or pores. Our preliminary work on applying GISAXS to *in-situ* monitoring the grain or pore growth in the sol-gel derived SnO₂ nanostructures has shown its great potential in this area. Physical models will need to be developed to interpret the GISAXS results.

II. Quantitative assessment on magnetic and ferroelectric properties of VP-soft-eBL prepared nanopatterns

In this dissertation, functionality assessment on nanopatterns of magnetic and ferroelectric oxides is carried out using AFM-based techniques, i.e., MFM and PFM. Since the spontaneous magnetization for a CoFe₂O₄ nanostructure is heavily dependent on its crystallographic characteristic, it can be expected that proper microstructural engineering strategy may enhance the magnetic performance of such nanostructures. Therefore a quantitative knowledge on the magnetic behavior of individual CoFe₂O₄ pattern is required. This can be realized by obtaining

macroscopic measurement results in standard magnetometers such as VSM (Vibrating Sample Magnetometer) or SQUID (Superconducting Quantum Interference Device), followed by averaging the magnetization with respect to the number of patterns contained on the sample. For this purpose, samples need to be patterned with high density and over large area in order to get reasonable signal/noise ratio.

The macroscopic measurement can be hard to apply on ferroelectric nanopatterned systems due to the difficulties in depositing the top electrodes and applying electric field. Alternatively, quantitative PFM measurements should be utilized with very careful data interpretation. PFM measurement will be particularly indispensable to probe the so-called “geometric frustration” phenomena in the 2D ferroelectric grids discussed in chapter 4. Preliminary PFM work on such grids has confirmed their piezoelectricity and observed domain switching under in-situ poling, as shown in figure 7.1. Domain imaging is under the way to help visualize the domain distribution across the pattern and particularly in the node areas. With the capability of VP-soft-eBL, one can build a wide range of accessible artificial lattice geometries and even introduce rationally designed defect structures in such lattices. The combination of VP-soft-eBL patterning with highly site-specific PFM therefore enables a full-spectrum investigation of the geometric frustration with artificial ferroelectric lattices.

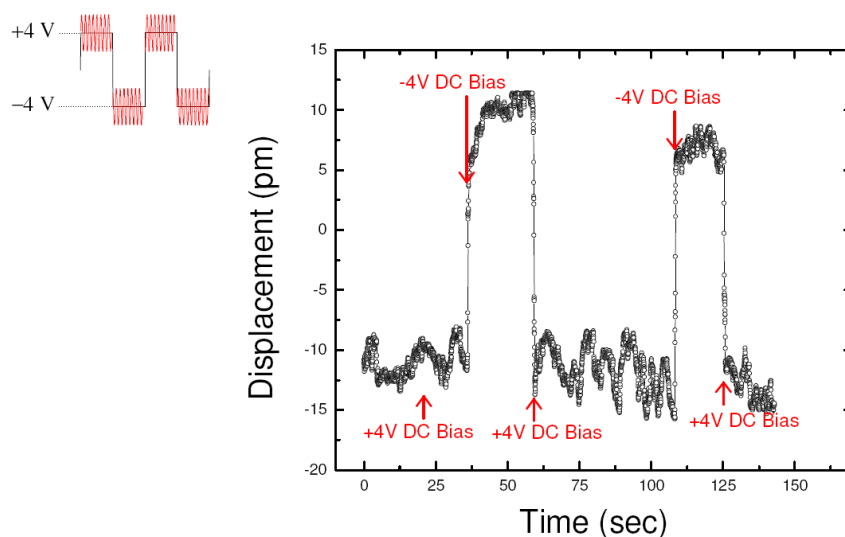


Figure 7.1: In-situ domain switching measurement performed by poling the patterns with an applied voltage on the PFM tip. The sample is 100 nm-wide BTO 2D grid on (001) Nb:STO substrate. Inset shows a schematic of the DC bias ($\pm 4V$) applied to the pattern and the AC signal (sine wave of 2V amplitude at 43 kHz) used to probe the piezoresponse. Contributor: Aravind Vasudeva Rao, Gopalan group, Pennsylvania State University.

Besides the wide-open opportunities in obtaining site-specific microstructural and functional information from the VP-soft-eBL nanostructures, efforts can also be extended in the following areas:

- Control of the interface bonding between the two different oxides in multiferroic heterostructures to achieve strain-mediated coupling phenomena;
- Optimization of sol-gel recipe and/or the thermal treatment portfolio to achieve preferred microstructure with shorter time and under lower temperature;
- Expanding the VP-soft-eBL in patterning non-oxide nanostructures or oxide/organic hybrid architectures.

APPENDICES

APPENDIX 4.1 DEDUCTION OF THE FINAL FORM OF Q(x, y)

4.1.1 Q(x, y) for line patterns

$$\begin{aligned}
 Q(x, y) &= Q_s \iint_{u \ v} P_{_LHV}(x-u, y-v) f(u, v) dudv \\
 &= Q_s \iint_{u \ v} \sum_{i=-K}^K U(x-u-id, y-v) f(u, v) dudv \\
 &= Q_s \sum_{i=-K}^K \iint_{u \ v} U(x-u-id, y-v) f(u, v) dudv \\
 &= Q_s \sum_{i=-K}^K \int_{x-id-W/2}^{x-id+W/2} \int_{y-L/2}^{y+L/2} f(u, v) dudv \\
 &= Q_s \sum_{i=-K}^K \int_{x-id-W/2}^{x-id+W/2} \int_{y-L/2}^{y+L/2} \frac{1}{(1+\eta)\pi} \left[\frac{1}{\alpha^2} \exp\left(-\frac{u^2+v^2}{\alpha^2}\right) + \frac{\eta}{\beta^2} \exp\left(-\frac{u^2+v^2}{\beta^2}\right) \right] dudv \\
 &= Q_s \sum_{i=-K}^K \frac{1}{4(1+\eta)} \left[\left(\operatorname{erf}\left(\frac{x-id+W/2}{\alpha}\right) - \operatorname{erf}\left(\frac{x-id-W/2}{\alpha}\right) \right) * \left(\operatorname{erf}\left(\frac{y+L/2}{\alpha}\right) - \operatorname{erf}\left(\frac{y-L/2}{\alpha}\right) \right) \right. \\
 &\quad \left. + \eta \left(\operatorname{erf}\left(\frac{x-id+W/2}{\beta}\right) - \operatorname{erf}\left(\frac{x-id-W/2}{\beta}\right) \right) * \left(\operatorname{erf}\left(\frac{y+L/2}{\beta}\right) - \operatorname{erf}\left(\frac{y-L/2}{\beta}\right) \right) \right]
 \end{aligned}$$

4.1.2 Q(x, y) for grid patterns

$$\begin{aligned}
 Q(x, y) &= Q_s \iint_{u \ v} P_{_GHV}(x-u, y-v) f(u, v) dudv \\
 &= Q_s \iint_{u \ v} \left(\sum_{i=-K}^K U_x(x-id, y) + \sum_{j=-N}^N U_y(x, y-jd) \right) f(u, v) dudv
 \end{aligned}$$

$$\begin{aligned}
&= Q_s \left[\sum_{i=-K}^K \iint_{u \ c} U(x-u-id, y-v) f(u, v) dudv + \sum_{j=-N}^N \iint_{u \ c} U(x-u, y-v-jd) f(u, v) dudv \right] \\
&= \frac{Q_s}{4(1+\eta)} \left[\sum_{i=-K}^K \left\{ \left(\operatorname{erf}\left(\frac{x-id+W/2}{\alpha}\right) - \operatorname{erf}\left(\frac{x-id-W/2}{\alpha}\right) \right) * \left(\operatorname{erf}\left(\frac{y+L/2}{\alpha}\right) - \operatorname{erf}\left(\frac{y-L/2}{\alpha}\right) \right) \right. \right. \\
&\quad \left. \left. + \eta \left(\operatorname{erf}\left(\frac{x-id+W/2}{\beta}\right) - \operatorname{erf}\left(\frac{x-id-W/2}{\beta}\right) \right) * \left(\operatorname{erf}\left(\frac{y+L/2}{\beta}\right) - \operatorname{erf}\left(\frac{y-L/2}{\beta}\right) \right) \right\} \right. \\
&\quad \left. + \sum_{j=-N}^N \left\{ \left(\operatorname{erf}\left(\frac{x+L/2}{\alpha}\right) - \operatorname{erf}\left(\frac{x-L/2}{\alpha}\right) \right) * \left(\operatorname{erf}\left(\frac{y-jd+W/2}{\alpha}\right) - \operatorname{erf}\left(\frac{y-jd-W/2}{\alpha}\right) \right) \right. \right. \\
&\quad \left. \left. + \eta \left(\operatorname{erf}\left(\frac{x+L/2}{\beta}\right) - \operatorname{erf}\left(\frac{x-L/2}{\beta}\right) \right) * \left(\operatorname{erf}\left(\frac{y-jd+W/2}{\beta}\right) - \operatorname{erf}\left(\frac{y-jd-W/2}{\beta}\right) \right) \right\} \right]
\end{aligned}$$

APPENDIX 4.2 DERIVATION OF EM FOR PROXIMITY PARAMETER DETERMINATION

The marginal distributions $p(\beta, \eta | \{e_s\}, \alpha^{i-1}, Q_c^{i-1})$ and $p(\alpha, Q_c | \{e_s\}, \beta^{i-1}, \eta^{i-1})$ can be assumed as Gaussian distributions. In practice, they are approximated with Dirac distributions for simplicity. For example, $p(\beta, \eta | \{e_s\}, \alpha^{i-1}, Q_c^{i-1}) = \delta(\beta - \beta^{i-1}, \eta - \eta^{i-1})$. That is, for each step of the first EM, the distribution of β and η is assumed to be concentrated on the derived β^{i-1}, η^{i-1} from the previous step in the second EM. Hence, equation 4.13 becomes:

$$\begin{aligned}
K(\alpha, Q_c, \alpha^{i-1}, Q_c^{i-1}) &= \iint_{\beta, \eta} \log p(\{e_s\}, \beta, \eta | \alpha, Q_c) \delta(\beta - \beta^{i-1}, \eta - \eta^{i-1}) d\beta d\eta \\
&= \log p(\{e_s\}, \beta^{i-1}, \eta^{i-1} | \alpha, Q_c)
\end{aligned} \tag{4.13a}$$

Next, we assume each $p(\{e_s\}, \beta^{i-1}, \eta^{i-1} | \alpha, Q_c)$ is a Gaussian distribution, i.e., assuming the observed data is corrupted with independent white noise, as follows:

$$p(\{e_s\}, \beta^{i-1}, \eta^{i-1} | \alpha, Q_c) = \frac{1}{\sqrt{2\pi}\sigma} e^{-|Q(W/2 + e_s, d/2) - Q_c|^2 / 2\sigma^2}$$

Thus equation 4.13a becomes:

$$\begin{aligned} K(\alpha, Q_c, \alpha^{i-1}, Q_c^{i-1}) &= \log \prod_{s=1}^S \frac{1}{\sqrt{2\pi}\sigma} e^{-|\hat{Q}(W/2 + e_s, d/2) - Q_c|^2 / 2\sigma^2} \\ &= -\sum_{s=1}^S \frac{\left| \hat{Q}\left(\frac{W}{2} + e_s, \frac{d}{2}\right) - Q_c \right|^2}{2\sigma^2} - S \log(\sqrt{2\pi}\sigma) \end{aligned} \quad (4.13b)$$

where $\hat{Q}(W/2 + e_s, d/2)$ is computed by equation 4.9, with β and η fixed as β^{i-1} and η^{i-1} respectively.

Finally, based on equation 4.13b, $K(\alpha, Q_c, \alpha^{i-1}, Q_c^{i-1})$ is maximized in M-step when the parameters α and Q_c minimize $\sum_{s=1}^S \left| \hat{Q}\left(\frac{W}{2} + e_s, \frac{d}{2}\right) - Q_c \right|^2$. That is, equation (4.14) gives

$$(\alpha, Q_c) = \arg \min_{\alpha, Q_c} \sum_{s=1}^S \left| \hat{Q}\left(\frac{W}{2} + e_s, \frac{d}{2}\right) - Q_c \right|^2$$

The second EM for estimating β and η from the grid pattern with α and Q_c as missing data can be derived in the similar fashion, with

$$(\beta, \eta) = \arg \min_{\beta, \eta} \sum_{s=1}^S \left| \tilde{Q}\left(\frac{W}{2} + e_s, \frac{d}{2}\right) - Q_c \right|^2$$

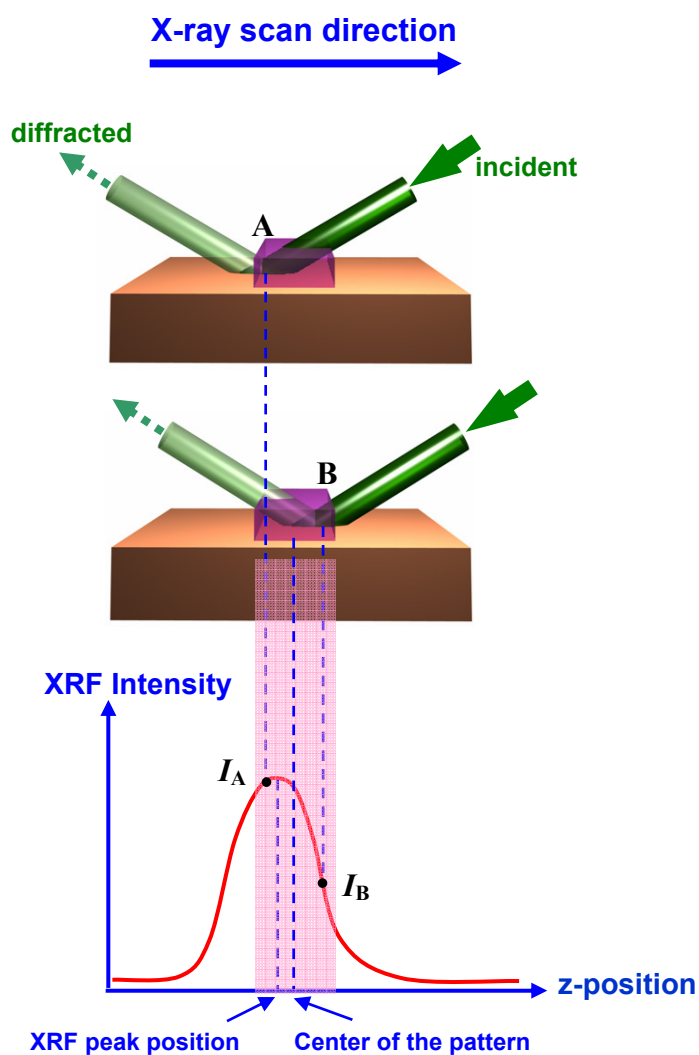
where $\tilde{Q}(W/2 + e_s, d/2)$ is computed by equation 4.10 with α and Q_c fixed as α^{j-1} and Q_c^{i-1} respectively, which are the estimated values from the previous step in the first EM.

APPENDIX 6.1 EXPLANATION OF XRF PEAK POSITION OFFSET IN FIGURE 6.10

Both incident beam and diffracted beam, when interacting with sample, may contribute to the XRF signal. The XRF yield of a certain element is therefore determined by the intensity of each beam as well as their interaction volume with the sample (diffracted beam is much weaker than the strong incident beam). Figure below schematically illustrates the incident x-ray beam on two symmetric positions with respect to the center of the pattern. In case of a non-perpendicular incidence (e.g., 35.824° incident angle used in our experiment), the total contribution of the incident and diffracted beams to the Co $K\alpha$ fluorescent signal is different on different side of the line, e.g., the XRF intensity is higher at spot A than at spot B. Therefore, the Co $K\alpha$ XRF intensity achieves a maximum before the incident beam reaches the actual center of the pattern.

The broadening of the XRF peak is the result of the convolution between the beam profile and the shape of the nanopattern. It should be pointed out that the beam sizes causing fluorescence is different from that causing diffraction. The full microbeam profile contributes to the fluorescence scan. On the other hand, only the narrow central region of the divergent beam fan contributes to the diffraction profile. This may explain why the broadening of XRF peak is

much larger than the FWHM width of peaks in ROI-1 and ROI-2 plots. Actually, the expected broadening of ROI-1 and ROI-2 peaks for incident angle of 35.824° and the nominal probe size of 200 nm can be calculated to be around 770 nm. This value corresponds very well to the measured FWHM of ROI-1 and ROI-2 peaks (700~800 nm).



Schematic illustration of XRF intensity change with incident beam position

APPENDIX 6.2 CALCULATION OF X-RAY ABSORPTION BY CFO NANOPATTERN

The x-ray transmission after passing through a thin film with thickness of x is given by:

$$T = \exp(-\mu \cdot x)$$

Here μ is the linear absorption coefficient of the film material. Using this equation, the absorption of x-ray by the CFO epitaxial pattern is roughly calculated by considering the pattern as a 50 nm single crystal thin film and assuming the incoming and outgoing x-rays both form 35.824° angles with the surface of the film. The total x-ray path inside CFO is:

$$x = 2 \times 50 / \sin(35.824^\circ) = 170.853 \text{ nm} = 1.70853 \times 10^{-5} \text{ cm}$$

The linear absorption coefficient can be calculated through the mass absorption coefficients (μ/ρ) of Co, Fe and O atoms as follows:

$$\mu(\text{CFO}) = \rho_{\text{CFO}} \times \left(\frac{\mu}{\rho}\right)_{\text{CFO}} = \rho_{\text{CFO}} \times [w_{\text{Co}} \cdot \left(\frac{\mu}{\rho}\right)_{\text{Co}} + w_{\text{Fe}} \cdot \left(\frac{\mu}{\rho}\right)_{\text{Fe}} + w_{\text{O}} \cdot \left(\frac{\mu}{\rho}\right)_{\text{O}}],$$

where w represents the weight fraction of each element in CFO, and ρ_{CFO} is the density of CFO (5.3 g/cm^3). The (μ/ρ) values of Co, Fe and O atoms at 10.08 keV are $184.1 \text{ cm}^2/\text{g}$, $170.6 \text{ cm}^2/\text{g}$ and $5.952 \text{ cm}^2/\text{g}$, respectively (from: <http://physics.nist.gov/>). The weight fractions of these elements are: $w_{\text{Co}} = 0.25118$, $w_{\text{Fe}} = 0.47606$, $w_{\text{O}} = 0.27275$. Inserting the value of w , μ/ρ and ρ_{CFO} in the above equation, $\mu(\text{CFO})$ is calculated to be $682.8768 \frac{1}{\text{cm}}$. Therefore the transmission is calculated to be 0.9884 and the absorption by CFO is $A = 1 - 0.9884 = 0.0116$.

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