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Atom Probe Tomography Analysis of Low-Dimensional Electronic Materials and Heterostructures

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Xiaochen Ren

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ABSTRACT

Atom Probe Tomography Analysis of Low-Dimensional Electronic Materials and Heterostructures

Xiaochen Ren

Atom probe tomography (APT) was used to analyze doping and alloying in low-dimensional electronic materials including thin film heterostructures, van der Waals materials, and colloidal quantum dots (QDs).

Firstly, APT was used to reveal structure-property relationship for low-dimensional thin film semiconductors used in electronic and opto-electronic devices. APT was shown to be capable of revealing buried interfaces, evaluating alloying distribution, and determining spatial correlations between dopants. APT, correlated with high-resolution X-ray diffraction (XRD) and micro-photoluminescence (micro-PL), was used to analyze indium distribution in continuous and discontinuous InGaN quantum wells (QWs) to identify factors contributing to the increase in internal quantum efficiency (IQE). Relative to the control growth, hydrogen dosing leads to narrower and discontinuous quantum wells of lower indium content with more abrupt interfaces, which contributes to an increased radiative recombination rate by increasing the electron-hole wavefunction overlap, as revealed by
simulations. Hydrogen dosing also selectively etches QWs near defects, which contributes to higher IQE by keeping carriers away from defects and thus reducing non-radiative recombination. APT analysis was also used to determine the Ag dopant distribution in a Ta$_2$O$_5$-based low energy switching memristor device. By manually tuning the laser energy to avoid fracture caused by different evaporation fields, the Ta$_2$O$_5$:Ag layer was analyzed and the distribution of Ag atoms evaluated. Based on the APT results and electrical performance data, a switching mechanism based on conductive tunneling paths instead of the continuous traditional conductive filaments was proposed for the memristor device. This research indicates the potential for APT analysis used in memristor devices.

A proof-of-principle application of APT analysis of doping in 2D materials was demonstrated for the first time by analyzing Ag doping in (PbSe)$_5$(Bi$_2$Se$_3$)$_3$ and Cu doping in Bi$_2$Se$_3$. APT analysis shows that Ag dopes both Bi$_2$Se$_3$ and PbSe layers in (PbSe)$_5$(Bi$_2$Se$_3$)$_3$, and correlations in the position of Ag atoms suggest a pairing across neighboring Bi$_2$Se$_3$ and PbSe layers. Density functional theory (DFT) calculations confirm the favorability of substitutional doping for both Pb and Bi and provide insights into the observed spatial correlations in dopant locations. APT analysis also shows that Cu exists within the layer and between layers in Bi$_2$Se$_3$. Results suggest that van der Waals interactions are strong enough to hold layers together during field evaporation, at least for Bi$_2$Se$_3$. APT analysis shows that Ag dopes both Bi$_2$Se$_3$ and Bi$_2$Se$_3$; however, van der Waals interactions make atoms in the same monolayer tend to be evaporated together, limiting the spatial resolution of resolving atomic layers. This work revealed the influence of bonding anisotropy on field evaporation.
In order to expand the applications of APT for low-dimensional electronic materials, novel sample preparation methods were developed. For transition metal dichalcogenides (TMDs), van der Waals interactions are generally not strong enough to hold layers together during field evaporation. Therefore, a conformal coating was applied on sharpened tips, reducing tip fracture during analysis. This method enables APT analysis of S doping in MoTe$_2$. Sample preparation methods were also developed for APT analysis of few-layer TMDs in order to correlate their electrical properties and their composition distributions. Contrast can be easily lost during sharpening for few-layer TMDs embedded in Ag films, so ALD SnS coating on TMDs was used to increase the contrast. The feasibility of ALD SnS as coatings was proved by APT analysis. The next step is to measure the W distribution in W$_x$Mo$_{1-x}$Te$_2$, and understand how the W distribution can trigger metal-semiconductor transition in W$_x$Mo$_{1-x}$Te$_2$. The application of APT analysis was also expanded to colloidal core-shell QDs. Colloidal core-shell QDs were analyzed by APT to investigate the role of interface abruptness in suppressing the blinking of photoluminescence. An encapsulation method was used to prepare APT specimens from QDs. After considering criteria for encapsulation materials, available atomic layer deposition (ALD) coatings were tested as encapsulation layers. ZnO enabled the identification of individual CdS/CdSe QDs and gives an upper-bound on the width of the core-shell interface of $\sim$1.2 nm, although with significant overlapping in the mass spectrum that degrades resolution. The difference in evaporation field between the QDs and encapsulants is smallest for ALD SnS among materials tested.
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CHAPTER 1

Introduction

Electronic materials are utilized as core elements for electronic and optoelectronic devices. Electronic materials have laid the foundations for our modern world and substantial research effort on electronic materials is now focused on low-dimensional electronic materials. For example, Si has enabled entire telecommunication and computer industries as the essential material in complementary metal-oxide-semiconductor (CMOS) devices. In accordance with Moore’s Law, the characteristic length of CMOS devices now shrinks into nanometers, thus research attention was attracted to the understanding of how Si performs at the nano-scale.

In order to understand the properties of low-dimensional electronic materials and to improve the performance of low-dimensional electronic materials based devices, it is important for a metrology measurement to reveal nano-scale features in three-dimensions, such as buried interfaces and dopant distribution in nanostructures. The two currently standard metrology tools are transmission electron microscopy (TEM) and secondary ion mass spectrometry (SIMS). TEM is a 2D projection technique, thus it cannot resolve structures in the direction of the electron beam; the lateral resolution of SIMS is limited by its primary beam size, which is approaching 40 nm. In short, both TEM and SIMS fail to achieve true 3-D characterization at the subnanometer scale. Atom probe tomography (APT) is a technique for imaging 3-D composition distributions with combined high spatial resolution (down to 0.2 nm) and high chemical sensitivity (down
to a few ppm). APT’s capability makes it an important metrology tool for studying the structure-property relationship in low-dimensional electronic materials. The Lauhon group was the first to expand the application of APT to nanowires. There has also been efforts in APT analysis of thin films. In this thesis, APT’s capability for analyzing low-dimensional electronic materials is further explored for thin films, and expanded to van der Waals layers and heterostructures and colloidal quantum dots (QDs).

Chapter 2 is an introduction to APT. APT exploits field evaporation to remove surface atoms from needle-shaped specimens under high electric field. The chemical identity and position of an evaporated ion can be determined by a time of flight (TOF) measurement and a position-sensitive detector, respectively. The sample preparation methods for fabricating needle-shaped specimens and commonly used analysis methods are summarized in this chapter. Because thin/ultrathin electronic materials are the main focus of this thesis, the technical challenges and motivations for APT analysis of thin/ultrathin electronic materials are discussed.

Chapter 3 and Chapter 4 describe APT analysis of thin film electronic materials. The research in Chapter 3 resulted from a collaboration with Sandia National Laboratory. This chapter describes correlated APT, high-resolution X-Ray diffraction (HRXRD) and micro-photoluminescent (micro-PL) analysis of indium distributions in continuous and discontinuous quantum wells (QWs). The introduction of hydrogen to the carrier gas during growth of the GaN spacer can boost the efficiency of QWs, but the resulting QWs are discontinuous, leading to errors in measuring the indium composition by HRXRD. APT was used to accurately determine the indium content and distribution, revealing changes in QWs morphology responsible for the increased efficiency. Besides, APT results
improve the HRXRD fitting in continuous QWs. Chapter 4 describes APT analysis of Ag dopant distribution in a Ta$_2$O$_5$-based low switching energy memristor device. The research is in collaboration with the Joshua Yang group in Massachusetts University. The buried nature of Ag atoms in the Ta$_2$O$_5$ layer presents challenges for TEM to resolve the Ag distribution. APT analysis reveals that Ag atoms are uniformly distributed in regions close to the top electrode, and informs a proposed mechanism for switching between stable resistance states.

Chapter 5 and Chapter 6 describe APT’s application for analyzing 2D layered materials (van der Waals layers and heterostructures). The research is funded by CHiMaD and involved collaborations with NIST and the Kanatzidis group in Northwestern University. Chapter 5 describes the first report of APT analysis of doping in 2D materials, establishing the spatial resolution for APT analysis of 2D materials. The accurate determination of dopant distribution in (PbSe)$_5$(Bi$_2$Se$_3$)$_3$ and Bi$_2$Se$_3$ can potentially help understand the origin of superconductivity in these two doped materials. Chapter 6 describes sample preparation method development for APT analysis of transition metal dichalcogenides (TMDs). APT specimens from bulk TMDs suffer from fracture due to their weak interlayer interactions and relatively high evaporation fields. A novel sample preparation method was introduced to improve the yield, leading to the successful APT analysis of bulk S-doped MoTe$_2$ and revealing the uniform distribution of S dopants. APT analysis of TMDs few-layers was hindered by the difficulty to target the few-layer TMDs in the sharpening step. It was proposed to solve this challenge by ALD sulfide deposition onto TMDs to enhance the contrast during sharpening.
Chapter 7 describes efforts in APT analysis of zero-dimension electronic materials: colloidal core-shell quantum dots (QDs). It was funded by a DOE SISGR in collaboration with Los Alamos National Laboratory. Colloidal core-shell QDs were analyzed by APT to investigate the role of interface abruptness in suppressing the blinking of photoluminescence. Different sample preparation methods were evaluated and tested. ZnO encapsulation enabled the identification of individual CdS/CdSe QDs and gives an upper-bound on the width of the core-shell interface of $\sim1.2$ nm. The difference in evaporation field between the QDs and encapsulants is smallest for ALD SnS among materials tested.

Finally, Chapter 8 summarizes APT analysis of low-dimensional electronic materials in this thesis and provides an outlook on promising directions for continued research in this area.
CHAPTER 2

Introduction to Atom Probe Tomography

One major goal in material characterization is to determine the position and of every atom in a material to enable the understanding of structure-property relationships down to the atomic scale. Atom probe tomography (APT) is one of the few instruments that can approach this goal with its capability of combining spatial resolution down to 0.2 nm in three-dimensions and chemical sensitivity of a few ppm. The history of APT traces back to the invention of field ion microscope (FIM) by E. W. Müller in 1951. Müller, Panitz, and McLane invented the first APT in 1968 by combing a FIM and a time-of-flight (TOF) mass spectrometer. With the development of high-speed electronics for rapid data collection, position-sensitive micro-channel plate (MCP) detectors, pico- and femtosecond lasers, focused ion beam (FIB) based modern sample preparation methods, and advanced data analysis techniques, APT has come a long way as manifest in the state-of-the-art local-electrode atom probe (LEAP) used in this work. A detailed review of the history of APT can be found in various publications and books. In this chapter, a brief introduction to APT is presented, covering APT working principles, modern sample preparation methods, commonly used analysis methods and technical challenges for APT analysis of thin/ultrathin electronic materials.
2.1. APT Working Principles

In general, APT exploits the physical phenomenon of field evaporation to remove surface atoms from the apex of the needle-shaped specimen under high electric field. A TOF measurement is performed during the field evaporation to determine the chemical identity (mass-to-charge ratio) of the evaporated ions. The position-sensitive detector can record where the evaporated ion collides with the detector; when a reconstruction algorithm is applied, the position on the detector can be transformed to the position of the ion in the specimen before evaporation.

2.1.1. Field Evaporation

Field evaporation is the sublimation of atoms from a surface under very intense electric field, and was first discovered by Müller\cite{11} in 1956. Although the process has been known for more than 60 years, a comprehensive quantum mechanical understanding of this process has not yet been achieved. However, thermodynamic considerations can cast light on why and how atoms evaporate. The discussion below is based on thermodynamic considerations for field evaporation of metals.

Figure 2.1 shows the potential energy of an atom/ion at a distance of x from a surface. As shown in this figure, the electric field caused by a positive bias reduces the energy barrier for an atom to escape the surface (from $Q_0$ to $Q(F)$). There are two widely cited models for how atoms are ionized and escape from the surface: the image hump theory\cite{11} and the charge exchange theory\cite{13}. The image hump theory assumes that the atom is fully ionized at a critical distance before it escapes the surface; the charge exchange theory assumes that the ionization and escape happen simultaneously. However, both
models assume that a surface atom is directly changed to a n-times-charged ion, failing to explain ion charge state variation with varying field evaporation conditions. Haydock and Kingham later showed that an evaporated ion can be further ionized by tunneling of electrons from the ion back to the surface, during a process known as post-ionization. As discussed above, the mechanism of field evaporation is not entirely clear even for metals, and can be even more complex for semiconductors and dielectrics.
2.1.2. APT Operation

The first step for APT analysis is to achieve a high electric field for field evaporation, which is on the order of 10 V/nm. Such a high electric field can be obtained by applying a positive bias on a needle-shaped specimen tip with a diameter less than \( \sim 100 \) nm. The electric field on the surface of a metal tip can be estimated as

\[
F = \frac{V}{K_f \times R}
\]

(2.1)

where \( F \) is the electric field at the apex of the tip, \( V \) is the applied voltage, \( R \) is the radius of the tip and \( K_f \) is the field factor, which is a constant that accounts for the tip shape. Thus, for a tip with a diameter less than 100 nm, a few kV bias is needed to achieve the necessary electric field.

In order to perform the TOF measurement, the departure moment of an ion from the tips surface is precisely controlled by either laser pulsing or voltage pulsing. The evaporation rate can be expressed as:

\[
R = A \times \exp\left(-\frac{Q(F)}{kT}\right)
\]

(2.2)

where \( R \) is the evaporation rate, \( A \) is a constant, \( Q(F) \) is the energy barrier for field evaporation and \( T \) is the temperature of the tip. To achieve pulsed field evaporation, \( Q(F) \) can be reduced by voltage pulsing; this is the technique that was first demonstrated. However, voltage pulsing requires the specimen to have a high electrical conductivity, so its application is typically limited to metal samples. The evaporation rate can also be increased by delivering thermal energy to the tip; this can be achieved by illumination with
a pulsed laser. Because laser pulsing is not limited by the conductivity of the specimen, it is now most widely used.\textsuperscript{[12], [16]}

TOF measurements record the time between a pulse and the moment the ion hits the detector. The potential energy acquired by an ion ($neV$) can be equated to its kinetic energy ($mv^2/2$) by assuming that the initial velocity is zero. The velocity of an ion can be considered constant during the whole flight ($L/t_{flight}$) since the potential energy can be considered to immediately convert to kinetic energy, so one can get the mass-to-charge ratio by equating the energies:

$$\frac{m}{n} = 2eV \times \left(\frac{L}{t_{flight}}\right)^2$$

\subsection*{2.1.3. Reconstruction}

In APT analysis, reconstruction is a process to convert the detector position and event order ($X, Y, N$) into original coordinates ($x, y, z$) in the specimen before evaporation, which consists of a magnification transformation of $(X, Y)$ to $(x, y)$ and a depth transformation of $N$ to $z$. The current standard methodology is based on a point projection model.\textsuperscript{[17]} As shown in Figure 2, the model assumes that the tip is in a hemisphere-on-cone shape, with a sphere of radius $R$ on a cone with a shank angle of $\alpha$. The reconstruction algorithm based on the point projection model is built in the commercially available IVAS software package. Although the assumptions made in this model are not usually well met, this method can work well to reproduce the known features once the fitting parameters are well tuned.
Limitations and improvements will be not discussed in this thesis because all reconstructions in this thesis are produced using the standard model and were found to work suitably well. However, an understanding of these limitations and improvements is important for APT analysis of more complicated material systems with heterogeneous interfaces. A detailed discussion can be found in the review paper discussing reconstructions in APT.\cite{18}

### 2.2. Sample Preparation for APT

The high electric field enabling field evaporation can only be practically achieved via geometric field enhancement of the sharp needle-shape specimen with a diameter less than 100 nm, so the sample preparation is a key step for the success of APT analysis. The general goal for APT sample preparation is to fabricate a tip with the following features: (1) the tip needs to be sharp enough (usually $< 100$ nm) to achieve a high electric field
and has the needle shape assumed in the reconstruction model for reliable reconstructions; (2) the tip needs to be mechanically strong enough for a stable field evaporation; (3) the feature of interest cannot be too far from the top of the tip. Electropolishing is a useful method to prepare metal APT samples. This technique has been developed since the birth of APT and is still widely used due to its easy, fast and inexpensive nature. A detailed introduction to electropolishing can be found in APT books and will not be discussed here. This chapter is focused on the APT sample preparation methods developed in the last 15 years that have enabled the rapid advance of APT analysis of non-metallic materials.

2.2.1. Mounting of Semiconductor Nanowires

A nanowire is a nanostructure with the diameter of 10 to 100 nm and the length of the order of a micrometer. Nanowires are naturally suitable for APT analysis due to their needle-like shapes, diameters and lengths. The first example of APT analysis of nanowires was demonstrated by Perea et al. by analyzing nanowires directly grown on a flat substrate.[3] Follow-up research from Perea et al. showed that it is easier to find the nanowires and align them in LEAP by growing nanowires vertically on top of microposts.[19] However, nanowires are often grown in dense forests or arrays and need to be isolated for APT analysis.

An early strategy for isolating individual nanowires for ATP analysis was developed by Agrawal et al.[20] as shown in Figure 2.3. In this method, the first step is to transfer nanowires from the substrate to the edge of one half of a transmission electron microscopy (TEM) grid which is cut into two halves by a razor blade. The cut edge of half grid is scraped along the substrate surface and nanowires are detached from the substrate and
transferred onto to the half grid. Ideally, there will be several isolated nanowires with sufficient length and diameter protruding from the cut edge (Figure 2.3a). The second step is to attach the target nanowire onto a manipulator tip. For example, Figure 2.3b shows a nanowire attached on a tungsten tip on a nanomanipulator. The tungsten tip is put into contact with the nanowire and then the nanowire is welded onto the tip with electron
beam deposited platinum. Then the tip is slowly raised and withdrawn to minimize the possibility that the nanowire will fracture in the middle. Finally, the tungsten tip with the attached nanowire is mounted on a LEAP puck for APT analysis.

Nanowires can also be picked directly from the substrate when it is necessary to target a specific nanowire for APT analysis. Riley created a method to select a nanowire from a densely covered growth substrate. As shown in Figure 2.3c, the nanomanipulator tip approached the base of the selected nanowire with the stage tilted 40° and made contact with the nanowire. Platinum was deposited by an electron beam on a region overlapping the nanomanipulator tip and half of the nanowire at the point of contact. Once the selected nanowire was secured with platinum deposition, the nanomanipulator pushed the nanowire forward in the direction marked by the red arrow until the nanowire detached from the substrate. The next step transferred the nanowire to a TEM half grid. The nanowire was placed into contact with the grid with precise control of the nanomanipulator and then welded onto the grid with sequential platinum depositions to ensure that this weld was more firm than the weld between the nanowire and the nanomanipulator tip. Finally the nanomanipulator was moved backward slowly to break the weld between the nanowire and the nanomanipulator tip and leave the nanowire on the grid as in Figure 2.3d. Koelling et al. recently developed a method to use a short nanowire as the nanomanipulator tip to pick up a selected nanowire. The procedures are basically the same as in Riley’s method, but the use of a short nanowire as the nanomanipulator tip can potentially reduce the stress and damage introduced during picking and mounting the selected nanowire.


2.2.2. FIB Milling Method

Commercial FIB systems are widely used in materials science, and APT specimen preparation methods have been developed based on FIB milling. This method can be applied to all materials and provides precise selection of the regions of interest. An example of the standard process is shown in Figure 2.4 illustrating how APT specimens were prepared for the continuous InGaN/GaN quantum wells samples in Chapter 3. Firstly, a capping layer was deposited to protect the selected region of interest (ROI) from Ga ion damage during the subsequent steps. The capping layer can be a bar of ion beam deposited platinum on top of electron beam deposited platinum or a blanket deposition of sputtered metal film (Pt in this case) (Figure 2.4a). The choice of the thickness of the capping layer depends on the sharpening step, with the capping layer completely removed once the ideal diameter is reached. The second step is to extract the ROI from the sample. The material on the top, bottom and left sides of the platinum bar was removed by Ga ion milling (the stage tilted at 22°) to form an undercut wedge, with only the right side still connected to the sample. An Omniprobe approached the wedge and was welded to the wedge by ion beam deposited platinum, and then the right side of platinum bar was cut free to enable the transfer process as shown in Figure 2.4b. Next, the wedge was transferred onto a Si micropost by the Omniprobe. A portion of the wedge was welded onto the Si micropost and cut off from the rest, as in Figure 2.4b. Then angular sharpening patterns provided by Cameca were used to sharpen the material on the Si post to a needle-shape tip gradually. Sharpening was stopped when the capping material was completely removed; the diameter of the tip should be less than 100 nm at this time. Finally, the tip was exposed to Ga ion beam of 2 kV and 28 pA at a magnification of 15 kX for 10 seconds. This step
can remove the damaged surface layer while only implanting Ga ions with a negligible distance (1-2 nm) due to the low energy. There are usually no obvious changes in the SEM images before and after the final cleaning step. Additionally, this damage region with a thickness of 1-2 nm is typically outside the field of view.

![Figure 2.4](image)

**Figure 2.4.** An example of FIB milling method to prepare APT samples. (a) ROI was selected and covered with a bar of ion beam deposited platinum on top of a layer of sputtered platinum blanket deposition. (b) ROI was extracted with the help of Omniprobe. (c) ROI was mounted onto a Si post. (d) Angular sharpening to mill the ROI into a tip with a diameter less than 100 nm.

For analyzing thin/ultrathin films, samples need to be analyzed in rotated geometries. By rotating 90°, the sample can be analyzed in cross-section, which can increase the analysis volume of the ROI and improve the yield when the layers in the film have significant differences in evaporation field. By rotating 180°, the sample can be analyzed
in bottom-up geometry, which is often used when the sample lacks inversion symmetry or the ROI is difficult to approach in APT analysis from normal orientation, e.g., when interfaces between the sample surface and the ROI lead to fracture. In order to prepare samples in rotated geometries, a thick sacrificial capping layer (more than 500 nm) is usually first deposited on top of the sample surface. The thick capping layer can help center the near-surface ROI in the final tip for cross-section geometry or keep the near-surface ROI away from the platinum welding in bottom-up geometry.

Figure 2.5. (a) A schematic of ARM, from Lawrence, et al.\textsuperscript{24} (b) A SEM image of a wedge attached on the manipulator probe of the ARM.

The rotation process is performed with the help of an axial rotating manipulator (ARM)\textsuperscript{24}. Figure 2.5a shows a schematic of the ARM, consisting of a stage which is comparable to a SEM stub in size and a manipulator probe which can rotate along its own long axis. After the wedge was extracted from the sample, it was welded onto the manipulator probe as shown in Figure 2.5b. Then the ARM was taken out from FIB and the manipulator probe was rotated to the desired angle. Next, the ARM was put back in the FIB and the left-side of the wedge was re-attached onto the Omniprobe with the
right-side cut free from the manipulator probe. After the above process, the wedge was transferred onto Si posts and sharpened in the same manner as the standard method. Different materials were analyzed in the cross-section geometry in Chapter 6 and Chapter 7 to increase the yield and analysis volume; the results will be discussed in detail there. The bottom-up geometry is not used in this thesis.

2.2.3. Coating on Pre-sharpened Tips

Although the FIB milling method can be applied to all materials in principle, some materials, such as polymers, are challenging to mill under the Ga ion beam. The soft nature of polymers will cause non-uniform milling rates, resulting in the formation of pits and voids.\cite{25} For insulating polymers, a significant drift of the sample will happen during milling, making problems even worse. In order to study polymer fragmentation behavior in APT analysis, Prosa et al.\cite{26} developed two techniques to deposit polymer films onto a pre-sharpened metal tip for APT analysis without the use of FIB. In both techniques, an aluminum wire was electropolished to a tip with the diameter less than 100 nm to work as the pre-sharpened tip. Aluminum is chosen because it has good wettability with the studied polymer and does not react in the fabrication environment. The first technique is dip deposition. Poly(3-alkylthiophene)s were dissolved in chloroform to form a 1 wt% solution and then a drop of the solution was put on a substrate. The pre-sharpened tip then approached the drop from the top until just penetrating the surface of the drop. Evaporation of the solvent will lower the surface of the drop and leave 200 nm thick film on the tip surface. The second method is electrospray ionization deposition. The aluminum tip was positioned off-axis of the spray plume and approximately 12 cm from
the spray tip. The polymer was dissolved in chloroform to form a 0.01 wt% solution and the solution was loaded into the spray tip. The solutions were drawn to the end of the tip by capillary action with a DC voltage of 15 kV applied. A spray of 2 µL solution can also result a 200 nm thick film on the tip surface. Although the final diameter of the tip is nearly 500 nm in diameter, the deposited polymer film by both methods can be evaporated well in APT analysis due to the relatively low evaporation field of the polymer.

The concept of depositing materials onto a pre-sharpened tip was adopted by the APT community and applied to other materials. Tedsree et al.\textsuperscript{[27]} analyzed core-shell Ag/Pd nano-catalyst particles using APT by attracting nanoparticles onto a pre-sharpened Pt-Rh tip via electrophoresis. The Pt-Rh tip was dipped into a droplet of a solution of dispersing core-shell Ag/Pd nanoparticles in methanol. Because the nanoparticles possess a negative charge on surfaces, they can be attracted to the Pt-Rh tip when a positive voltage is applied to the tip. This method can be applied to other nanoparticles as long as the tip does not react with the solution and has a voltage polarity opposite to the surface charge of nanoparticles. However, this method does not allow precise control of the number of nanoparticles attached to the tip. Relatively rough surfaces can form even when nanoparticles are closely packed on the tip surface, making the shape of the final tip deviate significantly from the hemisphere-on-cone shape assumed in the reconstruction. This deviation can have an appreciable impact on the spatial resolution of the analysis. Among the several publications using electrophoresis to attach nanoparticles onto a pre-sharpened tip, only the work from Tedsree et al. achieved atomic-resolution.\textsuperscript{[27]} Other reports observed an aggregation of known elements in a volume much larger than the size of a single nanoparticle.\textsuperscript{[28, 29]} To make this technique more useful, further studies
are needed to understand how the distribution of nanoparticles on the tip surface can influence the spatial resolution on the reconstruction.

Another example is to study the microstructure of thin films by depositing thin films onto Si microposts. In this study, thin-film Ge$_{40}$S$_{60}$ 80 nm thick was deposited by flash evaporation on pre-sharpened silicon microposts (PSM M36 by CAMECA) followed by a silver layer of 30 nm thick by thermal evaporation. The goal of the research was to study the microstructure of optically induced dissolution and diffusion of Ag into Ge$_{40}$S$_{60}$ thin film, so the deposited film on Si microposts was exposed in a halogen lamp (150 W) under argon atmosphere. APT analysis reveals two regions with distinct compositions in the thin film and a columnar structure of the as-deposited film preserved during the optically induced dissolution and diffusion process. The columnar structure, with Ag enriched, was believed to be the preferred locations for the growth of conducting filaments.

2.3. Commonly Used Analysis Methods

Many different methods have been developed to analyze the three-dimensional (3D) data acquired by APT. Due to the large size of the data sets, these analysis methods are usually performed on high-end workstations using IVAS software. Below is an introduction to the methods that were used in this thesis.

2.3.1. 3D Grid Analysis: Isoconcentration Surfaces and Proximity Histogram

A 3D grid in concentration space is the foundation to explore 3D compositional features in APT data. The grid is specified by defining voxel (small 3D volume blocks) size and delocalization. The voxel sizes are chosen by balancing errors due to counting statistics
and the needed spatial resolution. Reducing the voxel size increases the spatial resolution but also increases the statistical error in concentration, whereas larger voxel sizes can reduce the error in concentration but at a cost of degraded spatial resolution. Since the positions of the voxel boundaries do not perfectly avoid the positions of the atoms, it is also necessary to decide how to assign atoms on boundaries into adjacent voxels. A widely used method is delocalization, which is to share the atom on the boundaries among the neighboring voxels by a delocalization transfer function. For example, IVAS uses a Gaussian transfer function to partition each atom between voxels. To note, a 3D grid will be automatically created in IVAS and the concentration in each voxel will be estimated whenever a POS file is imported.

Isoconcentration surfaces are usually used to visualize the morphology and composition of features formed by solute atoms within the matrix material. Isoconcentration surfaces, also known as isosurfaces, are contour maps in 3D space that connect the surfaces representing a predetermined threshold concentration in the created 3D grid. In IVAS, isosurfaces can be created using single ions, decomposed ions or ion combinations based on ionic or atomic concentration, ionic or atomic counts, or any user-defined ionic or atomic ratio. Once the isosurfaces are created, the roughness of each surface can be calculated; APT data inside or outside selected surfaces can also be isolated to form a new POS file for better visualization.

The proximity histogram, also known as proxigram for short, calculates local concentration profiles with respect to the shortest distance of an atom from an interface (i.e. the surface normal intersecting the atom), with a positive sign if the atom is in a region of higher concentration than the interface or a negative sign if the atom is in a region
of lower concentration than the interface. The initial reference interface is based on an isoconcentration surface. A proximity histogram is calculated by firstly generating a histogram of the proximity of all atomic positions to the interface and then normalizing the histogram to a local composition profile by the total atom numbers in each bin of the histogram. The proxigram is a very powerful tool for analyzing variations in concentration near non-planar or buried interfaces, a capability unique to APT. When applied to planar structures, a proxigram can distinguish composition gradients from surface roughness and is in that way superior to 1D concentration profiles. An example comparing proxigram and 1D composition profile analysis can be found in Section 3.3.1.

2.3.2. Spatial Distribution Maps (SDM)

Spatial distribution maps (SDM) record all position vectors between a species of interest and a predetermined center species. Specifically, for every atom \( i \) of the center species, the relative position of atom \( j \) of the species of interest \((\Delta x_{ij}, \Delta y_{ij}, \Delta z_{ij})\) is recorded. In theory, the result is a 3D histogram of the relative positions of every atom pair from \( i \) to \( j \). In practice, the maximum length of vectors is usually limited to a prescribed value because APT can only provide accurate short-range atomic order; the 3D histogram is visualized by a 2D SDM projected to a plane and a 1D SDM projected to an axis. 2D SDM analysis requires the higher spatial resolution for the collected dataset compared with 1D SDM analysis; thus, 2D SDM is usually performed for the analysis of metal samples while 1D SDM is widely used for the analysis of all samples.

One straightforward application of SDM is finding the crystal lattice to enable calibration of the reconstruction. As discussed in Section 2.1.3, even the best reconstructions do
not achieve the perfect arrangement of detected ions, so it is desirable to have a method
to evaluate the quality of a reconstruction. The SDM can typically resolve the atomic
interplanar spacing along the analysis direction when the analysis was conducted with
appropriate evaporation parameters; reconstruction parameters are tuned to make the
interplanar spacing match the known lattice spacing. It is generally accepted that once
the interplanar spacing matches the known lattice spacing, the long-range order of the
reconstruction is reliable in the analysis direction, enabling accurate analysis of features
in the original specimen.

SDM is also very useful for observing short range ordering. For example, APT resolves
the L12 ordered structure in Al3Sc precipitates in an aluminum matrix; the claim that
the precipitate consists of the alternating planes of either 100% aluminum atoms or 50%
aluminum and 50% scandium atoms in the <100> direction was confirmed by SDM
analysis showing that the spacing of the Sc–Sc atoms is twice the spacing of the Al–Al
atoms.[17] SDM can also be used to determine the site occupancy of solute elements under
some conditions. Marquis and co-workers showed that Nb is positioned on Ti planes in
γ−TiAl containing 2 at.% Nb by analyzing Al–Al, Nb–Al, Ti–Ti and Nb–Ti SDMs.[33] In
this thesis, SDM was used to determine the Ag dopant distribution in (Bi2Se3)3(PbSe)5,
showing that Ag atoms are distributed in both Bi2Se3 and PbSe layers; SDM was also
used to distinguish intercalation and substitution of Cu in Bi2Se3.

SDM also plays an important role in a variety of other analyses, including quanti-
fying trajectory aberrations, correcting lattice strain, quantifying spatial resolution, and
measurement of detection efficiency.[34]
2.3.3. Frequency Distribution Analysis (FDA)

Frequency distribution analysis (FDA)\[35\] is used to determine the uniformity of solute distribution in a specimen. FDA is performed by dividing the atoms in the APT 3D dataset into voxels with a fixed number of atoms. The choice of the number of atoms in each voxel is a trade-off between counting errors and measurement resolution as discussed in Section 2.3.1. The concentration of the element of interest is calculated in each voxel, and then the frequency of occurrence of voxels is plotted against concentration in a histogram. The histogram is compared with binomial distribution to determine whether the solute distribution is consistent with a random distribution.

For a binomial distribution, the expected number of voxels with \(i\) solute atoms of interest is \(F(i)\). It is the product of the number of voxels \(N_\nu\) by the probability \(P(i,N_b)\) of finding \(i\) solute atoms of interest in the voxel with \(N_b\) atoms. \(F(i)\) is given by:

\[
F(i) = N_\nu \times P(i,N_b) = N_\nu \times \frac{N_b!}{i!(N_b - i)!} p^i (1 - p)^{N_b - i}
\]

where \(p\) is the probability of success in a Bernoulli trial, which can be estimated by the average concentration of the solute atoms of interest. Whether the distribution of solute atoms is uniform can be tested by a statistical \(\chi^2\) test. \(\chi^2\) is defined as:

\[
\chi^2 = \sum_{i=1}^{n} \frac{(O(i) - F(i))^2}{F(i)}
\]

where \(F(i)\) is the expected number of occurrences of the class \(i\), \(O(i)\) is the experimentally observed number of occurrences of the class \(i\), and \(n\) is the number of classes. To make a valid statistical comparison, the choice of \(N_b\) should guarantee that \(O(i)\) is larger than 5.
for each case. The null hypothesis is that there is no statistically significant deviation between the distribution of solute atoms of interest and a binomial distribution. A p-value can be calculated for a $\chi^2$ distribution with a degree of freedom of $n - 1$ and a critical value of $\chi^2$ as just calculated. The null hypothesis will be rejected if the p-value is larger than a confidence level of $\alpha$. More details of the $\chi^2$ test for APT analysis can be found elsewhere.[10, 17]

2.3.4. Radial Distribution Function (RDF)

Radial distribution function (RDF) analysis is used to statistically determine the density of a species of interest around a given solute species, which can provide insight into the typical cluster size. RDF, at a radius of $r$, is defined as the normalized average concentration of a species of interest $i$ around a given species $X$:[36]

$$RDF(r) = \frac{<C_i^X(r)>}{C_i^0} = \frac{1}{C_i^0} \sum_{k=1}^{N_X} \frac{N_i^k}{N_{tot}^k}$$

(2.6)

where $C_i^0$ is the overall concentration of the species $i$, $N_X$ is the number of species $i$ atoms in the analyzed volume, $N_i^k$ is the number of species $i$ atoms within a radial shell with distance of $r$ to the centered $K$th $X$ species atom, and $N_{tot}^k$ is the number of all atoms within that shell. A RDF value of 1 means that the average concentration of species $i$ in a shell around species $X$ is the same as the overall concentration of species $i$, which suggests a uniform distribution of species $i$ around species $X$. Any RDF values less than 1 suggests that there is a negative correlation between species $i$ and species $X$; in other words, species $i$ atoms tend to stay away from species $X$ atoms. Any RDF values larger than 1 indicate a positive correlation between species $i$ and species $X$, with species $i$ atoms...
tending to aggregate around species $X$. If a RDF analysis of species $X$ around species $X$ is performed, a positive correlation between species $X$ and species $X$ will then suggest the formation of cluster. Due to possible ion trajectory effects and counting errors, a RDF within $r < 0.2$ nm may not be interpretable\cite{36}, so only RDF analysis of $r \geq 0.2$ nm is presented in this thesis.

In Chapter 5, a 2D RDF analysis was developed in order to study the origin of “Ag–Ag” pairing. The code for the 2D RDF can be found in Appendix A. All other RDFs in this thesis were performed by IVAS software.

2.4. APT for Thin/Ultrathin Layers of Electronic Materials

There are general challenges to be faced in APT analysis of thin/ultrathin layers of electronic materials:

(1) The limited field of view. Due to the continuous efforts to increase the field of view of APT by Cameca, the LEAP 4000 system can typically analyze a volume of $50 \times 50 \times 100$ nm$^3$. Such a field of view is large enough to observe any nm-scale phenomenon, such as clustering and atomic ordering; however, any features larger than 100 nm, such as lateral variation of one element in the thin film, is difficult to be captured by APT.

(2) Layers with different evaporation fields. For thin/ultrathin layers of electronic materials, especially when they are used in optoelectronic and electronic devices, layers of different materials (from metals, semiconductor to oxide dielectrics) can be used and the evaporation fields of these materials can be very different. Analysis through interfaces of greatly different evaporation fields often leads to fracture. Even when the evaporation in
LEAP is continuous through an interface, the spatial resolution of the reconstruction is often degraded due to the “local magnification” \cite{37} effect.

(3) Weak interactions between layers. The whole tip is under significant mechanical stress induced by electrostatic pressure during field evaporation and the stress has been proposed to play an important role in tip fracture\cite{38}. In some layered “2D” materials, the layers are held together by weak van der Waals interactions, and there is a high probability of fracture by exfoliation at the fields necessary for field evaporation.

In this thesis, these challenges will be addressed in a major effort to advance APT analysis to thin and ultrathin layers of electronic materials. The challenge of limited field of view was met when analyzing discontinuous InGaN/GaN quantum wells (Chapter 3) and it has been solved by correlating APT with micro-PL and AFM. Layers of different evaporation field became a problem for APT analysis of a TaO$_x$-Ag memristor device (Chapter 4) and APT analysis was extended to the desired regions by increasing laser energy although the whole device structure was not captured due to fracture. Chapter 6 discusses efforts to develop new sample preparation techniques to solve problems created by weak van der Waals interactions. Besides these general challenges, this thesis also discusses how weak van der Waals interactions influence the evaporation process of ultrathin layers in Chapter 5.
CHAPTER 3

Correlated HRXRD, micro-PL and APT Analysis of
Continuous and Discontinuous InGaN/GaN Quantum Wells

InGaN/GaN quantum wells (QWs) are the foundation of commercial solid state lighting, due to the high light-emission efficiency and tunable band gap of InGaN. In lighting applications, the efficiency as expressed in lumens per watt is an extremely important metric, and improvement of the internal quantum efficiency (IQE) of radiative recombination within the QWs remains a target for improving the overall efficiency. The further improvement of IQE is highly dependent on the understanding of structure-property relationship at the atomic scale, which requires a measurement of atomic-scale indium distribution. However, standard metrology methods, such as high resolution X-Ray diffraction (HRXRD) and transmission electron microscopy (TEM) cannot achieve such a measurement. For example, the introduction of hydrogen to the carrier gas during growth of the GaN spacer has been shown to boost the IQE of QWs grown by metal organic chemical vapor deposition (MOCVD) recently, but the resulting QWs are discontinuous, i.e. they exhibit nm-scale gaps in InGaN layer. Standard metrology methods measure the averaged composition between indium rich regions and gaps in such a structure, failing to reveal variations in indium distribution. The unknown indium distribution prevents the optimization of IQE by indium distribution engineering. In this chapter, correlated HRXRD, APT, and micro-PL were used to characterize
continuous and discontinuous InGaN QWs. APT was used to accurately determine the indium content and distribution, which improved the HRXRD fitting in continuous QWs and identified changes in QW morphology responsible for the blueshift and increased IQE of discontinuous QWs; hydrogen dosing can also etch defects through active InGaN QWs, which plays an important role in improving IQE by keeping carries away from defects and thus reducing non-radiative recombination. This chapter is based on the following publication: Appl. Phys. Lett. 107, 022107 (2015).

### 3.1. InGaN/GaN Quantum Wells

InGaN/GaN quantum wells (QWs) are the active regions for light emitting diode (LED) based solid state lighting (SSL). The first efficient blue LED with InGaN QWs were developed in the early 1990s, following the achievement of high quality GaN growth and p-type conductivity. Since then, the efficiency of LED based SSL continues to be improved. Today, with efficacies of certain products nearing 150 lumens per watt, SSL can be more efficient than any other lighting technology. For the invention of efficient blue light-emitting diodes, which have enabled bright and energy-saving white light sources, the 2014 Nobel Prize for physics was awarded to Isamu Akasaki, Hiroshi Amano, and Shuji Nakamura.

A typical structure of phosphor coated InGaN/GaN QWs LED is shown in Figure 3.1. Electrons and holes are injected through electrodes and combine with each other in InGaN/GaN QWs to emit blue light. The blue light travels through a phosphor layer, partially converted into green and red light, and is emitted as a white light. The overall
efficiency is ca. 30% with sub-efficiencies of approximately 50%, 70%, and 85% for the blue LED, phosphor, and human eye response, respectively.\textsuperscript{40}

\subsection{InGaN Material Properties}

III-Nitrides are direct-bandgap materials that include GaN, InN, AlN, and their alloys. The wurtzite structure is the most thermodynamically stable structure for III-Nitrides. The bandgap of InGaN can be tuned in entire visible spectrum (Figure 3.2). GaN has a bandgap of 3.5 eV with lattice parameters $a = 3.189 \text{ Å}$ and $c = 5.185 \text{ Å}$ and InN has a bandgap of 0.78 eV with lattice parameters $a = 3.545 \text{ Å}$ and $c = 5.730 \text{ Å}$.\textsuperscript{54} The bandgap of InGaN is nonlinearly dependent on the content of indium. The nonlinearity is typically expressed as:
(3.1) \[ E_g(In_xGa_{1-x}N) = (1 - x) \times E_g(GaN) + x \times E_g(GaN) - b \times x \times (1 - x) \]

where \( x \) is the concentration of indium and \( b \) is the bowing factor. However, there is no agreement on the magnitude of the bowing. Possible reasons for the large spread of reported bowing factor values will be discussed in Section 3.3.2 and a more precise measurement of bowing factor will be given.

Figure 3.2. InGaN bandgap vs. in-plane lattice spacing. The bandgap of InGaN can be varied from the entire visible spectrum. The line connecting GaN and InN is corrected by bowing factor from linear.

InGaN is unlike III-V arsenide and phosphide semiconductors in that it can emit light efficiently at a high defect density. Because of the enormous lattice mismatches of InGaN with existing substrates, InGaN/GaN QWs typically exhibit a high density (up to \( 10 \times 10^{10} \text{ cm}^{-2} \)) of threading dislocations (TDs) running along the growth direction terminated by a V-shaped pit at the growth surface. For III-V arsenide and phosphide semiconductors, no band edge light emission would be expected at such a high defect
density. The extraordinarily high efficiency at high defect density for InGaN/GaN QWs is believed to be caused by two mechanisms: (1) excitons are strongly localized in InGaN/GaN QWs due to compositional fluctuations or even self-formed InGaN quantum dots; (2) V-shaped pits form a potential barrier due to sidewalls with smaller thickness and thus higher band gap, which keeps carriers from recombining nonradiatively at TDs. A detailed understanding of these mechanisms is essential for controlling and engineering indium distribution and defects in InGaN/GaN QWs in order to further boost light emission efficiency.

3.1.2. Standard Metrology Methods

HRXRD is the most commonly used technique to infer indium composition and measure layer thickness in InGaN/GaN QWs due to its non-destructive nature and rapid analysis. Usually a high-resolution \( \omega/2\theta \) scan is performed around the (0002) reflection of GaN. The lattice spacing of InGaN and the layer thickness can be obtained by simulating the measured scattering profile, assuming that indium distribution is uniform in QWs and the interfaces between InGaN and GaN are flat and chemically abrupt. The relatively simple kinematic theory, which is adequate for most purposes, gives the measured intensity:

\[
I = \frac{\sin^2(\pi kNT)}{\sin^2(\pi kT)} \left\{ f_{\text{InGaN}}^2 \frac{\sin^2(N_{\text{InGaN}}d_{\text{InGaN}}\pi k)}{\sin^2(N_{\text{InGaN}}\pi k)} + f_{\text{GaN}}^2 \frac{\sin^2(N_{\text{GaN}}d_{\text{GaN}}\pi k)}{\sin^2(N_{\text{GaN}}\pi k)} \\
+ 2f_{\text{InGaN}}f_{\text{GaN}} \cos(\pi kT) \frac{\sin(N_{\text{InGaN}}d_{\text{InGaN}}\pi k)}{\sin(N_{\text{InGaN}}\pi k)} \frac{\sin(N_{\text{GaN}}d_{\text{GaN}}\pi k)}{\sin(N_{\text{GaN}}\pi k)} \right\}
\]

where \( k = 2\sin \theta/\lambda \), \( N \) is the number of QWs, \( N_z \), \( d_z \) and \( f_z \) are the number of atomic planes, atomic plane spacing and mean atomic scattering factors in the layer \( z \),
respectively (where \( z \) is InGaN or GaN). More advanced dynamical theory, used by most commercial simulation software, can measure more precise values for the lattice spacing of InGaN and layer thickness. Once the lattice spacing of InGaN is determined, indium composition can be obtained using the following equation, assuming that the out-of-plane lattice parameter of InGaN follows Vegard’s law and that InGaN layers are fully strained in-plane to the GaN layers:

\[
x = \frac{1 - \nu}{1 + \nu} \left( \frac{d_{\text{InGaN}} - d_{\text{GaN}}}{d_{\text{InN}} - d_{\text{GaN}}} \right)
\]

where \( \nu \) is the Poisson’s ratio, and \( d_z \) is the out-of-plane lattice spacing (where \( z \) is InGaN, GaN or InN). HRXRD analysis is typically based on indium distribution models with assumptions as mentioned above; the accuracy of these assumptions and their influence will be discussed in Sector 3.3.1.

TEM is another useful tool to characterize InGaN/GaN QWs, measuring both indium composition and indium distribution. In particular, scanning transmission electron microscopy (STEM) can deliver better resolution than TEM, which is important to image the QW structures. Indium composition can be measured by dispersive X-ray (EDX) spectroscopy, electron energy loss spectroscopy (EELS), Z-contrast high-angle annular dark-field (HAADF) STEM or the combination of them. Despite the fact that STEM provides a wealth of information on the indium distribution in QWs, there are also limitations. First, the electron beam might damage the sample, leading to the
formation of indium-rich clusters, and this compromises measurement of indium segregation. Second, STEM images are a 2D projection along the electron beam direction, and therefore average information along this direction.

3.1.3. APT for analysis of InGaN/GaN QWs

Although APT has a long track record of analyzing metals, APT has been applied to III-nitride materials more recently, with the first report in 2007. A detailed review of early findings from APT analysis of InGaN/GaN quantum wells can be found in Chapter 3 of Dr. Riley’s thesis. Briefly, APT was mainly used to investigate the hypothesis of carrier localization due to indium fluctuations. For example, APT was used to detect indium clusters by FDA analysis, with the majority of reports excluding the formation of indium clusters in c-plane InGaN/GaN QWs. APT was also utilized to analyze the QW interfaces, revealing monolayer fluctuations in QW width which may also play a role in carrier localization.

A fundamental concern in APT analysis of InGaN/GaN QWs is the reliability of the analysis. The evaporation behavior of InGaN during APT is rather complex due to the distinct evaporation characteristics of group-III and group-V species and the varying polarity along different crystallographic directions in wurtzite crystal. It was proposed that a reliable measurement of indium composition is achievable because Ga atoms and In atoms have a similar evaporation field (Ga: 15V/nm, In: 13V/nm). This hypothesis was confirmed experimentally by examining the influence of surface structure and polarity on the In mole fraction extracted from APT reconstructions of InGaN QWs
with three different crystal orientations. This work validated that APT can provide a reliable measurement of the indium mole fraction and distribution in InGaN/GaN QWs.

More recent comprehensive studies of InGaN/GaN QWs involving APT have focused on correlated analysis of optical and structural properties to understand the factors that limit efficiency. Riley and co-workers reported the correlated APT, STEM, and cathodoluminescence spectroscopy (CL) analysis of InGaN/GaN QWs in nanowire array LEDs. Nonpolar QWs grown on side-facets of nanowires were found to share many characteristics with high quality planar nonpolar QWs in fluctuations of indium distribution, QWs width fluctuations and Mg distribution in p-InGaN canopy layer. Correlated APT and CL measurements also revealed that variations in indium composition along the side-facet of QWs lead to increased light emission wavelength, indicating the promising application for white light. Another interesting correlated study was reported by Rigutti and co-workers. By correlating micro-PL, STEM and APT, they evaluated a single nano-object containing a set of InGaN/GaN quantum wells for the first time. The development of the methodology is important for the dynamical study of the micro-PL decay in time-resolved measurements on single nano-object.

3.1.4. Challenges and Motivations

Despite the successful commercialization of InGaN/GaN QWs based LEDs, efficiency improvements remain desirable. One key remaining challenge is to further boost IQE, which in principle can approach 100%, by advanced design of indium distribution and precise control in QWs growth; another is to push the blue light into green and yellow
light,\textsuperscript{[76]} which is critical for the development of color-mixing LEDs without the use of low-efficient phosphor conversion layer.

APT is a great tool for understanding 3D indium distribution in atomic-scale and providing knowledge for solving remaining challenges of InGaN/GaN QWs. However, due to the limited field of view, APT needs to be correlated with other characterization methods to provide a full picture of InGaN/GaN QWs. The mechanisms for controlling indium incorporation and improving efficiency using hydrogen dosing revealed in this chapter by correlated APT, HRXRD and micro-PL analysis of continuous and discontinuous QWs is important for resolving the first challenge and is also promising in the application of synthesizing high quality QWs to emit green and yellow light.

\section*{3.2. Materials Synthesis and Characterization Methods}

\subsection*{3.2.1. Chemical Vapor Deposition of InGaN/GaN QWs}

The continuous and discontinuous quantum wells samples were grown by metalorganic chemical vapor deposition (MOCVD) on c-plane sapphire substrates in a Veeco D125 reactor by Dr. Dan Koleske at Sandia National Laboratory. Both samples were grown using identical procedures except that a hydrogen dose was applied after the growth of each QW for the discontinuous QW sample. Several $\mu$m-thick GaN template layers were first grown on each sapphire substrate using trimethylgallium (TMG) and ammonia (NH$_3$). HRXRD measurements showed that these template layers had dislocation densities of $\sim 7 \times 10^8$ cm$^{-2}$. An InGaN underlayer with low indium concentration ($\sim 3\%$) was then grown on each template using trimethylindium (TMIn), TMGa and NH$_3$. Next, GaN barrier layers were grown followed by InGaN QWs to form a superlattice structure with
five QWs. Each QW was grown at 745 °C for 1.8 min then capped with GaN at 745 °C for 0.5 min to deplete the excess indium present on the QW surface. After the growth of the GaN cap layer, the temperature is increased to 800 °C over 0.5 min with the TMGa flow on and held at 800 °C for 5 min to complete the GaN barrier. For the discontinuous QW sample, 2.0 SLM hydrogen was introduced into the reactor during the growth of the initial GaN capping layer and then shut off for the remainder of the GaN barrier growth. The hydrogen exposure was the only difference in the growth procedure between the continuous and discontinuous QW samples. After the growth of the superlattice, a thicker GaN cap (∼30 nm) was grown near 900 °C to smooth the surface and facilitate atom probe tomography (APT) sample preparation.

### 3.2.2. Characterization Methods

Centimeter-scale Photoluminescence (PL) measurements were performed using a Nanometries RPM2000 PL Mapper equipped with 325 nm HeCd laser at approximately where HRXRD scans were performed. The micro-PL measurements were performed using a WITec Alpha300R confocal microscope equipped with a 405 nm laser. 24 × 24 µm maps were generated with 0.2 s integration time and 300 nm step size under excitation power of 4.2 µW which was focused to a spot size of ∼550 nm by a 100× objective with a numerical aperture of 0.9.

High resolution X-ray diffraction (HRXRD) measurements were performed by Dr. Daniel Koleske at Sandia National Laboratories. High-resolution ω/2θ scans were performed and recorded around the (0002) reflection of GaN for both samples using a Panalytical Xpert MRD X-ray diffractometer. Diffraction simulations were performed using
a dynamical simulation software, Panalytical XPert Epitaxy 4.0. Thick GaN layers were used as substrates in all simulations. Original models assume indium distribution is uniform in QWs and the interfaces between InGaN and GaN are flat and chemically abrupt and more advanced models for indium distribution were developed based on APT results.

To correlate optical properties and indium composition locally, site-specific focused ion beam (FIB) liftout and sharpening methods were used for both continuous and discontinuous samples. An example of the discontinuous QWs sample is shown in Figure 3.3 to illustrate how the procedures were performed. Pt deposition, liftout and sharpening work was done using a FEI FEI Helios Nanolab SEM/FIB system. Firstly, Pt L-shaped markers were deposited using electron-beam induced deposition (EBID) to align the micro-PL map with FIB lift-out. The Pt L-shaped markers were shown as extremely low-intensity regions in the integrated intensity map (Figure 3.3a) and can be clearly observed as "bumps" in SEM image (Figure 3.3b) after the sample was coated with 100 nm Ni protective layer by ion-beam sputtering deposition. The next step is to select regions of interest (ROIs) from micro-PL mapping. Selected ROIs covering low-intensity and high-intensity regions were marked with small EBID Pt squares on top of a rectangular platinum protective layer of 200 nm by ion-beam induced deposition (IBID) (Figure 3.3b). These small EBID Pt squares provide targets in the final sharpening step. Then, a liftout procedure was performed by cutting ROIs out of the discontinues QWs sample using a high Ga⁺ ion beam and transferring ROIs onto Si posts with the help of Omniprobe (Figure 3.3c-e). A detailed description of the liftout procedure with specific Ga⁺ ion beam voltages and currents can be found in Section 4.1 of Dr. Riley’s thesis. Finally, the liftout samples were sharpened by targeting small EBID Pt squares. Sharpening was performed with
annular milling patterns with different internal diameter from CAMECA Company using 30 keV \( \text{Ga}^+ \) ion beams under 93 pA and 48 pA currents. Sharpening was stopped when the diameters of specimens were less than 100 nm, followed by a “cleaning” step by exposing the entire specimen to 2 keV \( \text{Ga}^+ \) ions under 28 pA current for 10 seconds at 15 k\( \times \) magnification. (Figure 3.3e)

![Image](image-url)

**Figure 3.3.** Site-specific FIB sample preparation procedures to correlate optical properties and indium composition locally. (a) The integrated intensity map of micro-PL mapping. (b) ROIs were identified and marked with small EBID Pt squares. (c-e) ROIs were extracted and transferred onto Si posts with the help of Omniprobe. (f) An example of specimens sharpened into need-shaped tips with diameters less than 100 nm.

APT was performed using a LEAP 4000X Si system under conditions of 0.05 pJ laser pulse energy, 250 kHz pulse frequency, 0.002 ions/pulse target detection rate, and
a background temperature of 28 K for both samples. Reconstructions were done using a commercial software package IVAS with the following parameters: image compression factors of 1.70–1.80, detection efficiency of 0.5, and tip profiling with sphere-cone ratios of 1.60–1.90. The sum of the Ga–Ga spatial distribution maps (SDMs) generated in all of the GaN barrier layers show good agreement with the spacing of the gallium layers along the [0001] direction with mean absolute error of 2.7% for the continuous QW sample and 6.0% for the discontinuous QW sample.

3.3. Correlated Analysis of Continuous and Discontinuous QWs

![Figure 3.4.](image.png) (a) Schematic of continuous and discontinuous QWs. (b) Room temperature PL spectra of continuous and discontinuous QWs. HRXRD data (black line) and abrupt interface model fits (red line) for (c) continuous QWs and (d) discontinuous QWs.
Schematics of continuous and discontinuous QWs are shown in Figure 3.4a. Gaps exist in discontinuous QWs as a result of hydrogen dosing. Figure 3.4b shows the room temperature PL spectra for both continuous and discontinuous QWs. The PL peak is at 468 nm (446 nm) with a full width at half maximum (FWHM) of 28 nm (24 nm) for continuous (discontinuous) QWs. The intensity of the discontinuous QWs is 50% greater than that of continuous QWs. Assuming that the light extraction efficiency is the same for continuous and discontinuous QW samples (since the GaN capping layer is the same for both samples), the IQE of discontinuous QWs is therefore 50% higher. Figure 3.4c and Figure 3.4d show HRXRD scans and fittings based on abrupt interface model. Optimal fits to the continuous QWs find a thickness of 3.1 nm and an indium composition of 0.145. For the discontinuous QWs, the indium composition was determined to be 0.084 with an assumed thickness of 2.7 nm. Fitting the discontinuous QWs in this manner underestimates the true indium mole fraction because it averages over the indium-rich regions and gaps.

3.3.1. APT and HRXRD Analysis of Continuous QWs

A more accurate and useful picture of the indium distribution in continuous QWs was determined by APT. Measured APT profile of indium composition was used to assess the accuracy of the HRXRD fit and to refine the fitting model. Figure 3.5a is a 3D reconstruction of the continuous QWs, with blue dots representing indium atoms and grey surfaces representing the 2.0 at% indium isosurfaces. All five quantum wells are well-defined with no evidence of damage during sample preparation. Frequency distribution analysis (FDA) was performed to access the uniformity of the indium distribution within
QWs with voxels containing 200 ions each. The measured indium distribution was shown as blue dots and the perfect binomial distribution was shown in black dashed line in Figure 3.5b. At a confidence level of 95%, the distribution of indium atoms shows no deviations from a binomial distribution, which suggests a random alloy. So the assumption of uniform indium distribution in QWs made in HRXRD fitting is reasonable. The 1D indium mole fraction profile (Figure 3.5c) shows a superlattice period of 12.0 ± 0.5 nm, a maximum indium mole fraction of 0.18 ± 0.01, and a FWHM of 2.2 ± 0.1 nm. To compare more directly with the rectangular QW shape assumed in the HRXRD fitting, we fit the APT profiles to a symmetric Heaviside step function to find an average indium mole fraction (within the FWHM) of 0.15 ± 0.01 and QW width of 2.9 ± 0.1 nm. These values agree with the HRXRD fitting results. Hence the superlattice spacing, average QW composition, and QW width are well described by the HRXRD measurements, but a QW composition profile must be assumed.

In addition, the indium composition profile extracted from the APT data shows that the upper QW interface is actually more diffuse (Figure 3.5d). The asymmetry is not an artifact of the APT analysis because symmetric indium profiles were previously observed in other samples using similar APT conditions. The more diffuse upper interface is believed to result from indium segregation during QW growth. Indium atoms accumulate on the surface during growth of the InGaN layer, enabling the excess indium to diffuse into the GaN barrier layer and producing an asymmetric profile. This asymmetric profile can dramatically change the potential profile and reduce the efficiency of InGaN/GaN QWs.
Figure 3.5. (a) APT reconstruction of continuous QWs with 2.0 at% indium isosurfaces. (b) FDA analysis of indium distribution within 6.0 at% isosurfaces. (c) 1D indium concentration profile of a cylindrical region of interest in the center of the reconstruction. (d) Indium composition proximity histogram (blue line) averaged over five upper 2.0 at% indium isosurfaces. The blue arrow indicates the growth direction. The black line is an approximation of the histogram in 0.5 nm bins.

The measured QW composition profiles were binned and used to constrain the HRXRD analysis (Figure 3.5d shows the 0.5 nm bins). The goodness of the HRXRD fits is quantified by the mean-absolute error (MAE) as described by Wormington et al.\[80\], giving MAE values of 0.219, 0.195 and 0.183 for the rectangular, 1.0 nm bin, and 0.5 nm bin profiles, respectively (Figure 3.6). Thus, the HRXRD models refined by APT profiles represent an improvement in the analysis of continuous QWs. The trapezoid model by
Lee et al.\cite{81} is an intermediate approach that also improves fitting compared to the assumption of rectangular quantum wells.

![Figure 3.6](image)

Figure 3.6. Two fitting profiles generated by binning APT data were used for HRXRD fitting. The mean-absolute error values demonstrate improved fits compared with the assumption of abrupt interfaces (rectangular profile).

3.3.2. APT and micro-PL Analysis of Discontinuous QWs

Prior to APT analysis of the discontinuous QWs, Pt bars were deposited as markers for correlated analysis, and micro-PL mapping was conducted to assess the uniformity of the sample. Figure 3.7a shows an optical image of the surface of the discontinuous QW sample, with a square indicating where the PL mapping was performed. The black
spots are the well-known V-defects in InGaN QWs,[82, 83] and the right panel of Figure 3.7a is a map of the PL peak center-of-mass. Specimen lift-out and APT was performed on regions avoiding V-defects but otherwise covering all ranges of the variation of PL emission to be able, in principle, to avoid sampling bias. Figure 3.7b is a reconstruction of the discontinuous QW sample. The top two QWs are discontinuous, and the bottom three QWs are continuous. We note that the term “continuous” refers to the appearance of the QW within the field of view of the atom probe reconstruction. None of the QWs are expected to extend across the entire wafer, and all will exhibit gaps that define coalesced islands of InGaN that are much larger than the APT field of view. Figure 3.7c is a 1D indium mole fraction profile showing the superlattice period of 11.9 ± 0.6 nm and QWs with full-width at half maximum (FWHM) of 1.6 nm, which is less than that of the continuous QW sample. The maximum and average indium mole fraction in the continuous portion of the discontinuous QWs is 0.16 ± 0.01 and 0.13 ± 0.01, respectively, which is comparable to the values of the continuous QW sample.

Unlike the measurements such as XRD and Rutherford Backscattering Spectroscopy, APT can analyze the indium-rich regions and gaps separately, and determine the indium mole fraction in indium-rich regions without averaging over the gaps. This capability is useful for understanding the effects of hydrogen dosing. Compared with continuous QWs, discontinuous QWs are narrower and contain less indium (Figure 3.8a). Considering a 10–90% composition change as the interfacial abruptness, the abruptness of lower interface is nearly the same for continuous QWs (0.9 nm) and discontinuous QWs (0.8 nm). However, the upper interface of discontinuous QWs (1.4 nm) is more abrupt than that of continuous QWs (2.0 nm) as a result of hydrogen exposure, which removes excess indium
on the growth surface by forming a volatile compound. Another useful application of APT’s capability in determining indium-rich regions without averaging over the gaps.
is to improve the measurement the bowing factor. As introduced in Section 3.1.1, the bowing factor bridges bandgap and indium composition. So an accurate measurement of bow factor requires both an accurate measurement bandgap and an accurate measurement of indium composition. By locally relating APT and micro-PL measurement, the bowing factor was measured to be $2.20 \pm 0.15$ eV. The wide spread of reported bowing factors (1.0–6.0 eV) can be attributed to the possible inaccurate measurement of indium compositions. For example, GaN filled gap in InGaN layers were also observed without hydrogen dosing; common characterization techniques, such as HRXRD, will significantly underestimated the indium composition, thus resulting an overestimated bowing factor.

3.4. Discussion: Mechanisms of IQE improvement in Discontinuous QWs

IQE can be express as:

\begin{equation}
IQE = \frac{B \times n^2}{A \times n + B \times n^2 + C \times n^3}
\end{equation}

where $B \times n^2$ is the radiative recombination rate, $A \times n$ is the non-radiative Shockley-Read-Hall (SRH) recombination rate and $C \times n^3$ is the non-radiative Auger recombination rate. Below is a detailed discussion how the radiative and non-radiative recombination rate is changed in discontinues QWs by hydrogen dosing.

3.4.1. Radiative Recombination

To explain the difference in radiative recombination rate between continuous and discontinuous QWs, the indium mole fraction profiles (Figure 3.8a) were imported into the
Figure 3.8. (a) Averaged proximity histograms for continuous QWs (purple line) and discontinuous QWs (red line). The two proximity histograms are used as input for simulation. (b) Nextnano$^3$ simulation of a single quantum well for continuous QWs (solid lines) and discontinuous QWs (dashed lines). The black lines are valence bands and conductions bands and the red lines are electron and hole wavefunctions.

Schrodinger-Poisson solver nextnano$^3$ to simulate the band profiles and wavefunctions of electrons and holes. As shown in Figure 3.8b, the discontinuous QWs have a slightly larger bandgap as a result of the lower indium composition, which explains the blue-shift
of the PL spectrum. We also observe that the separation of electrons and holes is smaller for discontinuous QWs; the square of ground-state electron and hole wavefunction overlap is 0.09 for continuous QWs and 0.13 for discontinuous QWs. The larger overlap indicates that the discontinuous QWs should, all other factors being equal, have a higher radiative recombination rate\cite{85}, which would contribute to the observed higher IQE.

### 3.4.2. Non-Radiative Recombination

Of course, any reduction in non-radiative recombination may also contribute to the improved IQE. At the low excitation power used here, Auger recombination can be ignored\cite{86}, so one expects defect-related non-radiative (SRH) recombination to dominate non-radiative recombination. Atomic force microscopy (AFM) shows that there are two kinds of defects existing (Figure 3.9a), which are named “small defect” and “large defect”; and a schematic of these two kinds of defects in QWs is shown according to their size and depth. The large defect goes through QWs layers, thus it can keep carrier from defect, which is why regions around large defects are brighter in integrated micro-PL mapping (Figure 3.9b). Smaller defects end in QWs layers and act as SRH recombination centers, so regions around small defects are darker in the integrated micro-PL mapping. A comparison of SEM images of the surfaces of continuous and discontinuous QWs shows that the density of defects is similar for both QWs but the ratio of large defects is higher for discontinuous QWs (61.9% in discontinuous QWs vs. 38.6% in continuous QWs). This phenomenon can be explained as indium near small defects was preferentially etched, changing small defects into large defects and reducing defect-related SRH recombination rate. This is another reason for the IQE improvement of discontinuous QWs.
3.5. Summary

In summary, correlated APT and photoluminescence analysis of continuous and discontinuous InGaN QWs enables and refines the measurement of indium mole fraction and identifies factors contributing to the increase in IQE. Relative to the control growth, hydrogen dosing leads to narrower quantum wells of lower indium content with more abrupt interfaces, which contributes to an increased radiative recombination rate by increasing the electron-hole wavefunction overlap, as revealed by simulations. Hydrogen dosing also etch defects through QWs layer, which contributes to higher IQE by keep carrier from defects thus reducing non-radiative recombination.
Figure 3.9. (a) AFM measurements of two kinds of defects, which are named “small defect” and “large defect” according to their size and depth, and the schematic of these two kinds of defects. (b) An integrated intensity map from micro-PL mapping and its correlated SEM image. (c) SEM images of the surfaces of continuous and discontinuous QWs.
CHAPTER 4

APT Analysis of A Low-Energy Memristor

The memristor (short for memory resistor) was first proposed in conception by Leon Chua in 1971[87] as another fundamental passive circuit element besides the resistor, capacitor and inductor. Since it was experimentally achieved in 2008 by researchers from Hewlett-Packard Company,[88] memristor research has attracted considerable attention. Nowadays, the memristor has become one of the most promising device candidates for next-generation computing beyond complementary metal-oxide semiconductor (CMOS) technology, including non-volatile memory[89, 90, 91, 92], and neuromorphic computing[91, 93, 94, 95].

APT has been demonstrated as a powerful tool for characterizing CMOS devices,[96, 97, 98, 99] but it has not yet been applied to memristor devices. In this chapter, APT was used to explore the structure and to help understand the switching mechanism of a memristor utilizing Ag doped Ta$_2$O$_5$ as the active layer, which is the first low-energy memristor that can be operated at both low voltage and low current while maintaining stable resistance states. The design, fabrication, electron microscopy imaging and electrical property measurements were performed by Jung Ho Yoon under the supervision of Professor Jianhua (Joshua) Yang at the University of Massachusetts. APT measurements and analysis were performed at Northwestern University and are the focus of this chapter. A manuscript, including the APT results, but focusing on electrical measurements,
4.1. Introduction

4.1.1. Challenges for Achieving Low-Energy Memristors

Despite numerous laboratory demonstrations of memristor applications, large-scale commercialization of memristors has not been achieved. One major obstacle is the lack of a low-energy memristor that can be switched at both low voltage and low current between stable resistance states. These properties are especially critical for a memristor to operate together with a selector in a 1S1R (1 selector and 1 memristor) structure, which is likely the only scheme that can fully realize the scalability potential of memristors in both 2D and 3D for ultimate device density. A memristor device has two states: OFF state (high resistance) and ON state (low resistance). The operation of a traditional memristor device usually involves an “electroforming” process, a one-time application of high voltage or current to produce a significant change of electronic conductivity. This “electroforming” process is responsible for huge device to device variance in electrical performance and should be avoided for large scale commercialization. In addition, the large voltages and currents used in electroforming can also induce permanent damages to the selector device in 1S1R cells. An ideal low-energy memristor should be operated without an “electroforming” process, which indicates that the pristine state and the OFF state have a similar resistance level. More importantly, a low-energy memristor should simultaneously achieve low switching voltage (e.g. < 1 V) and a low switching current (e.g. < 30 µA), which are critical for achieving a low energy and high
density computing system utilizing the state of the art selectors or driving transistors that operate at sub 1 V.

Either low switching voltage or low switching current (but not both simultaneously) has been obtained in valence change memory (VCM) cells with oxides, such as HfO$_x$, TaO$_x$, TiO$_x$ and other metal oxides.\cite{89, 104, 105} The switching in such devices is induced predominantly by the motion of oxygen (e.g. oxygen anions or vacancies), which has good retention characteristics but requires either a large switching voltage or current due to a relatively large diffusion barrier for oxygen in oxides.\cite{104, 105} Low voltages together with low currents have been observed in electrochemical metallization (ECM) cells with traditional electrolytes such as Ag$_2$S and other chalcogenides.\cite{106, 107, 108} Unfortunately, those devices suffer from unstable resistance states because the switching is induced by the motion of cations (e.g. Ag and Cu), for which the diffusion barrier to hold the resistance states under zero electrical bias is relatively low in the traditional electrolytes. Therefore, a combination of VCM and ECM provides an opportunity to engineer a device that can be switched with both low voltage and low current, and at the same time maintains stable resistance states.

4.1.2. Motivation

In this chapter, the advantages of combining VCM and ECM for low-energy memristors are demonstrated by utilizing cations such as Ag to obtain a medium diffusion barrier in TaO$_x$. The stable resistance states are maintained by pre-configuring metal species (Ag in this case) into the oxide matrix during the fabrication process instead of electrically driving them into the oxide during the first electrical operation. The developed new type of
memristor based on Ag doped Ta$_2$O$_5$ can achieve the required performance characteristics for large-scale commercialization, with low current below 30 µA and simultaneously low voltage $\sim \pm 0.7$ V in switching operations.

A measurement of the concentration and 3D distribution of Ag in TaO$_x$ oxides is essential to provide a controlled fabrication scheme and to understand the mechanism of switching and maintenance of stable resistance states. For this purpose, APT analysis was performed on fabricated memristor devices to evaluate the concentration and distribution of Ag atoms. Despite the huge differences in evaporation field between the protecting layer (Pd) and the top electrode (TE) Ta, the Ag doped Ta$_2$O$_5$ layer was successfully analyzed before the tip fractured at the Ta$_2$O$_5$/bottom electrode (BE) interface. APT analysis established the concentration of Ag in the Ta$_2$O$_5$ layer to be $\sim$8%, and revealed that Ag atoms are uniformly distributed in regions close to TE in the OFF state. These observations support a proposed switching mechanism discussed in Section 4.3.4.

4.2. Experiments

4.2.1. Fabrication and Electrical Measurements

Standard photolithography and lift-off processes were used for top Ta and bottom Ru electrodes to fabricate a 5 µm by 5 µm cross-bar type device (Figure 4.1a). Using a sputtering system (Orion 8, AJA international), 4.5-nm-thick Ta$_2$O$_5$:Ag (8%) film was deposited by RF co-sputtering with Ar:O$_2$ (4:1) gas ambient at room temperature on a 20-nm-thick Ru/2-nm-thick Ta patterned BE, where the Ru BE and adhesion Ta films were deposited by DC sputtering, respectively on the SiO$_2$/Si substrate. Then, Ta TE
and Pd layer for blocking the oxidation of Ta were electron-evaporated. A schematic of each layer with its thickness is shown in Figure 4.1b.

Figure 4.1. (a) An optical microscopy image of the fabricated cross-bar memristor devices. (b) Schematic showing each layer with its thickness in one memristor device.

4.2.2. Device Characterization

The cross-section of the Ta/Ta$_2$O$_5$:Ag/Ru device was evaluated using high-resolution TEM (Titan transmission electron microscopy, FEI). The electrical behavior of the fabricated device was measured using a B1500 semiconductor parameter analyzer (Keysight) for DC measurement and B1530 (Keysight) for pulse measurement, respectively, and bias was applied to the TE while the BE was grounded.

APT (LEAP 4000X Si, CAMECA) analysis was performed to reveal the Ag concentration and distribution of the films. Ni was sputtered onto the top of the devices as a protective layer. Then FIB milling method was used to prepare samples for APT analysis, targeting the edges of the electrodes, which have the highest electric field during switching. Electron beam deposited Pt was placed on the edge as markers as in Figure
4.2a. The marker can be clearly seen when the extracted wedge was transferred onto Si posts (Figure 4.2b). Sharpening was centered on the marker.

![Figure 4.2](image)

Figure 4.2. (a) A SEM image of the cross-bar memristor devices, with 4 ROIs marked by electron beam deposited Pt. (b) A SEM image of a portion of the extracted wedge weld on a Si post, ready to be sharped; the marker can be clearly seen. The red circles illustrate the same Pt marker.

APT was performed at 250 kHz pulse frequency, a 0.005 ions/pulse target detection rate and a background temperature of 50 K. Laser pulse energy was tuned from 30 pJ to 70 pJ to suppress any rapid voltage increase. 7.8 M hits were collected for the data reported. Reconstructions were performed using the commercial software package IVAS using the tip-profile method with an image compression factor (ICF) of 1.8.

4.3. Results and Discussions

4.3.1. Morphology and Switching Characteristics

The cross-section of a memristor device with a stack structure of Ta/Ta₂O₅:Ag/Ru is shown in a high-resolution transmission electron microscopy (TEM) image in Figure 4.3a, where the inset presents a microscopic top view of the patterned device. The Ta TE,
amorphous Ta$_2$O$_5$:Ag layer, and Ru BE can be clearly seen in the micrograph, where the Ta/Ta$_2$O$_5$:Ag and Ta$_2$O$_5$:Ag/Ru interface are also clearly defined. However, it is difficult to observe the Ag distribution in the TEM image.

Figure 4.3b presents the resistance switching I–V curves of the Ta/Ta$_2$O$_5$:Ag/Ru memristor device. The general switching sequences are shown by the purple dashed arrows and the numbers, including a SET process (OFF state to ON state) and RESET process (ON state to OFF state). A compliance current ($I_{cc}$, the allowed maximum current) of 10 $\mu$A was used during SET switching to protect the device. The I–V sweep measurement started with a positive bias applied to the TE, while the Ru BE was grounded, as indicated by the 1st Set curve (labeled with open square symbols). The pristine state of the device was in OFF state with high resistance. As the voltage increased to 0.7 V, the current suddenly jumped to the applied $I_{cc}$ (10 $\mu$A) and the device was switched to the ON state. Upon reversing the bias polarity to the negative direction, the current increased to about 30 $\mu$A and then suddenly dropped at $\sim$−0.7 V to a similar current level of the pristine state, which was the Reset process. The subsequent switching loops repeat the switching curves of the 1st Set and Reset well within a normal variance. As can be seen from the I–V curves, the device shows low operation voltages of $\sim \pm 0.7$ V and a low switching current below 30 $\mu$A.

The endurance of the device was tested by repeating the switching operations. Figure 4.3c presents the results up to $5 \times 10^7$ cycles. As shown in the figure, there is no significant change in the resistance for both ON state and OFF state in the operations, i.e. stable resistance states are maintained in the device. Based on the electrical performance of the
memristor device, it can be concluded that a low-energy memristor operating at both low voltage and low current with stable resistance states has been achieved.

4.3.2. APT Measurement of the Device

As shown in Figure 4.3a, the Ag distribution in the amorphous Ta$_2$O$_5$ layer was not clearly overserved in the TEM image. Thus, APT was used to analyze the 3D distribution of Ag atoms in the Ta$_2$O$_5$ layer of a device on the OFF state. A layer of 100 nm Ni was deposited on top before FIB milling to protect the device from ion beam damage. Since the distribution of Ag atoms is highly influenced by the electric field, lift-out processes targeted an ROI at the edge of the electrode where the electric field is strongest. Figure 4.4a is a schematic of the region targeted for lift-out. Tips were fabricated as discussed in Section 4.2.

One can observe from Figure 4.4a that the composition of the tip is very complex. According to calculations from Tsong, the evaporation fields of Ni (35 V/nm) and
Figure 4.4. (a) A schematic of the position and composition of the fabricated tip with the black line indicating the shape of the tip. (b) APT reconstruction of a specimen analyzed by manually controlling laser power, with blue dots for Ni, yellow dots for Pd, gray dots for Ta and orange dots for Ta$_2$O$_5$.

Pd (37 V/nm) are very close, so the interface between Ni and Pd is believed to be stable. However, the evaporation field of Ta (96 V/nm) is extremely high, so the interface between Pd and Ta has a high chance of fracturing due to the stress induced by the rapid voltage increase during APT analysis. This prediction was confirmed by initial experiments with the LEAP system in auto-control (normal operation mode for most experiments), specifically the voltage increases rapidly when the Ta layer is exposed, followed by tip fracture. These initial experiments resulted in the collection of only Ni and Pd ions, whereas the ROI is the Ta$_2$O$_5$:Ag layer. In order to extend APT analysis into the Ta$_2$O$_5$:Ag layer, a new strategy was adopted. As the Ta layer was exposed, the laser power was manually increased (from 30 pJ to 70 pJ) to keep the voltage constant. This reduced the rate of tip fracture and resulted in a successful analysis of the Ta$_2$O$_5$:Ag
layer as shown in Figure 4.4b. However, the entire tip was not captured. When the BE Ru (evaporation field 41 V/nm) is exposed, the high laser power leads to the preferential and rapid evaporation of Ru ions, resulting a fracture at the Ta$_2$O$_5$:Ag/BE interface. To achieve full tomographic imaging of the inner structure in the memristor device, cross-section sample preparation is likely necessary.

### 4.3.3. Analysis of Ag distribution

A closer look at the reconstruction is shown in Figure 4.5a in order to determine the Ag distribution, where Ag atoms were presented by green dots. The first step is to determine in which layers Ag atoms are located. A first impression from Figure 4.5a is that Ag atoms are in all three regions of interest (ROI 1, ROI 2 and ROI 3). However, mass spectrum analysis, rather than observing the reconstruction, is needed to determine whether there are certain atoms in a ROI due to the existence of background ions. Figure 4.5 b-d show the mass spectra from 100 Da to 115 Da (Ag$^+$ ion in 107 Da and 109 Da) for ROI 1, ROI 2 and ROI 3, respectively. In these three mass spectra, Pd$^+$ ions (102 Da, 104 Da, 105 Da, 106 Da, 108 Da, 110 Da) were observed due to significant trajectory aberrations of Pd$^+$ ions caused by different evaporation fields between layers. However, an obvious Ag$^+$ peak is only observed in ROI 3. Hence, Ag atoms are only located in the Ta$_2$O$_5$ layer and the green dots in ROI 1 and ROI 2 are background ions.

Next, the Ag distribution along the layer stacking direction was analyzed in an ROI indicated by the red rectangle in Figure 4.5a. A 1D concentration profile along the red arrow is shown in Figure 4.5e, divided into 3 regions. Region I is the interface between Ta and Ta$_2$O$_5$; the width of Ag concentration profile is attributed to interface broadening.
caused by the difference in evaporation fields. Region II shows the Ag concentration in the Ta$_2$O$_5$ layer is $\sim$ 8%. In Region III, the Ag concentration decreases as the distance from the TE increases, consistent with the suggestion that Ag atoms tend to segregate at the growth interface of the Ta$_2$O$_5$ layer to minimize the surface energy between Ag and Ta$_2$O$_5$\cite{95}. No data were collected beyond Region III due to fracture of the interface between Ta$_2$O$_5$ and the Ru BE$_i$. The Ag concentration profile is in agreement with SIMS measurements.\cite{100}

Finally, the uniformity of Ag atoms in Ta$_2$O$_5$ layer was evaluated by radial distribution function (RDF) analysis. The Ta$_2$O$_5$:Ag layer was first isolated by isosurfaces with a Ag concentration of 4\%, and the RDF was performed in the isolated regions (Figure 4.5f). No obvious deviations from 1 can be found in the RDF of Ag–Ag, indicating that Ag atoms are uniformly distributed in Ta$_2$O$_5$ layer and no cluster is formed in the region close to the TE.

One concern on the measured Ag distribution is that the high electric field applied during APT analysis can cause the redistribution of Ag atoms. However, the high electric field can only penetrate a few angstroms into the surface of the tip for oxide dielectrics, because the strong electric field can reduce the band gap of oxide dielectrics, leading to metallization of the oxide surface.\cite{109} So the electric field in APT analysis is believed not to cause Ag redistribution on a scale of $\sim$100 nm for the reconstruction of the tip. Experimentally, the concern can be address by analyzing the memristor device in different orientations. If the electric field during APT analysis has no influence, the Ag distribution from different orientations should be the same. Analysis at different orientations is beyond the scope of this chapter and was not performed.
Figure 4.5. (a) A smaller region of the reconstruction in Figure 4b, with the size of 50 nm by 45 nm. Ag atoms are represented by green dots. (b-d) Mass spectra for ROI 1, ROI 2 and ROI 3, respectively. (e) 1D concentration profile of Ag in a ROI shown in the red rectangle in the bottom-left corner of (a). (f) Radial distribution function of Ag in Ta$_2$O$_5$ layer.
4.3.4. Proposed Mechanism

The analyses above inform understanding of possible switching mechanisms. Figure 4.6 illustrates the proposed distribution of Ag atoms in the pristine state (equivalent to the OFF state) and the ON state (caused by the migration of Ag). In the pristine state, the concentration of Ag is higher near the TE region and some Ag nanoparticles (nano-seeds) are embedded on the Ru surface. The gradient in Ag concentration is supported by the 1D concentration profile near TE in APT analysis. The formation of Ag nanoparticles embedded in Ru is based on the fact that there is no mutual solubility between Ag and Ru, so Ag atoms tend to aggregate to minimize the surface energy between Ag and Ru. The Ag enriched region near the TE acts as a virtual Ag electrode analogous to the intentionally deposited Ag layer in conventional conductive bridging random access memory (CBRAM) structures. When a positive bias is applied to the TE, a small fraction of the Ag ions migrate towards the BE, resulting in a conductive tunneling path. In contrast to conventional CBRAM, a sub-critical concentration of Ag is pre-dispersed in the oxide layer during sample fabrication. As a result, less Ag migration is needed to produce conductive tunneling paths. Conductive tunneling paths can be formed via discontinuous Ag clusters in the new memristor, in contrast to traditional CBRAM devices where strong continuous conductive filaments are needed and typically observed. After the Set process, when a negative bias is applied to the TE, Ag ions are driven back towards the TE. This reduces the Ag cluster sizes (and possibly numbers), increases the distances between them, and thereby disrupts the conductive tunneling paths to switch the device back to the OFF state. Unfortunately, the proposed Ag clusters were not captured by APT analysis due to the fracture of the tip near the interface between
Ta$_2$O$_5$:Ag and BE Ru. However, the formation of Ag clusters is supported by the tunneling conduction mechanism in ON state revealed by additional electrical measurements which are discussed in detail in the submitted manuscript.\[100\]

Figure 4.6. Schematic diagrams illustrating the distributions of Ag atoms in (a) the pristine state (equivalent to the OFF state) and (b) the ON state (caused by the migration of Ag) in Ta/Ta$_2$O$_5$:Ag/Ru memristor device.

4.4. Summary

In summary, by combining the advantages of VCM and ECM, a low-energy Ag-doped Ta$_2$O$_5$ memristor device was proposed and experimentally demonstrated to switch with low current and voltage while maintaining stable resistance states. APT analysis was used to determine the Ag distribution in the low energy memristor device. By manually tuning the laser energy to avoid fracture caused by different evaporation fields, the Ta$_2$O$_5$:Ag layer was analyzed by APT and the distribution of Ag atoms evaluated. Based on the APT results and electrical performance data, a switching mechanism based on conductive tunneling paths instead of the continuous traditional conductive filaments was proposed for the Ta/Ta$_2$O$_5$:Ag/Ru stack structure. The low switching current and voltage make
the memristors highly compatible with two-terminal selectors. The results open up an avenue to engineer memristors for high-density and low-energy applications.
CHAPTER 5

APT Advances to 2D Limit: Feasibility and Resolution for APT Analysis of 2D Layered Materials

The feasibility of APT analysis of 2D layered materials is explored in this chapter. Considering that the weak interlayer van der Waals interactions in 2D layered materials might result in tip fractures, a family of 2D layered materials, \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_{3m}\), was chosen to be studied due to the possibility in tuning their interlayer interactions. Doped \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\), \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_6\), and doped \(\text{Bi}_2\text{Se}_3\) were analyzed. The results for doped \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\) and doped \(\text{Bi}_2\text{Se}_3\) are presented in this chapter and the results for \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_6\) can be found in the supporting information online\(^{[111]}\). For Ag doped \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\), sub-nm spatial resolution was achieved and used to identify layers. Analysis revealed that the Ag dopants were distributed in both PbSe and Bi\(_2\)Se\(_3\) layers, and that a spatial correlation exists between Ag atoms in adjacent PbSe and Bi\(_2\)Se\(_3\) layers. For Cu doped Bi\(_2\)Se\(_3\), APT was used to show that both intercalated and substituted Cu atoms exist.

5.1. Introduction

5.1.1. 2D Layered Materials

Broadly, 2D layered materials can be defined as materials with weak interlayer bonding, typically van der Waals bonding, with the potential to be exfoliated to isolated monolayers.
The bulk forms of 2D layered materials have been demonstrated in a wide range of applications. For example, graphite, MoS\(_2\) and hexagonal boron nitride (h-BN) have been widely used as surface lubricants.\[112, 113, 114, 115\] Bi\(_2\)Se\(_3\), Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\) have been studied as topological insulators, promising for quantum computing.\[116, 117, 118\] Monolayers of 2D materials have been extensively studied after the discovery of graphene.\[119\] and presently monolayers have been used for various applications, such as transistors,\[120\] photodetectors,\[121\] photovoltaics,\[122\] etc.

5.1.2. APT for Evaluating Doping in 2D Materials

Impurity doping plays an important role in engineering the electronic properties of traditional semiconductor materials, and is beginning to be explored in 2D materials to modulate carrier density and impart magnetic properties. For instance, Nb can be incorporated into the lattice of MoS\(_2\) in chemical vapor transport (CVT) growth and tune the n-type semiconducting MoS\(_2\) to be p-type semiconducting, enabling vertical p-n junctions.\[123\] Nitrogen doped graphene can be synthesized via chemical vapor deposition (CVD) on copper foil substrate with NH\(_3\) introduced during growth, and the carrier density is controlled by the nitrogen dopant density.\[124\] Similarly, Mn doped MoS\(_2\) can be grown via CVD on graphene substrate,\[125\] which can introduce magnetic properties into MoS\(_2\) monolayers according to DFT studies.\[126, 127, 128\] Despite the above success in doping 2D materials, it remains a challenge to dope 2D materials in a controlled manner in order to tailor the electronic properties. Furthermore, it makes the challenge harder without an appropriate method to measure the dopant distribution, ideally with 3D atomic resolution, in both bulks and isolated layers. Determination of the dopant location is an
important step in improving understanding of the material synthesis and properties that could enable fundamentally new types of electronic properties and devices.

Common characterization tools, such as Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and Secondary ion mass spectrometry (SIMS) fail to solve this challenge. TEM and STEM have been used to assess the in plane dopant distribution in 2D materials.\cite{123, 125, 129, 130, 131} For example, Gong, et al.\cite{131} imaged Se-doped MoS$_2$ using STEM in high-angle annular dark field mode. Individual atoms can be identified by Z-contrast for MoS$_2$ monolayers and AB-stacking bilayers, providing direct maps of the dopant atom distribution. Unfortunately, due to the projection nature of STEM, this method cannot be applied to anything thicker than a few-layers. SIMS can reach atomic-scale resolution in depth profiling 2D materials as demonstrated by Chou et al.\cite{132} They revealed the locations of residuals in exfoliated graphene monolayers on h-BN using SIMS. However, the atomic resolution is only achieved in the depth direction and the lateral resolution is hundreds micrometers, failing to generate a 3D distribution of dopants.

APT has been used to characterize the dopant distribution in nanowires\cite{133, 134}, thin films\cite{135} and FinFET devices\cite{97, 98}. Considering its success in achieving atomic resolution with ppm chemical sensitivity, it is a good candidate for solving the key challenge of measuring dopant distribution in 2D materials although it had not been applied to analyze doping in 2D materials prior to this thesis work.
5.1.3. Challenges

2D materials are defined by their weak interlayer interactions, which might be a concern for APT analysis of these materials. Tips are under significant stress during APT analysis,\textsuperscript{[136]} and specimens with weak bonding are more subject to fracture. Additionally, the quality of APT analysis for stacked hereto-monolayers is under question because obvious reconstruction artifacts present in APT analysis of multilayers, usually leading to the broadening or missing layers.\textsuperscript{[137, 138, 139]} In 2D layered materials, dopants can be located in substitutional or interstitial sites within layers, or between layers (intercalation), which adds complexity for APT determination of dopant locations. In order to evaluate the data quality of APT analysis of 2D layered materials, the following questions were be addressed:

1. Are van der Waals interactions enough to hold tips together during APT analysis?
2. What spatial resolution can be achieved for APT analysis of 2D layered materials?
3. Is it possible for APT to resolve whether dopants are located within the layer or between layers?

\((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_{3m}\) is a family of homologous materials that consists of \(m\) layers of \(\text{Bi}_2\text{Se}_3\) alternating with a layer of \(\text{PbSe}\).\textsuperscript{[140]} The bonding strength between \(\text{PbSe}\) and \(\text{Bi}_2\text{Se}_3\) layers is larger than that between \(\text{Bi}_2\text{Se}_3\) layers according to DFT calculations,\textsuperscript{[111]} which makes the average interlayer interactions tunable by varying \(m\). Furthermore, the \(m=2\) phase is a topological insulator,\textsuperscript{[141]} whereas the \(m=1\) phase is semi-metallic and can be made superconducting by Ag doping.\textsuperscript{[142]} In this material system, one could in principle create an interface between a superconductor and topological insulator, which has been proposed to host Majorana fermions.\textsuperscript{[143]} However, the distribution of Ag dopants
in \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\) was not clear, preventing the understanding of the origin of superconductivity in the material system. Thus, APT was used to determine the location of Ag dopants in \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\). Ideally, the determination of dopant locations can in turn contribute to the scientific question of the origin of superconductivity.

\(\text{Bi}_2\text{Se}_3\) can be viewed as the limit of \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_{3m}\) with \(m\) approaching infinity. In terms of properties, \(\text{Bi}_2\text{Se}_3\) is a topological insulator\(^{[116]}\) whereas Cu doped \(\text{Bi}_2\text{Se}_3\) is a superconductor\(^{[144]}\). Superconductivity in \(\text{Cu}_x\text{Bi}_2\text{Se}_3\) is believed to arise from intercalated Cu atoms (Cu atoms between layers)\(^{[144]}\) but the ratio of intercalated Cu atoms is unknown due to experimental limitations in characterizing the atomic scale dopant distribution. APT analysis of Cu doped \(\text{Bi}_2\text{Se}_3\) can test the capability of APT to distinguish dopants within the layer versus dopants between layers. The possibility of quantitative analysis of the ratio of intercalated Cu dopants was also explored.

5.2. Ag Doping in \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\)

In this section, the tomographic mapping of dopants in layered 2D materials is reported with atomic sensitivity and subnanometer spatial resolution using atom probe tomography (APT). APT analysis shows that Ag dopes both \(\text{Bi}_2\text{Se}_3\) and \(\text{PbSe}\) layers in \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\), and correlations in the position of Ag atoms suggest a pairing across neighboring \(\text{Bi}_2\text{Se}_3\) and \(\text{PbSe}\) layers. Density functional theory (DFT) calculations confirm the favorability of substitutional doping for both Pb and Bi and provide insights into the observed spatial correlations in dopant locations. This section was based on the publication: Nano Lett. 16, 6064 (2016)\(^{[111]}\).
5.2.1. Sample Preparation and Experiments

Ag doped \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\) was grown by solid state synthesis in the Kanatzidis group. PbSe and \(\text{Bi}_2\text{Se}_3\) were first grown, then Ag, PbSe and \(\text{Bi}_2\text{Se}_3\) were weighted in a nominal composition \(\text{Ag}_x\text{Pb}_5\text{Bi}_6\text{Se}_{14}\) (\(x \sim 1\), corresponding to a nominal Ag atomic concentration of 0.038) and ground thoroughly. The mixture was sealed in an evacuated quartz tube and loaded in a tube furnace. The furnace was first heated to 950 °C over 12 h and then held at this temperature for 12 h. Subsequently, the furnace was cooled to 650 °C over 80 h and then shut off. The crystal structure in Figure 5.1a shows alternately stacked \(\text{Bi}_2\text{Se}_3\) and PbSe layers, and the weak interlayer bonding is revealed by the fracture surface observed in scanning electron microscopy imaging (Figure 5.1b).

Specimens for atom probe tomography (APT) analysis were prepared using standard focused ion beam (FIB) lift-out and sharpening procedures, with the analysis direction perpendicular to (001) planes. The final specimens were sharp needle-shaped tips with diameters less than 100 nm (Figure 5.1c). APT was performed using a LEAP 4000X Si with a 355 nm laser at 250 kHz pulse frequency, a 0.005 ions/pulse target detection rate, a background temperature of 28 K, and laser pulse energies between 1 and 30 pJ. Of the pulse energies tried, 30 pJ gave the best spatial resolution. Among 10 tips fabricated, 6 tips were successfully analyzed without fracture. Reconstructions and further analysis were conducted using the commercial software package IVAS, and the 2D RDF analysis was performed with the MATLAB codes shown in Appendix A. Simulation of radial distribution functions was done by importing the simulation results into IVAS.
Figure 5.1. (a) Crystal structure of (PbSe)$_5$(Bi$_2$Se$_3$)$_3$ with alternating PbSe and Bi$_2$Se$_3$ layers. (b) Top view SEM image of the (PbSe)$_5$(Bi$_2$Se$_3$)$_3$ crystal. (c) SEM image of a sharpened tip.

All electronic structure calculations were carried out at NIST by collaborators based on density functional theory (DFT) using the projector augmented wave method as implemented in the plane-wave code VASP.\textsuperscript{145, 146, 147, 148} For the structural relaxations and energy calculations, the optB88-vdW-DF functional was employed, which includes van der Waals (vdW) interactions.\textsuperscript{149, 150, 151, 152} Relaxations of the structures were performed until the forces and in-plane stresses were below 5 meV/Å and 0.01 GPa, respectively. The Brillouin zone integration was performed using k-point meshes with > 32 points/Å and a Gaussian smearing with a width of 0.05 eV. Such a k-point mesh and a cutoff energy of 550 eV ensures convergence of the total energies to better than 1 meV per unit cell. (PbSe)$_5$(Bi$_2$Se$_3$)$_3$ adopts a layered structure with monoclinic space group $P21/m$, where PbSe and Bi$_2$Se$_3$ layers are separated by weak van der Waals forces. The lattice parameters obtained from DFT structural relaxations, $a = 15.984$ Å, $b = 4.1915$ Å, $c = 21.4727$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 97.475^\circ$, are within 2.5% of the experimentally measured values\textsuperscript{142}. 
5.2.2. APT Results and Analysis

Figure 5.2a presents the SEM images of a tip before and after APT analysis, showing that the tip shape does not change significantly during evaporation. The smooth evolution of the tip shape suggests that the stacked 2D layers do not suffer severe reconstruction artifacts as traditional multilayers,\[137, 138, 139]\] and an accurate 3D tomographic mapping of the stacked 2D layers is possible. Figure 5.2b shows a three-dimensional reconstruction of the overall specimen and a region of interest (ROI) defined by a cylinder, mapping Bi atoms as blue dots, Pb atoms as green dots and Ag atoms as red dots. Alternating layered regions enriched in Bi and Pb atoms are visible in the entire reconstruction, and occur with the expected periodicity based on the crystal structure in Figure 5.1a.

A major motivation for APT doping analysis is the ability to detect single ions with very high spatial resolution. The laser conditions were chosen to optimize the spatial resolution in the analysis direction and 30 pJ delivered the best results among the conditions tried. The spatial resolution can be obtained from SDM analysis. A better spatial resolution is associated with a SDM which can correctly reflect the crystal structure and has higher peak amplitude. How to define spatial resolution of APT analysis of 2D materials by SDM analysis is discussed in Appendix B. The mass spectrum for the 30 pJ condition is shown in Figure 5.2c. No impurity peaks were detected, and the signal-to-noise level establishes an upper bound of 100 ppm. Peaks for Bi\(^+\)/Pb\(^+\) and Bi\(^++\)/Pb\(^++\) ions can be separated despite the small mass difference between Bi (209 Da) and Pb (204 Da, 206 Da, 207 Da, 208 Da). Peaks for complex ions, such as BiSe\(^+\) and PbSe\(^+\), BiSe\(_2\)^{++} and PbSe\(_2\)^{++}, overlap due to the large spread of Se isotopes (74 Da to 82 Da).
Figure 5.2. (a) A comparison of tip shapes before and after APT analysis, showing that the tip shape does not change significantly. (b) The distribution of Bi (blue), Pb (green) and Ag (red) atoms in the overall reconstruction and in the region of interest (ROI) defined by a cylinder, showing that layers are resolved. (c) Mass spectrum taken at 30 pJ laser pulse energy.
The overlap in peaks in the mass spectrum mixes the assignments of a small fraction of the complex ions, leading to some artificial spatial overlap of Bi and Pb elements (Figure 5.3a). However, Ag is only detected as Ag$^+$ ions, which do not overlap with other ions in mass spectrum. Therefore, the 1D concentration profile of Ag does not suffer from spatial overlap as discussed later. Despite the Bi and Pb overlap, alternating Bi$_2$Se$_3$ and PbSe layers are resolved in Figure 5.3a. For a more quantitative statistical analysis of the spatial resolution, we performed a spatial distribution map (SDM) analysis by only counting non-overlapped Bi$^+$/Pb$^+$ and Bi$^{++}$/Pb$^{++}$ ions for Bi/Pb. Figure 5.3b presents the SDM of atoms in the vertical direction of the reconstruction using Bi atoms as the reference species. Briefly, a SDM reports the distribution of one species relative to other atoms of the same or different species. The peak distance in the Bi–Bi profile shows the lattice spacing to be 1.65 nm in the analysis direction, in agreement with the crystal structure. Furthermore, the peaks at ±0.85 nm in the Bi–Pb profile indicate that Bi atoms and Pb atoms are separated statistically from each other, i.e., Bi$_2$Se$_3$ layers and PbSe layers are resolved by APT analysis.

The 1D concentration profile of Ag in Figure 5.3a shows two peaks in a lattice period, with large peaks in the same positions as the Pb peaks and small peaks in the same positions as the Bi peaks, indicating that Ag atoms are located in both PbSe and Bi$_2$Se$_3$ layers. SDM analysis of the Bi-centered Ag distribution (Bi–Ag profile, Figure 5.3b) shows more clearly that there are peaks at 0 nm and ±0.825 nm. The peaks at ±0.825 nm confirm that Ag atoms reside in the PbSe layers while peak at 0 nm implies that Ag atoms also reside in the Bi$_2$Se$_3$ layers. To determine the local concentration of Ag in Bi$_2$Se$_3$ and PbSe layers, the one-dimensional composition profile between the two lines in
Figure 5.3. (a) 1D concentration profiles in the region of interest shown in Figure 5.2b, with dashed black lines indicating a distance of 10 lattice constants. (b) SDM of atoms relative to Bi atoms (curves are offset by 0.5 units each for clarity). (c) 1D concentration profile of Ag obtained by averaging the data shown in (a) over 10 lattice constants, with error bars giving the standard deviation.
Figure 5.3a was broken up into 10 segments, with the length of each segment equal to the lattice constant. The 10 segments were averaged together to determine the local Ag concentration (Figure 5.3c). The atomic concentration of Ag is 3.5% in the Bi$_2$Se$_3$ layer and peaks at 4.5% in the PbSe layer. Approximately 54% (46%) of the Ag atoms are detected in the Bi$_2$Se$_3$ (PbSe) layers. This direct measurement of local concentration is one of the most important capabilities of APT.

5.2.3. DFT Simulation

To provide further insights into the Ag distribution, first-principles DFT calculations were used to search for energetically favorable configurations of Ag atoms. A substitution of Ag atoms on Pb and Bi sites is expected due to the similarity in the covalent radii and valencies. The nominal concentration of 0.038 can be simulated by substituting 2 Ag atoms in the 50 atoms monoclinic primitive cell of (PbSe)$_5$(Bi$_2$Se$_3$)$_3$ resulting in a 0.040 nominal concentration of Ag. The formation energies, $\Delta E_{Ag}^i$, of all configurations with the two Ag atoms restricted to Pb-sites in the PbSe layer (45 configurations), Ag atoms restricted to Bi-sites in the Bi$_2$Se$_3$ layer (66 configurations), and Ag atoms distributed equally between Pb-sites and Bi-sites (120 configurations) were computed. Schematics of configurations with Ag restricted to Pb-sites, Bi-sites and equally distributed in the Pb- and Bi-sites are shown in Figure 5.4a. $\Delta E_{Ag}^i$ of the $i$th configuration is given by:

$$\Delta E_{Ag}^i = E_{Ag}^i - E - n_{Ag} \times \mu_{Ag} + n_{Pb} \times \mu_{Pb} + n_{Bi} \times \mu_{Bi}$$
where $E_{Ag}^{i}$ is the energy of the Ag substituted $(\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3$ crystal in the $i$th configuration and $E$ is the energy of the perfect $(\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3$ crystal. The number of Ag atoms in the crystal is denoted by $n_{Ag}$ and the number of these Ag atoms on the Pb- and Bi-sites is denoted by $n_{Pb}$ and $n_{Bi}$, respectively. The phase diagram of PbSe-Bi$_2$Se$_3$ system indicates that all the constituent phases are in molten state at the 1223 K synthesis temperature of the crystal, hence the chemical potential of Ag, Pb and Bi atoms, $\mu_{Ag}$, $\mu_{Pb}$, $\mu_{Bi}$, respectively, are taken to be the energies of the isolated atoms.

Figure 5.4b shows the formation energies of the configurations plotted against the distance between the Ag atoms. The distance between the Ag atoms is computed by ignoring the self-images in the periodic images. The formation energies of configurations with Ag atoms equally distributed on the Pb- and Bi-sites are significantly lower than those with Ag atoms restricted to the Pb-sites or Bi-sites only. Figure 5.4c shows the thermodynamic probability of occurrence of the $i$th configuration computed as:

\[
P_i = \frac{\exp(-\frac{\Delta E_{Ag}^{i}}{k_BT})}{\sum_{j=1}^{231} \exp(-\frac{\Delta E_{Ag}^{j}}{k_BT})}
\]

where $k_B$ is the Boltzmann constant and the temperature $T = 300$ K. At room temperature, configurations with Ag in both layers account for more than 99.99% of the total probabilities. Even at temperatures as high as 923 K, configurations with Ag in both layers account for more than 97.57% of the total probabilities. Thus, the DFT calculations support the experimental observation that Ag dopants are distributed between both Pb and Bi layers.
Figure 5.4. (a) Schematics of example configurations of Ag dopant atoms with Ag restricted to Pb sites, Bi sites, and equally distributed between Pb and Bi sites, respectively. (b) Defect formation energies of different configurations of Ag dopants plotted against distance between pairs of Ag atoms. (c) Probabilities of occurrence of Ag–Ag configurations at 300 K.

For the analysis above, all 231 possible configurations were simulated for the primitive cell of (PbSe)$_5$(Bi$_2$Se$_3$)$_3$. We note, however, that the Ag–Ag distance in the periodic images in the y-direction is restricted to the length of the y-lattice vector, i.e. 4.26 Å; larger
supercells are preferred to avoid artificial interactions between the dopant sites, which in the “real” material do not share the translational symmetry of the lattice. \[^{154}\] However, a supercell that is \(1 \times 2 \times 1\) times larger than the primitive cell will not only have larger number of total atoms, but will also require simulating \(^{44}C_4 = 135751\) configurations (4 Ag atoms to be arranged in 44 cation sites). Since simulating all the configurations is beyond the capacity of present-day computational resources, collaborators simulated 9 representative configurations of a \(1 \times 2 \times 1\) supercell.\[^{111}\] It was found that the configurations where Ag atoms are distributed in both the layers have lower formation energies, consistent with experimental findings. However, the limitations on computing all relevant configurations preclude explanation of certain details, such as why Ag is uniformly distributed in Bi\(_2\)Se\(_3\) layers but not in PbSe layers as shown in Figure 5.3c.

A structural analysis of all the 231 configurations reveals that Ag dopants distort the lattice of the crystal and the configurations with lowest formation energies have minimal distortion in the crystal. A Bader charge analysis of the configurations shows that the low energy configurations have localized charge modulation around the Ag dopants. Large distortions in the lattice planes are expected when \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\) is doped with a high concentration of Ag. This has been experimentally observed in the form of an instability when \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\) is doped with 25\% Ag\[^{28}\]. Most likely, these distortions are mediated by significantly lower charge of the Ag atoms in comparison to that of Bi and Pb cations.
5.2.4. Correlations in the Distribution of Ag Atoms

The observation of sharp peaks in the probability distribution of Figure 5.4c raises the question of whether there are correlations in the distribution of Ag atoms within and between layers. In other words, does the presence of an Ag atom influence the probability of finding another Ag atom nearby? To investigate correlations in the Ag distribution, the Ag–Ag radial distribution function (RDF) was generated from the APT data (Figure 5.5a). A RDF gives the probability of finding an atom B surrounding atom A as a function of distance.\[36, 155\] The RDF was generated using data from the center of the reconstruction, which has been shown to improve the resolution,\[155\] and is plotted for distances greater than 0.2 nm because ion trajectory effects complicate interpretation at smaller distances.\[36\] The experimental Ag–Ag RDF shows an increased probability of finding Ag atoms $\sim7$ Å apart, implying a pairwise correlation in Ag dopant distribution. The average distance from a given Ag atom to the next closest Ag atom is less than the average distance between Ag atoms. The significance of the variations in the experimental RDF can be evaluated by comparing with the fluctuations in RDFs of 10 simulated data sets of the same size but with randomly distributed Ag atoms (“+” markers, Figure 5.5a). Clearly, the spatial correlations observed in the APT data are not present in a random alloy.

To investigate whether the spatial correlations come from Ag atoms within or between layers, 2D RDF was performed. 2D RDF was adapted from traditional 3D RDF, counting the atoms in a circular shell rather than atoms in a spherical shell as illustrated in Figure 5.5c. The 2D RDF analysis was performed using the MATLAB code in the Appendix A. Bi-layers, Pb-layers and mixed regions were isolated from the reconstruction as shown
Figure 5.5. (a) Ag–Ag radial distribution function (RDF) from APT reconstruction compared with that of Ag atoms randomly substituted for Bi and Pb atoms. Crosses show data points from individual distribution functions, and the gray line shows the average of 10 simulated distribution functions. (b) ROI and selection of Bi-layer, Pb-layer and mixed region. (c) Schematic of 2D RDF. (d) 2D RDF from Bi-layers (blue), Pb-layers (green) and mixed regions (red).

in Figure 5.5b, and a 2D RDF was performed for each isolated layer. Results of Ag–Ag 2D RDFs were generated by averaging 10 Bi-layers, 10 Pb-layers and 10 mixed regions and the results are shown in Figure 5.5d. The error bars show the uncertainty arising
from counting statistics, *i.e.* the finite number of counts within a particular distance bin. The Ag–Ag 2D RDF was not significantly larger than 1 for Ag atoms in Pb layers (blue) and Bi layers (green). However, for Ag atoms in the mixed regions (red), *i.e.* Ag atoms between Pb and Bi layers, there is a significant positive correlation at Ag–Ag distance of ~6 Å. Considering that the z coordinate was neglected, this correlation is in agreement with the positive correlation of Ag atoms with ~7 Å apart shown in Figure 5.5a. So it can be concluded that the Ag–Ag pairing occurs primarily between Ag atoms in adjacent Bi\textsubscript{2}Se\textsubscript{3} and PbSe sub-layers.

**5.2.5. Summary**

To summarize work on (PbSe)\textsubscript{5}(Bi\textsubscript{2}Se\textsubscript{3})\textsubscript{3}, the feasibility of APT analysis of 2D layered materials was demonstrated and the layered structure of (PbSe)\textsubscript{5}(Bi\textsubscript{2}Se\textsubscript{3})\textsubscript{3} was resolved in APT reconstructions, illustrating that APT can achieve subnanometer resolution for the vertical direction. Ag dopants are located in both PbSe layers and Bi\textsubscript{2}Se\textsubscript{3} layers. Additionally, spatial correlations were observed between Ag atoms, which is a 2D lateral in-plane feature. Resolving both vertical and lateral features proves that APT can achieve 3D subnanometer resolution for 2D layered material. Original experimental data can be found in Materials Database Facility, which is a database funded by CHiMaD with motivations to share data between material scientists and to accelerate materials design.
5.3. Cu Doped Bi$_2$Se$_3$

5.3.1. Sample Preparation and Experiments

Cu doped Bi$_2$Se$_3$ was synthesized by collaborators in the Kanatzidis group using a method reported previously.\cite{144} Briefly, stoichiometric mixtures of Bi (99.999%), Cu (99.99%), and Se (99.999%) for Cu$_x$Bi$_2$Se$_3$ ($x \sim 0.1$) were melted at 850 °C in a sealed ampoule. The ampoule was gradually cooled down from 850 °C to 620 °C and single crystals of Cu doped Bi$_2$Se$_3$ were grown during cooling. When growth was complete the ampoule was quenched in cold water. The single crystals were collected from the ampoule and cleaved along the basal plane.

Standard FIB lift-out and sharpening procedures were used to fabricate specimens for APT analysis. The APT analysis was performed along direction perpendicular to (001) planes using a LEAP 4000X Si with a 355 nm laser. The conditions for the experiments were 250 kHz pulse frequency, a 0.008 ions/pulse target detection rate, a background temperature of 30 K, and laser pulse energies between 2 pJ and 10 pJ. Reconstructions and analysis were performed using the commercial software package IVAS and the correlation histogram\cite{156} analysis of multiple hits was performed using MATLAB codes developed by Dr. Ivan Blum.

5.3.2. Results and Analysis

The magnetism of the synthesized sample was measured by Lei Fang in the Kanatzidis group at low temperature without applying a magnetic field (zero-field cooling). As shown in Figure 5.6a, the superconducting transition temperature is approximately 3.1 K, which is in agreement with the earlier report.\cite{144} The magnetic characterization confirms the
Figure 5.6. (a) the zero-field cooling measurement of the magnetism in low temperature. (b) A SEM image of a tip composed of Cu doped Bi$_2$Se$_3$ and the reconstruction of APT analysis of this tip. (c) A mass spectrum of APT analysis of Cu doped Bi$_2$Se$_3$.

superconductivity of the synthesized sample. Figure 5.6b shows an SEM image of the fabricated tip with a diameter less than 100 nm. The APT reconstruction of this tip is shown to the right of the SEM image, with purple, green and red dots representing Bi, Se
and Cu atoms, respectively. No layered structure can be observed in the reconstruction. The mass spectrum of the APT analysis is shown in Figure 5.6c. No unexpected impurity peaks were found in the mass spectrum. Four Cu-containing peaks, Cu$^+$, CuSe$^+$, CuSe$_2^+$ and CuSe$_2^{++}$, contribute to the total Cu concentration of $\sim$1.8%, which is close to the expected Cu concentration of 1.96% based on the nominal composition of Cu$_{0.1}$Bi$_2$Se$_3$.

![Graph showing SDMs of Bi, Se, and Cu atoms using Bi atoms as reference.](image)

Figure 5.7. SDMs of Bi, Se and Cu atoms using Bi atoms as reference.

Although it is known that superconductivity arises from intercalated Cu atoms rather than Cu atoms within the layer,\textsuperscript{144} the ratio of intercalated Cu atoms is still unknown. HRXRD cannot uniquely determine this ratio: Cu atoms within the layer can decrease the out-of-plane lattice spacing because Cu atoms are smaller than Bi atoms; intercalated
Cu atoms will definitely increase the out-of-plane lattice spacing. The success of SDM in determining the location of Ag atoms in \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\) described above motivates the application of SDM to identify intercalated Cu atoms. The SDMs of Bi, Se and Cu atoms in the vertical direction of the reconstruction using Bi atoms as the reference are shown Figure 5.7. The peak distance in the Bi–Bi profile shows the lattice spacing to be \(\sim 1\) nm in the vertical direction, which is in agreement with the reported crystal structure of Cu doped \(\text{Bi}_2\text{Se}_3\).\(^{144}\) Furthermore, the peak distance of the Bi–Se profile is also \(\sim 1\) nm and the Bi–Se profile is well aligned with the Bi–Bi profile, indicating that Se evaporation is correlated with Bi evaporation in the same \(\text{Bi}_2\text{Se}_3\) layer. Cu-containing complex ions may degrade the spatial resolution due to evaporation artifacts, such as dissociation during the flight to the detector. Thus, the SDM of Cu includes only \(\text{Cu}^+\) ions. SDM analysis of the Bi-centered Cu distribution shows clearly that there are peaks at \(\pm 1.5\) nm, \(\pm 1\) nm, \(\pm 0.5\) nm and 0 nm. The peaks at \(\pm 1\) nm and 0 nm are aligned with peaks in the Bi–Bi profile, suggesting that there are Cu atoms within the layer; while the peaks at \(\pm 1.5\) nm and \(\pm 0.5\) nm are between peaks in the Bi–Bi profile, suggesting that there are intercalated Cu atoms. These results suggest that Cu atoms exist in both sites. However, the noise level prevents the determination of the local Cu concentration, so the percentage of intercalated Cu could not be determined for doped Cu atoms. A possible solution is to simulate SDMs under different ratios of intercalation versus substitution, and then to determine the ratio by the best fit between the experimental Bi–Cu SDM and the simulation.
5.3.3. Summary

In summary, APT was successfully applied to the analysis of Cu doped Bi$_2$Se$_3$. Again, van der Waals interactions are strong enough to hold the tips together, enabling the successful analysis. Although no atomic layers were observed in the reconstruction, evidence for intercalated Cu atoms was found in SDM analysis. Unfortunately, the determination of a local Cu concentration was limited by the high noise level in the data. As discussed in Section 5.2.2., the spatial resolution of APT analysis of 2D materials is defined by statistical SDM analysis, so it can be claimed that sub-layer solution was achieved for APT analysis of Cu doped Bi$_2$Se$_3$.

5.4. The Influence of Van Der Waals Bonding on Atom Probe Tomography

The imaging of atomic planes requires a well-defined field evaporation sequence in which atoms from the edges of terraces are first to leave the surface.\cite{157, 158} Atomic planes are often observed in metals, but less often in semiconductors due to penetration of electric field.\cite{158} Although (PbSe)$_5$(Bi$_2$Se$_3$)$_3$ is semi-metallic, the weak van der Waals interactions between layers may result in the simultaneous evaporation of many atoms in the same layer, which will hinder the imaging of atomic planes within the layers. This assumption is consistent with the experimental observation that the fraction of multiple hits varies non-monotonically between 66% and 71% in steady evaporation. To our knowledge, APT has not been used previously to analyze 2D materials, with the exception of one recent report of impurity analysis in a graphene monolayer,\cite{159} where the imaging of atomic planes was not achieved. So it remains an open question whether atomic planes can be resolved in APT of 2D materials.
Cu atoms within a layer are strongly bonded with other atoms while Cu atoms between layers are weakly bonded (possibly by van der Waals interactions) with other atoms. The existence of Cu atoms in two different sites in Bi$_2$Se$_3$ provides a platform to study the influence of van der Waals interactions on the evaporation. However, it is impossible to isolate substitutional Cu atoms from all Cu atoms. Instead, the distributions of different Cu-containing ions were examined. The SDM of Cu$^+$ ions is already shown in Figure 5.7. The SDMs of CuSe and CuSe$_2$ clusters using Bi atoms as reference are shown in Figure 5.8. These two SDMs show peaks well aligned with Bi–Bi profile, indicating that
CuSe and CuSe$_2$ clusters are only from the Bi$_2$Se$_3$ layer. So Cu atoms in CuSe$_2$ and CuSe clusters are Cu atoms within the layer; Cu atoms in Cu$^+$ ions are from both sites.

Figure 5.9. (a) Correlation table of selected ions. (b) Correlation histogram for the mass spectrum shown in Figure 5.6b.

In order to understand the evaporation behavior of different ions, a multiple-hit analysis was performed using the MATLAB codes. The correlation table of selected ions was
shown in Figure 5.9a. The strongest correlation is between Cu\(^+\) and Cu\(^+\), which is a result of Cu\(_2^+\) ion decomposition. Clusters containing only Cu atoms are not stable and will decompose en-route to the detector. This is also why no Cu\(_2^+\) clusters were observed in the mass spectrum. Other strong correlations are between Bi\(^+\) and Se\(^+\), between Bi\(^+\) and Se\(_2^+\), and between Cu\(^+\) and Se\(_2^+\). These correlations also represent the decompositions of metastable clusters en-route to the detector. These decompositions manifest as trails\[156\] in the correlation histogram shown in Figure 5.9b.

The evaporation process can be pictured as following: intercalated Cu atoms are weakly bonded with Se atoms, so they tend to evaporate as Cu\(^+\) ions or Cu\(_2^+\) ions (which decomposed into Cu\(^+\) ions); Cu atoms within the layer are strongly bonded with Se atoms, so they tend to evaporate as clusters. However, some of the clusters decompose en-route to the detector. As a result, the SDMs of Cu-containing clusters resemble the Bi-Bi SDM, while the Cu\(^+\) ion SDM shows additional peaks representing intercalated Cu atoms. The phenomenon that dopants at different locations show different evaporation behaviors is unique for 2D layered materials, and has not been observed before for traditional materials.

5.5. Conclusion

In conclusion, the feasibility of APT analysis of 2D layered materials was first proved by APT analysis of Ag doped (PbSe)\(_5\)(Bi\(_2\)Se\(_3\))\(_3\) and Cu doped Bi\(_2\)Se\(_3\). The van der Waals bonds are strong enough to maintain APT tips without fracture for 60% of the time. APT analysis of Ag doped (PbSe)\(_5\)(Bi\(_2\)Se\(_3\))\(_3\) revealed that the Ag dopants were distributed in both PbSe and Bi\(_2\)Se\(_3\) layers. Corresponding DFT calculations were in agreement with the experimental results and inspired the discovery of a spatial correlation existing between
Ag atoms in adjacent PbSe and Bi$_2$Se$_3$ layers. The combination of APT and DFT can play an important role in understanding the structure-property relationship in the nm scale. APT analysis of Cu doped Bi$_2$Se$_3$ revealed that Cu atoms exist within the layer and between layers. Furthermore, SDM analysis and multiple-hit analysis revealed different evaporation behaviors for Cu atoms in these two different sites.
CHAPTER 6

APT analysis of TMDs Enabled by Novel Sample Preparations

The feasibility and spatial resolution of APT analysis of layered 2D materials was described in Chapter 5. In this chapter, APT analysis was applied to transition metal dichalcogenides (TMDs), a family of 2D materials attracting significant attention due to their unique electronic properties. However, APT specimens from bulk TMDs suffer from a high rate of fracture due to their weak interlayer interactions and relatively high evaporation fields. A novel sample preparation method was introduced for APT analysis of bulk S-doped MoTe$_2$, resulting the first successful application of APT for the analysis of TMDs. In addition, efforts were directed towards APT analysis of few-layer TMDs, but the yield was extremely low due to the difficulty of targeting TMDs in the sharpening step. ALD SnS was proposed to be deposited onto TMDs in order to enhance contrast during sharpening and it was found that ALD SnS evaporate smoothly in APT analysis.

6.1. Introduction

6.1.1. Doping and Alloying in TMDs

TMDs are a family of materials with the general formula of MX$_2$, where M is a transition metal and X is a chalcogen (S, Se or Te). TMDs consist of layers with the transition metal sandwiched by two chalcogen atoms. Atoms within the layers are strongly bonded by covalent bonding while atoms across the layers are bonded by weak interlayer van der Waals interactions. Additionally, the chalcogen atoms do not have dangling bounds, so the
layers are not especially chemically reactive. Bulk TMDs have been extensively studied in the past few decades as lubricants, but thin-layers isolated from bulk TMDs have quickly gained attention after the isolation of graphene\cite{119} by mechanical exfoliation. Thin-layers of TMDs have unique electronic properties due to the charge carrier confinement within two dimensions and are widely explored for novel electronic applications.\cite{120,160}

Despite numerous encouraging demonstrations of TMDs for novel electronic devices, the electronic properties of TMDs still benefit from engineering by doping or alloying for specific functionalities. For example, doping plays an important role in producing stable n- or p-type semiconducting behaviors. MoS$_2$, one of the most widely studied TMDs, is n-type in nature due to the existence of S vacancies; p-type MoS$_2$ can be obtained by surface charge transfer doping\cite{161} or substitutional doping of Nb for Mo\cite{123,129}. The achievement of p-type MoS$_2$ enabled a vertically stacked rectifying diode\cite{162}. Another example is bandgap engineering by alloying. Continuously tuned bandgaps have been demonstrated in MoS$_{2x}$Se$_{(1-x)}$ monolayers (x = 0∼1) grown by chemical vapor deposition\cite{163}. Alloying is also useful for the fabrication of in-plane or vertical TMD heterojunctions,\cite{164,165,166,167} which can be used to form lateral or vertical pn diodes for inverters. In short, doping and alloying enlarge the family of TMDs and enrich their applications for various electronic devices.

\subsection{6.1.2. Motivations}

In the family of TMDs, MoTe$_2$ has recently gained special attention because of its ambipolar conduction\cite{168} and semiconductor/semimetal phase transition\cite{169}. In this chapter, two MoTe$_2$ sample types are of particular interest:
(1) Bandgap engineering of MoTe$_2$ by S doping. The bandgap of semiconducting 2H MoTe$_2$ varies from 1.0 eV (bulk) to 1.1 eV (monolayer)$^{[170]}$ while the bandgap of semiconducting 2H MoS$_2$ varies from 1.29 eV (bulk) to 1.9 eV (monolayer)$^{[171]}$. Dop- ing MoTe$_2$ by S can tune the bandgap within visible and infrared spectrum, providing opportunities for new applications in opto-electronics. Besides, the superconductivity of semi-metallic 1T' MoTe$_2$ can be enhanced significantly by S doping.$^{[172]}$

(2) Phase transition of W$_x$Mo$_{1-x}$Te$_2$ induced by electrostatic gating. DFT calculations have indicated that W alloying can reduce the energy difference between the 2H semiconducting phase and the 1T' semi-metallic phase and the relative thermodynamic stability of a monolayer between these two phases can be reversed by a very small amount of charge.$^{[173],[174]}$ The synthesis of W$_x$Mo$_{1-x}$Te$_2$ with specific composition $x$ has been demonstrated by chemical vapor transport (CVT).$^{[175]}$

For both sample types, it is of interest to resolve the distribution of the doping or alloying atoms that determine the properties of TMD. In this chapter, the application of APT was pushed into the characterization of TMDs while the APT analysis results were expected to help understand the above two problems.

6.2. Sample Preparation

MoTe$_2$ and W$_x$Mo$_{1-x}$Te$_2$ were grown by Sergiy Krylyuk in the Functional Nanostructured Materials Group led by Albert Davydov in Material Measurement Laboratory of National Institute of Standards and Technology (NIST). S doped MoTe$_2$ was grown by a post-treatment process during the author’s visit to NIST in 2016.
In order to determine the distribution of doping and alloying distribution, both bulk and thin-layers need to be analyzed by APT. However, straight-forward APT sample preparation for both bulks and thin-layers failed as shown below. Thus, novel sample preparation methods were developed to enable the APT analysis of bulk TMD crystals and proposed to boost the yield of APT analysis of thin-layers.

6.2.1. Sample Growth

MoTe$_2$ and W$_x$Mo$_{1-x}$Te$_2$ crystals were grown using CVT with iodine or chlorine as the transport agent. Poly-crystalline MoTe$_2$ or W$_x$Mo$_{1-x}$Te$_2$ powders were synthesized by heating stoichiometric amounts of molybdenum (99.999%), tungsten (99.999%) and tellurium (99.9%) powders at 750 °C for 72 h in vacuum-sealed quartz ampoules. Single crystals of MoTe$_2$ (W$_x$Mo$_{1-x}$Te$_2$) were grown by mixing ~2 g of poly-crystalline MoTe$_2$ (W$_x$Mo$_{1-x}$Te$_2$) powders and a small amount of transport agents (iodine or chlorine) in a HF-etched and vacuum baked quartz ampoule with the internal diameter of 13 mm and the length of ~17 cm. After a few Ar flushes, the ampoule was sealed to a pressure of ~1 Pa. The CVT growth was carried out at 1000 °C for 7 days with poly-crystalline powders distributing along approximately a half-length of the ampoule, which is found to significantly increase both the yield and the size of MoTe$_2$ (W$_x$Mo$_{1-x}$Te$_2$) crystals. MoTe$_2$ crystals can be controlled to retain the 2H or 1T’ phase by slowly cooling the ampoule or quenching the ampoule in ice-water, respectively. W$_x$Mo$_{1-x}$Te$_2$ (x ~ 0.05) used in this chapter was 2H phase obtained by slowly cooling the ampoule.

S doping was performed by sealing S powders and 2H or 1T’ MoTe2 single crystals in a HF-etched and vacuum baked quartz ampoule. S powders and MoTe$_2$ single crystals were
kept in different ends of the sealed ampoule. S powders were kept at 120 °C to maintain sufficient S vapor pressure and MoTe₂ single crystals were kept at 950 °C to enable the incorporation of S into the MoTe₂ lattice. The ampoule was kept in the furnace for 3 days and then slowly cooled down to room temperature.

6.2.2. APT Samples of Bulk TMDs

Preliminary experiments to test the feasibility of APT analysis of bulk TMDs were performed using specimens directly prepared by the FIB milling methods in normal orientation and in cross-section. However, unlike tips of (PbSe)₅(Bi₂Se₃)₃ and Cu doped Bi₂Se₃, the fabricated tips of bulk TMDs do not withstand field evaporation. For example, tips of MoS₂ fractured in APT analysis when analyzed in a normal orientation (Figure 6.1a-b). When analyzed in cross-section, tips of MoS₂ split (Figure 6.1c-d). Although atoms on the split tip can be further field evaporated and a mass spectrum can be retrieved, no reliable reconstruction can be obtained because the irregular shape of the split tip. The observed splitting phenomena might suggest a way to field-exfoliate layered 2D materials, but it is not desired in APT analysis. Other TMDs (MoTe₂, WTe₂) behaved similarly to MoS₂ in APT analysis.

From DFT calculations[111], the van der Waals interactions are similar between MoS₂, (PbSe)₅(Bi₂Se₃)₃ and Cu doped Bi₂Se₃. However, MoS₂ is more difficult to field evaporate considering the evaporation field of Mo (65 V/nm) is much higher than Pb (20 V/nm) or Bi (18 V/nm).[73] This suggests that TMDs with low evaporation field (possibly for M = Ti, Zr, V, Cr, etc. in the MX₂ formula) are better candidates for APT using the straight-forward FIB milling sample preparation method.
For TMDs with a high evaporation field (for $M = Mo, W$ in the MX$_2$ formula), new sample preparation methods were developed to increase the mechanical strength of the fabricated tips. In this chapter, a conformal coating was used for this purpose. For the APT analysis of bulk S doped MoTe$_2$, the Si micropost array with the sharpened tips was put in a magnetron sputter system. 5 nm Ag was sputtered onto the sharpened tips with the Si micropost array consistently rotating during the deposition process. The confocal
coating increased the mechanical strength of the tips and enabled the successful APT analysis.

6.2.3. APT Samples of Few-Layer TMDs

The atomic-scale characterization of few-layer and monolayer TMDs is important for understanding of their structure-property relationships at the 2D limit. STEM-HAADF is very useful to determine the doping or alloying distribution in monolayer TMDs,[130, 176] but its application for few-layer TMDs is limited because its projecting nature. APT, with its capability to provide 3D elemental mapping, is a powerful tool for analyzing few-layer TMDs if a successful sample preparation method can be developed. Baik et al.[159] reported a sample preparation method for APT analysis of CVD grown monolayer graphene. The monolayer graphene was sandwiched between Ni and Cr layers and analyzed in cross section.

The sample preparation method for monolayer graphene was adopted for initial experiments on few-layer \( W_xM_{1-x}Te_2 \). However, few-layer TMDs could not be resolved in specimen SEM imaging, and targeting few-layer \( W_xM_{1-x}Te_2 \) in the sharpening step relies on the contrast between Ag layers and the Si substrate. Figure 6.2 shows the efforts to fabricate APT specimens using few-layer \( W_xM_{1-x}Te_2 \). Bulk \( W_xM_{1-x}Te_2 \) was mechanically exfoliated by the scotch tape method to few-layers on a Si substrate coated with 200 nm sputtered Ag. Another 200 nm Ag was sputtered on the top, covering \( W_xM_{1-x}Te_2 \) few-layers to form the sandwich structure. Cross section FIB milling method was performed to fabricate tips for APT analysis. Unfortunately, the contrast between Ag layers and the Si substrate was lost in the high magnification sharpening step (Figure 6.2d), making
it difficult to target the $W_xMo_{1-x}Te_2$ few-layers. Therefore the yield of this method was extremely low. (8 tips were fabricated and none of were targeted on the $W_xMo_{1-x}Te_2$ few-layers.)

![Image of SEM images](image)

**Figure 6.2.** (a) A SEM image of few-layer $W_xMo_{1-x}Te_2$ sandwiched between two sputtered Ag layer. (b-d) SEM images of the sharpening process. As the sharpening process continues, the contrast of Ag layers and Si substrate was lost.

An improvement on the sandwich method is to increase the thickness of the middle layer containing $W_xMo_{1-x}Te_2$ few-layers. It is proposed to coat the $W_xMo_{1-x}Te_2$ few-layers with atomic layer deposition (ALD) grown sulfide, which should have a good evaporation behavior when sandwiched between two Ag layers. As the ALD growth of SnS was developed in the Lauhon group in 2016, and the feasibility of ALD SnS as the coating material was tested. For this purpose, 10 nm ALD SnS was grown on a Si substrate
coated with 200 nm sputtered Ag. Similarly, another 200 nm Ag was sputtered on the top of the ALD SnS. FIB milling was used to fabricate cross-sectional APT specimens.

6.3. Results and Discussion

6.3.1. Bulk TMDs: S doped MoTe$_2$

Figure 6.3. (a) A schematic of Ag coated cross-sectional tips. (b) A SEM image of a tip after Ag deposition.

S doped MoTe$_2$ was analyzed by post-treatment of the CVT grown MoTe$_2$ as described in the sample preparation section. A schematic of the final tip is shown in Figure 6.3a. Tips were fabricated by the FIB milling method in cross section and then 5 nm Ag was sputtered onto the tips with the Si microposts array rotating in a sputter system to enable a conformal coating. Ag was chosen due to its good electrical and thermal conductivity. Figure 6.3b shows a SEM image of one tip after the Ag deposition. As shown in the SEM image, Ag was uniformly deposited onto the surface of the tip and the surface of the final tip was smooth with no obvious clusters formed. These features indicate that the deposition of Ag did not change the shape of the fabricated tip, making sure that the model assumed in the reconstruction is suitable for the final tip.
Figure 6.4. (a) Mass spectrum of S doped MoTe$_2$. (b) The distributions of Te, Mo and S in a reconstruction. (c) Radial distribution function (RDF) analysis of S–S distribution with the ROI indicated by the blue sphere in (b).
Moreover, the uniform deposition of Ag increased the strength of the tip, preventing the tips from splitting and thus enabling a successful analysis of the S doped MoTe$_2$ by APT. A tip coated with Ag was analyzed by APT under the conditions of 50 K background temperature, 0.5% detection rate and 50 pJ pulse laser energy. The mass spectrum of the analyzed tip is shown in Figure 6.4a. All the peaks in the mass spectrum are labelled accordingly. No Ag peaks were found because the thin Ag layer (5 nm) on the tip surface is out of the field of view. S dopants were observed and labelled in the mass spectrum. The concentration of S was measured to be 0.16%. No other impurities peaks were identified.

A reconstruction was performed using IVAS software package. The distributions of Te, Mo and S are shown in Figure 6.4b. From the reconstruction, no layered structure was found (layer was vertical in the cross section analysis). The distributions of Te and Mo were not uniform, with the densities of Te and Mo varying in space. The spatial variations of densities of Te and Mo are on the order of tens of nanometers, presumably caused by microfractures during the field evaporation. The distribution of S was relatively uniform in the reconstruction. A line feature in the S distribution is believed to be an artifact caused by a fracture of the tip. RDF analysis was performed to capture the short-range features in the distribution of S atoms. RDF analysis was targeted on the volume within the blue sphere with a radius of 15 nm, avoiding the artifact of the line feature. The RDF of S–S distribution is shown in Figure 6.4b. Although the variation of the RDF is large, there is no obvious peak or valley, indicating that the distribution of S is uniform on length scales of less than 3 nm.
6.3.2. Few-layer TMDs: SnS as the Coating Layer

As discussed in the sample preparation section, a coating layer can increase the yield of APT analysis of few-layer TMDs. The coating layer should have similar evaporation field as the Ag sandwich layers and should provide a good contrast in the sharpening process. To test feasibly of ALD SnS as the coating layer, 10 nm of SnS was grown by ALD at 120 °C and sandwiched by two Ag layers (Figure 6.5a). ALD SnS grown at 120 °C is amorphous and should be able to conformally coat TMDs few-layers. Figure 6.5b-c show SEM images of a tip in cross section before and after sharpening. From the SEM images, the ALD SnS layer can be clearly observed due to its different contrast with Ag layers. So ALD SnS layer can provide guidance during sharpening and the final tip can be easily centered on the ALD SnS layer (Figure 6.5c).

![Figure 6.5](image)

Figure 6.5. (a) A schematic of the test sample with 10 nm SnS layer sandwiched by two sputtered Ag layers. (b) A SEM image of a cross-section tip before sharpening. (c) The tip in (b) after sharpening.

The fabricated tips were analyzed in APT under conditions of 50 K background temperature, 1% detection rate and 20 pJ pulse laser energy. The mass spectrum of a successfully analyzed tip is shown in Figure 6.6a with peaks associated with S, Sn and Ag labelled. There are several unidentified peaks, which might come from organic residues.
left in the ALD SnS film. The background in the mass spectrum is high, which is also a suggestion of the existence of organic residues (organic residues can decompose in a quite wide range in the mass spectrum, leading to an overall increase in the mass spectrum background).

The distributions of S and Sn are presented in Figure 6.6b with pink dots representing S atoms and green dots representing Sn dots. Both S and Sn are in the center of the reconstructed tip; the pink and green dots on the sides are background counts. The reconstruction showing both S and Sn atoms confirms that S and Sn atoms were from the same regions, in other words, the ALD SnS layer. The interface between SnS and Ag was not smooth, which is attributed to the rough surface of the sputtered Ag but also suggests the conformal coating of ALD SnS. A 1D concentration profile was taken from a cylinder ROI in the reconstruction (Figure 6.6c). The variations of the concentrations of S, Sn and Ag also prove that the SnS layer was resolved by APT. These results proved the feasibility of ALD SnS as a coating layer for APT analysis of few-layer TMDs. SnS can provide a good contrast with Ag in SEM imaging, which enables targeting of the few-layer TMDs during sharpening.

These results proved the feasibility of ALD SnS as a coating layer for APT analysis of few-layer TMDs. SnS can provide a good contrast with Ag in SEM imaging, which enables targeting of the few-layer TMDs during sharpening.

6.4. Summary and Outlook

In summary, conformal coating of Ag on sharpened APT tips was used to increase their mechanical strength, enabling the first APT analysis of bulk TMDs with analysis of
Figure 6.6. (a) The mass spectrum of a tip with ALD SnS sandwich by two Ag layers. (b) S, Sn and S+Sn distributions in a reconstruction. (c) A 1D concentration profile in the ROI indicated in the S+Sn distribution.

S-doped MoTe$_2$. S was found to be doped into MoTe$_2$ with a concentration of 0.16%, and RDF analysis showed that S atoms were uniformly distributed. The feasibility of APT analysis of few-layer TMDs was also demonstrated. ALD SnS was used to coat few-layer
TMDs to increase the thickness and improve contrast with Ag layers during FIB sharpening. ALD SnS evaporated smoothly in a sandwich structured with two sputtered Ag layers. The APT analysis of TMDs, enabled by the sample preparation methods developed in this chapter, will make a broader impact when correlated with the measurement of electrical properties to generate knowledge of structure-property relationships for TMDs in the 2D limit.
CHAPTER 7

APT Analysis of Colloidal Quantum Dots in Various Encapsulation Materials

Colloidal core-shell quantum dots (QDs) were analyzed by APT to investigate the role of interface abruptness in suppressing the blinking of photoluminescence. Different sample preparation methods were evaluated and tested. After considering criteria for encapsulation materials, available atomic layer deposition (ALD) coatings were tested as encapsulation layers. ZnO enabled the identification of individual CdS/CdSe QDs and gives an upper-bound on the width of the core-shell interface of 1.2 nm, although with significant overlapping in the mass spectrum that degrades resolution. The difference in evaporation field between the QDs and encapsulants is smallest for ALD SnS among materials tested.

7.1. Introduction

7.1.1. Colloidal Quantum Dots

Quantum dots (QDs) are semiconductor nanoparticles whose radius is below the Bohr exciton radius in the bulk counterpart. The three-dimensional confinement of the exciton can modify the continuous energy bands of the bulk semiconductor to produce discrete electronic states in QDs, leading to strongly size-dependent electronic and optical properties. Colloidal QDs are QDs synthesized and dispersed in solution, and are typically
stabilized by a layer of organic surfactants.\textsuperscript{178} Since high-quality monodisperse colloidal QDs were first developed by Murray, Norris and Bawendi in 1993,\textsuperscript{179} there has been a continuous and growing interest in colloidal QDs as high quality emitters. Nowadays, various colloidal QDs, from individual nanocrystals to self-assembled QD arrays, have been explored in electronic and optoelectronic devices, including displays, field-effect transistors, thin film photovoltaics, light-emitting diodes, lasers and photodetectors.\textsuperscript{180, 181}

\subsection*{7.1.2. QD Blinking}

Colloidal QDs exhibit photoluminescence (PL) intermittency in emission, whereby a single colloidal quantum dot PL randomly switches between ON and OFF states under constant excitation,\textsuperscript{182} exhibiting fluctuations in PL intensity. These fluctuations (also known as blinking) limit the applications of QDs as single biological labels\textsuperscript{183} or as single-photon sources\textsuperscript{184}. Currently, the most widely accepted explanation for QD blinking is that QDs can be ionized under illumination (on $\rightarrow$ off) and subsequently neutralized (off $\rightarrow$ on).\textsuperscript{185} When a QD is neutral, a photon excites an electron-hole pair (exciton), which then recombines to give rise to PL; this process is known as radiative recombination. A QD can become ionized when a carrier in the exciton gets ejected photophysically or thermally and captured by a surface state, leaving the other carrier in the QD as an extra carrier. The extra carrier can trigger a faster, non-radiative Auger recombination process,\textsuperscript{186} strongly suppressing or even quenching PL. At some later time, the ejected carrier will return to the QD, restoring charge neutrality. However, how this reneutralization process occurs remains a mystery.
7.1.3. Towards Non-Blinking QD

A common approach to suppress or even eliminate QD blinking is to suppress QD ionization by eliminating trapping sites at the surfaces of QDs. Hohng et al. showed that passivation of QDs surfaces with thiol moieties suppresses QDs blinking significantly. Hohng et al. showed that passivation of QDs surfaces with thiol moieties suppresses QDs blinking significantly. \[187\] Another approach is to grow a thick shell on the QD core: two groups independently reported the suppression of blinking in CdS/CdSe QDs by the growth of thick CdS shells in 2008. Indeed, whether the ionization process occurs photophysically or thermally, the potential barrier provided by a thick shell reduces the probability that a carrier will escape to the surface.\[185\]

Another path to eliminate blinking is to eliminate the fundamental source of blinking, Auger recombination. If the non-radiative Auger recombination rate is slower than that of the radiative recombination for a charged exciton (trion), the ionized quantum dot will not switch to the off state. Based on calculations, Cragg and Efros pointed out that it is possible to increase the Auger recombination time in core-shell QDs, by controlling the alloy composition profile of the core-shell interface. Cragg and Efros pointed out that it is possible to increase the Auger recombination time in core-shell QDs, by controlling the alloy composition profile of the core-shell interface. \[190\] Later, gradient alloyed core-shell interfaces were achieved in CdS/CdSe core-shell QDs experimentally, suppressing Auger recombination completely. Later, gradient alloyed core-shell interfaces were achieved in CdS/CdSe core-shell QDs experimentally, suppressing Auger recombination completely. \[191, 192\]

7.1.4. Motivation

Colloidal CdS/CdSe quantum dots with thick CdS shells, known as giant QDs (GQDs) \[188\], were synthesized by collaborators in Los Alamos National Laboratory (LANL), demonstrating significantly suppressed blinking behavior. The thick shells, which reduce the chance for the excited carriers to be trapped by surface states, play an important...
but not necessarily exclusive role in the suppression of blinking. For example, alloyed core-shell interfaces can be formed during the growth of the thick shell, which may also significantly contribute to the suppression of blinking.

In order to develop a comprehensive understanding of mechanisms of blinking suppression, a measurement of core-shell interface abruptness in GQDs was pursued in this thesis work. Considering the curved and buried nature of the core-shell interfaces, such a measurement is only possible, in principle, with the 3D mapping capability and ppm level chemical sensitivity of atom probe tomography.

7.2. Sample Preparation for APT Analysis of Colloidal QDs

Due to their shape and small size (sphere with diameter <100 nm), colloidal QDs cannot be directly analyzed by APT via a standard FIB milling method. Indeed, colloidal QDs need to be attached to or buried in materials with a larger total volume to enable FIB sample preparation for APT analysis. In this chapter, sample preparation methods for APT analysis of nanoparticles are first reviewed for reference because nanoparticles have a similar shape and size as colloidal QDs. Then, by considering the features of colloidal QDs and the questions to answer, such as the core-shell interface abruptness, the encapsulation method was determined for preparing APT samples of colloidal QDs.

7.2.1. Sample Preparation Methods for APT Analysis of Nanoparticles

Nanoparticles share similar sizes and shapes with QDs, and they have been successfully analyzed by APT. A review of the sample preparation methods for APT analysis of
nanoparticles can provide valuable insight into the sample preparation for APT analysis of colloidal QDs. The common sample preparation methods for nanoparticles include:

1. **Electrophoresis.** A pre-sharpened tip was dipped into a solution of nanoparticles and biased oppositely to the surface charge of the nanoparticles. Then, nanoparticles were attracted to the surface of the pre-sharpened tip via an electrophoresis process. A low density of nanoparticles on the tip can be achieved by controlling the electrophoresis time, and the tip with nanoparticles can be used as a final tip for APT analysis. This method was mainly used for the study of catalytic nanoparticles.\[^{28, 193, 194, 195}\] Unfortunately, due to the rough surface of the final tip, most of the reported results failed to resolve individual nanoparticles.\[^{28, 194, 195}\]

2. **Encapsulation.** In this method, nanoparticles were deposited onto a flat substrate and encapsulated by a matrix or capping materials. Then a standard FIB liftout and sharpening procedures was used to fabricate tips for APT analysis. The encapsulation method has achieved the highest data quality so far. For example, Heck, et al. performed APT analysis of nanodiamonds by sandwiching them between two layers of Pt grown by atomic layer deposition (ALD) and the spatial resolution was good enough to resolve individual nanodiamonds. Similarly, Larson, et al. evaluated Pt nanoparticles encapsulated by a matrix of ALD Zn(Al)O.\[^{196}\] Individual Pt nanoparticles were observed in the reconstruction although the shapes of the Pt nanoparticles are irregular due to evaporation artifacts.

3. **Aggregates.** Nanoparticles tend to form aggregates when they are in the powder form. If nanoparticles in an aggregate can be “glued” together, a FIB liftout and sharpening procedure can be applied to fabricate APT tips. Felfer et al.\[^{197}\] reported a “gluing”
strategy by sharpening an aggregate using a low-energy Ga\(^+\) ion beam while simultaneously imaging the aggregate using a high electron beam voltage, with a constant stream of Pt precursor gas, \((\text{C}_5\text{H}_4)\text{CH}_3\text{Pt} (\text{CH}_3)_3\). The precursor can be decomposed to deposit Pt when it was hit by an electron or ion beam. Thus, Pt can be deposited into voids between nanoparticles during milling to hold the nanoparticles together. Because the high electron beam voltage can give rise to a high penetration depth for electrons, it produces the secondary electrons in the entire volume of the aggregate. Using this method, a core-shell structure of CoCuMn catalyst nanoparticles was successfully revealed by APT analysis.\(^{198}\) However, there are significant carbon impurities in the electron induced Pt deposition, leading to a deterioration in the spatial quality of the data.\(^{197}\)

7.2.2. Encapsulation Method for Colloidal QDs

The three sample preparation methods introduced above have achieved success for different nanoparticles. However, no colloidal QDs have been reported to be analyzed by APT. Thus, careful considerations need to be taken when choosing the appropriate method for colloidal QDs. The existence of organic ligands on the surface of QDs can significantly reduce the interaction between QDs and a metal surface, presenting challenges to the electrophoresis method. The goal of this study was to resolve the abruptness of the CdS/CdSe interface in GQDs, so the aggregates method was deemed insufficient to achieve the required high resolution. Instead, the encapsulation method was pursued.

The material to encapsulate GQDs should meet the following requirements: (1) the material should form a conformal coating, which is typically achieved by atomic layer deposition (ALD); (2) the material should have a good conductivity, which means that it
should be a semiconductor or a metal; (3) the material should have similar evaporation field as the GQDs; (4) the overlapping in the mass spectrum peaks of interest between the material and GQDs should be minimized.

7.2.3. Experiments for Sample Preparations

GQDs were synthesized via a successive ion layer adsorption and reaction (SILAR) approach in LANL. Briefly, the CdSe cores were prepared by the hot injection method and dispersed in hexane for shell growth. S precursors and Cd precursors were added alternatively, with the quantity calculated according to the volume increment of each monolayer shell. The final size of GQDs is \( \sim 15\,\text{nm} \).

A monolayer of the synthesized GQDs was deposited onto a Si substrate covered with 200 nm sputtered ZnO. The GQD monolayer was then exposed to oxygen plasma generated by Harrick Plasma PDC-32G under 200 mTorr for 10s. Different ALD materials were used to encapsulate GQDs. Finally, a protective layer was deposited on top of the ALD encapsulation material to form a “sandwich” structure. Figure 7.1a-b show top-view and cross-sectional SEM images of the sandwich structure, respectively. Standard FIB liftout and sharpening process was applied to the “sandwich” structure to fabricate tips for APT analysis. For ALD ZnO as the encapsulation material, cross-section liftout was performed (Figure 7.1c); for ALD Al\(_2\)O\(_3\) and SnS, normal liftout was performed (Figure 7.1d).
7.3. Results and Discussion

At the beginning of this study, only ALD oxides (ZnO, Al₂O₃, HfO₂, ZrO₂) were available at Northwestern. To achieve good conductivity, ZnO was first chosen as the encapsulation material. However, there is significant overlapping in mass spectrum between ZnO and GQDs. To avoid overlapping, Al₂O₃ was then tested as the encapsulation material, and was found to have a much larger evaporation field than GQDs. Later, ALD sulfides were developed in the Lauhon group at Northwestern and ALD SnS was used. It is worth noting that all GQDs monolayers received from LANL were deposited on sputtered on ZnO.
7.3.1. ALD ZnO as the Encapsulation Material

Figure 7.2. (a) A schematic of the fabrication of the sandwich structure and where the liftout was performed. A reconstruction showing the distribution of (b) Cd\(^{++}\), (c) CdSe\(^+\) and (d) CdS\(_2\)\(^+\). The sizes of the boxes in (b-d) are all 45 nm \(\times\) 45 nm \(\times\) 70 nm.

ZnO was first chosen as the encapsulation material because it is the most conductive of the ALD-available materials (ZnO, Al\(_2\)O\(_3\), HfO\(_2\), ZrO\(_2\)) at the beginning of this study. One problem with ZnO is that there exists significant overlap between ZnO related peaks and CdS/CdSe related peaks in the mass spectrum. For example, Zn\(^{++}\) and S\(^+\) are both at 32 Da and ZnO\(^+\) and Se\(^+\) are both at 80 Da. The initial hypothesis was that the
evaporation fields between ZnO and CdS/CdSe QDs are close enough to avoid spatial overlap, so the mass spectra would not overlap in spatially isolated the QDs regions.

Monolayer QDs were deposited onto sputtered ZnO and encapsulated with ALD ZnO as shown in the schematic in Figure 7.2a. 400 nm ZnO was then sputtered on top of the ALD ZnO to provide more material for the cross-section liftout. Cross-section liftout was chosen because the chance for a tip to survive in APT analysis is higher in this geometry than that in a normal direction. Four tips were fabricated and analyzed in APT. For one of the four tips, the QDs layer was successfully kept in the middle of the tip (Figure 7.1c). A reconstruction of this tip was shown in Figure 7.1b-d, illustrating the distribution of Cd\(^{++}\), CdSe\(^{+}\), and CdS\(^{2+}\), respectively. It can be seen that Cd\(^{++}\) ions are distributed in a strip region, where is the QDs layer. No QDs can be defined from the Cd\(^{+}\) ions distribution. Because S\(^{+}\) and Se\(^{+}\) overlaps with ZnO related peaks, CdSe\(^{+}\) and CdS\(^{2+}\) were used to identify the cores and shells of QDs. The distribution of CdS\(^{2+}\) is also diffuse, making it difficult to define QDs. However, the distribution of CdSe\(^{+}\) shows localized features, and three QDs can be defined from the CdSe\(^{+}\) distribution. For the other three tips, no QDs were observed in the reconstruction.

In order to investigate the spatial overlapping between QDs and ZnO, a region with the ion concentration of Cd\(^{+}\) greater than 20% was isolated, as shown in the left panel of Figure 7.3a. The right panel of Figure 7.3a is the distribution of CdSe\(^{+}\) in the isolated region, with isosurfaces of the CdSe\(^{+}\) concentration of 5%. A mass spectrum of the isolated region was shown in red in Figure 7.3b. Compared with the mass spectrum of ZnO from one of the three tips where QDs were not observed (green in Figure 7.3b), Cd\(^{++}\), CdSe\(^{+}\) and CdS\(^{2+}\) peaks are distinct, thus they can be used to identify the QDs layer, and even
Figure 7.3. (a) Isosurfaces of 20% ion concentration of Cd\(^{\pm}\) was used to isolate the QDs layer, and the distribution of CdSe\(^{\pm}\) in the isolated regions were shown on the right. (b) Mass spectra of the isolated region and pure ZnO. (c) Proximity histogram using the isosurface circled in (a) as reference.
individual QDs. However, in the isolated regions, the mass spectrum is still dominated by ZnO related peaks. This suggests that there is significant ion mixing in the isolated regions, which leads to the diffuse distribution of Cd\(^{++}\) and CdS\(_2\)^{+} peaks. Experimental results suggest that the evaporation field of ZnO is higher than that of CdS/CdSe QDs, so the spatial resolution of the collect data is not good enough to achieve atomic resolution for the CdS/CdSe core-shell interface. A proxigram analysis was performed using the isosurface circled in the right panel of Figure 7.3a, and the results are shown in Figure 7.3c. The width of CdS/CdSe core-shell interface was estimated to be \(\sim 1.2\) nm, which can be viewed as an upper-bound limit of the interface width.

### 7.3.2. ALD Al\(_2\)O\(_3\) as the Encapsulation Material

![Figure 7.4](image)

Figure 7.4. (a) A schematic of the fabrication of the sandwich structure and where the liftout was performed. (b) A reconstruction showing the distribution of Zn\(^{+}\) (gray), Cd\(^{+}\) (red) and Al\(^{+}\) (blue). (c) Cd\(^{+}\) isosurfaces of 26\%, showing two flattened QDs.

In order to solve the problem of mass spectrum and spatial overlap, ALD Al\(_2\)O\(_3\) was used as an encapsulation material to replace ALD ZnO. A schematic for the preparation of APT tips is shown in Figure 7.4a. FIB liftout was performed in normal direction because of
the difficulty of targeting the QD layer and the different milling rate between ALD Al₂O₃ and sputtered ZnO in the cross section configuration. A reconstruction is shown in Figure 7.4b, where the sandwich structure of ZnO/Al₂O₃:QDs/ZnO was resolved. However, the QDs layer is almost flat in the reconstruction. A closer look at the shape of QDs was performed using isosurfaces. As shown in Figure 7.4b, two QDs were isolated by the isosurfaces of Cd⁺ ionic concentration of 26%. These two QDs showed flattened features, with the Z dimension of only ~1nm.

![Figure 7.4](image)

Figure 7.4. (a) The tip before APT analysis, with a small region of ZnO on top. (b) The surface of the tip is Al₂O₃, and the voltage increases. (c) When the QD is exposed, it will be rapidly evaporated due to the high field. (d) The surrounding Al₂O₃ is barely changed during the evaporation of QDs.

The flattened QD profile is due to the fact that the evaporation field of Al₂O₃ is much greater than that of CdS/CdSe QDs. In the experiment, CdS/CdSe QDs were found to evaporate rapidly once they are exposed, which is indicative of the difference in evaporation fields. Figure 7.5 shows schematics to explain why QDs appear flat. A tip with only a small amount of ZnO on top (Figure 7.5a) was analyzed by APT. The ZnO on
top is evaporated, leaving the whole tip surface consisting of Al$_2$O$_3$ (Figure 7.5b). As the evaporation field of Al$_2$O$_3$ is relatively high, the voltage will increase to keep a constant evaporation rate. When the QDs are exposed (Figure 7.5c), the voltage is still at a high value, which leads to a rapid evaporation of the QDs with low evaporation field. Since the evaporation of QDs is so fast, the shape of the surrounding Al$_2$O$_3$ is barely changed, with an irregular surface left behind (Figure 7.5d). The remaining Al$_2$O$_3$ evaporates, but the evaporation is unstable due to the irregular shape. This explains why most Al$_2$O$_3$ was found beneath QDs and why voids were found in Al$_2$O$_3$ regions in Figure 7.4b.

![Figure 7.6](image)

Figure 7.6. (a) The mass spectrum of the whole reconstruction. (b) The mass spectrum from the regions where flat QDs were located. (c) The top view of Cd$^+$ and its 2D contour projection along z axis. (d) The top view of Se$^+$ (78 Da) and its 2D contour projection along z axis.

The advantage of Al$_2$O$_3$ is that it does not overlap with CdS/CdSe QDs in the mass spectrum. Figure 7.6a shows the mass spectrum of the whole reconstruction, where ZnO related peaks still dominate. The background level is higher compared with the tip using
entirely ALD ZnO, which can be attributed to the different thermal conductivity between Al₂O₃ and ZnO. CdSe⁺ and CdS₂⁺ peaks were no longer available for the identification of cores and shells. It would have been preferable to deposit colloidal QDs on a substrate without mass spectrum overlap, but the Si substrate coated with ZnO was the only sample provided. A close look at the mass spectrum from the regions where flattened QDs were detected is shown in Figure 7.6b. Se⁺ peaks should occur between 76 – 82 Da; despite the proximity of Zn₂O²⁺ and ZnO⁺ peaks, there is an obvious peak at 78 Da attributable to Se⁺. This peak can be used to locate the position of the cores of QDs. A top view of Cd⁺, Se⁺ (78 Da) and their contour plot of its density are shown in Figure 7.6c-d. Two identified QDs are marked with blue circles from the contour plot of Cd⁺. The cores of the two QDs can be seen in the contour plot of Se⁺ ions (78 Da) in Figure 7.6d. The width of core-shell interface in this case was estimated to be no narrower than in the analysis shown in Section 7.3.1.

7.3.3. ALD SnS as the Encapsulation Material

ALD sulfides are generally more conductive than ALD oxides and the evaporation field of ALD sulfides should be more similar to that of CdS/CdSe QDs. Hence, ALD sulfide coating was pursued when it became available. Figure 7.7a shows a schematic of the sandwich structure with ALD SnS as the encapsulation material. A layer of 200 nm Ag was sputtered on top of ALD SnS because Ag has a similar evaporation field with ALD SnS and the interface between Ag and ALD SnS is stable, as suggested by results in Chapter 6. In the APT analysis process, the QDs layer evaporated smoothly, confirming that the evaporation field between ALD SnS and CdS/CdSe QDs are similar. Figure 7.7b-d show
the distribution of Cd\textsuperscript{++}, S\textsuperscript{+} and Se\textsuperscript{+} in a reconstruction, respectively. A quantum-dot-like aggregation can be observed in the distribution of Cd\textsuperscript{++} and S\textsuperscript{+}. Interestingly, the aggregation appears hollow. This might be due to the overlap of ZnO related peaks with Se\textsuperscript{+}, or due to the high background burying the Se\textsuperscript{+} peak. However, because the size of the aggregation varies depending on the reconstruction parameters, it is difficult to claim identification of a quantum dot. Another possibility is that the aggregation is several QDs and the empty region is ALD SnS.

The overall spatial resolution was not improved using ALD SnS as the encapsulation material in this experiment, even though the evaporation field of ALD SnS is similar to that of CdS/CdSe QDs. One shortcoming of this sample is that QDs were deposited
on sputtered ZnO, which dominated the mass spectrum (Figure 7.8). The laser energy needed for the evaporation of Ag and ALD SnS is lower than that of ZnO, leading to a higher voltage for evaporation compared with experiments in Section 7.3.1. The high voltage leads to the uncorrelated evaporation of the bottom ZnO (evaporation between pulses), resulting a high background in the mass spectrum shown in Figure 7.8a. The high background buried many important peaks, such as CdS$^+$, CdSe$^+$ and Se$^+$. That is why CdS$^+$, CdSe$^+$ and Se$^+$ are distributed in the ZnO regions in Figure 7.7b-d. The bottom ZnO leads to QDs were difficult to be defined in this case.
7.4. Conclusion and Outlook

This chapter summarizes a series of efforts to analyze colloidal CdSe/CdS QDs with APT. Different encapsulation materials were explored for the fabrication of APT samples. And the advantages and disadvantages were discussed for each encapsulation material. The most successful results were obtained using ZnO as the encapsulation material despite the significant overlap in the mass spectrum. The width of core-shell interface in colloidal CdS/CdSe QDs was measured to be \( \sim 1.2 \) nm.

Looking forward, ALD sulfides are promising encapsulation materials. An improvement in the sample preparation would be to deposite QDs on a ALD SnS substrate. It would also be worthwhile to measure such a sample in both cross-section and in normal directions. Another point is that larger QDs could potentially help in locating the QD monolayer in the cross-sectional FIB liftout.
CHAPTER 8  

Summary and Outlook

The understanding of structure-property relationship at the atomic scale is crucial for engineering low-dimensional electronic materials. As the continued feature size reduction and the introduction of new structures and materials present complexity and challenges in revealing atomic-scale features, the development of metrology tools becomes more important and urgent. Although the widely deployed tools such as TEM and SIMS are extending their limits in order to measure atomic-scale features, the introduction and application of new tools and methods is highly desirable. APT, as a characterization technique with 3D sub-nm resolution and ppm level sensitivity, has proved uniquely useful in analyzing nanowires and thin film electronic materials and is promising for other low-dimensional materials. In this thesis, the capability of APT for characterizing low-dimensional electronic materials is further explored for thin films and expanded to van der Waals layers and heterostructures, and colloidal quantum dots.

InGaN QWs are an essential component of solid-state lighting. The further improvement of the efficiency of InGaN QWs will significantly reduce energy consumption and CO$_2$ emissions. The efficiency improvement resulting from H$_2$ dosing during GaN growth was not well understood, inhibiting further engineering and optimization. APT, correlated with HRXRD and micro-PL, revealed that the increased efficiency can arise from the improved confinement of electrons and holes. Keeping carriers away from dislocations also plays a role. The 3D measurement of indium composition by APT is important
for understanding the InGaN at the atomic level. Looking forward, the findings can be applied to semi-polar and non-polar InGaN QWs for efficient green and yellow light emitting. Another concern raised in this research is the accuracy of the bowing factor values. Most reported bowing factor values are based on indium composition from macroscopic HRXRD measurements; however, it is shown in this thesis that HRXRD can underestimate indium composition, particularly when gaps exist. The value of bowing factor could be determined accurately by precise determinations of indium composition and the bandgap of InGaN at the same region in nm scale, for example, by correlating APT and cathodoluminescence.

The memristor is a promising foundation for next generation computing beyond CMOS technology, including non-volatile memory and neuromorphic computing. Despite its successful demonstration in labs, the memristor has not been industrialized. It is not yet clear what are the best materials and structures for memristors to be commercialized. One challenge is to precisely control the conductive path in order to maintain stable switching states. In this thesis, APT helps to determine the Ag dopant distribution in a Ta$_2$O$_5$-based low energy memristor device and informs the understanding of the switching mechanism. APT can make further impact in this area by analyzing the conductive path in memristor devices with different electronic materials. The 3D composition distribution mapping provided by APT can help the understating of the formation and dissociation of the conductive path, in order to precisely control it.

The discovery of graphene opened the world of 2D materials. Although various 2D materials are isolated and synthesized, it remains a challenge to control doping and alloying in 2D materials. The world of 2D materials is wide open to be explored by APT
analysis. The proof-of-principle application of APT to 2D materials was demonstrated for the first time by analyzing Ag doping in $(\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3$. APT analysis successfully resolved the layered structure with sub-nm resolution. Ag dopants were found to be located in both PbSe and Bi$_2$Se$_3$ layers with a paring correlation, in agreement with DFT results. Then efforts were directed to APT analysis of TMDs. Sample preparation methods were developed for APT analysis of both bulk and few-layers of TMDs to overcome challenges due to weak van der Waals interactions. Future directions are to correlate structure characterization by APT with electronic properties of TMDs. The two materials mentioned in this thesis, S doped MoTe$_2$ and W$_x$Mo$_{1-x}$Te$_2$, can be analyzed in this way in order to understand the effects of doping and alloying in TMDs. Additionally, the van der Waals heterostructures, such as $(\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_{3m}$, can provide a top-down method for stacking 2D layers if they can be exfoliated in a controlled manner. Similar materials, such as Franckeite, are being intensively studied recently.\[199, 200\]

Colloidal QDs have been studied for more than 25 years and have been widely applied in electronic and optoelectronic devices. However, QD blinking limits QDs applications as biological labels and degrades the performance of QDs in devices. GQDs with thick shells show reduced QD blinking, but the role played by the thick shells in GQDs is not clear. APT was used to investigate the role of interface abruptness in suppressing the blinking of photoluminescence. An encapsulation method was used to prepare APT specimens. Among the available ALD materials at the beginning of the study, ALD ZnO encapsulation enabled the identification of individual CdS/CdSe QDs and gives an upper-bound on the width of the core-shell interface of 1.2 nm. The difference in evaporation field between the QDs and encapsulants is smallest for ALD SnS among materials tested. The encapsulation
method was shown to be successful, although the choice of ZnO encapsulation is not ideal. ALD sulfides, such as SnS, should be further studied as encapsulants in order to achieve atomic-resolution of the core-shell interface.

After exploring the application of APT to a range of low-dimensional materials, we are better positioned to predict what samples can be analyzed. The samples that can be successfully analyzed are most often conductive, with relatively high mechanical strength. If a material does not share these two features, additional sample preparation is needed to introduce the missing features. One example is the conformal coating around TMDs tips to increase mechanical strength. Ideally, one could predict whether a material can be analyzed before the experiment, which may possible as we better understand the field evaporation process both experimentally and theoretically. The ultimate limit of APT analysis is another open question. In terms of spatial resolution, the limit of APT is different for different materials, e.g. atomic layers can be routinely resolved for metals but not be resolved for van der Waals heterostructures in this thesis. As the material system becomes more complex, such as in complex electronic devices with multiple interfaces system, more artifacts tend to arise, which require further effort to understand and correct. In terms of identifying clusters, the detection efficiency of the LEAP 4000 system is currently around 50%, which prevents the identification of cluster of a few atoms. The ability to detect small clusters is better for LEAP 5000 system with the detection efficiency of 80%.

In summary, APT is a powerful and useful tool in analyzing low dimensional electronic materials. Besides the academic research, APT is gradually being accepted by industry. For example, Intel, the semiconductor industry leader, has one atom probe system to
help fabricate better micro-processors. As the APT user community becomes larger and larger, and the APT technique evolves, APT will have even greater impact in materials characterization as an irreplaceable metrology tool.
References


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APPENDIX A

MATLAB Code for 2D Radial Distribution Function (2D RDF)

A brute-force search, which systematically searches all possible candidates and checks whether each candidate is a solution, is used in this thesis for 2D RDF because the dataset is small for slices of 2D layers. The code is as followings:

```matlab
% The code below is for calculating 2D RDF for 10 Bi layers. Pos file for Bi layers were selected from reconstruction and named as Bi1.pos, Bi2.pos, ..., Bi10.pos
% all data is stored in a dataset D
% D(i)= {x,y,z,m}

%input
step = 0.1; % step size (nm)
r = 2; % radial distance (nm)
R = 30; % the size of ROI (nm) R>r
a=106.5; b=108.5; a1=108.5; b1=109.5; %a, b define centers ion in mass spectrum, this code only works for single type of ion
c= 106.5; d=108.5; c1=108.5; d1=109.5; % c,d define surrounding ions in mass spectrum

bin = floor(r./step); % bin size
layers =10;
RDF.Sum = zeros(bin,1);
for mm=1:layers
    str = sprintf('Bi%d.pos',mm);
    fileID = fopen(str,'r');
    [D,T] = fread(fileID,[4,Inf],'float','b');
    fclose(fileID);
    D=D.';

    % selecting ROI to avoid data on the side
    len = length(D); % the size of dataset
    ADD=zeros(len,1);
    C = [D ADD];
    for ii=1:len
        if C(ii,1).^2+C(ii,2).^2 <= (R-r).^2 & C(ii,5)=1;
        end
```

% ```
end

% count ion of interest
   \( t = 0 \); % number of center ion in effective region
for \( i = 1 : n \)
   if (\( C(i, 4) > a \) \& \( C(i, 4) < b \) \| \( C(i, 4) > a1 \) \& \( C(i, 4) < b1 \) \& \( C(i, 5) == 1 \))
      \( t = t + 1 \);
   end
end

\( n = \text{zeros}(t, \text{bin}); \) % number of surrounding ions around center ion \( i \), at distance \( r \)
\( nt = \text{zeros}(t, \text{bin}); \) % number of total ions around center ion \( i \), at distance \( r \)

% calculate the concentration surrounding every center ion at distance \( r \)
\( \text{s_conc} = \text{zeros}(t, \text{bin}); \) % concentration surrounding center ion at distance \( r \)
\( \text{nn} = 0; \) % numbering of center ion
for \( i = 1 : n \)
   if \( C(i, 5) == 1 \)
      if (\( C(i, 4) > a \) \& \( C(i, 4) < b \) \| \( C(i, 4) > a1 \) \& \( C(i, 4) < b1 \)) % identify center ion
         \( \text{nn} = \text{nn} + 1; \) % counting center ion
         for \( kk = 1 : \text{bin} \)
            for \( j = 1 : n \)
               if not (\( j == i \))
                  distance_square = \( (C(i, 1) - C(j, 1))^2 + (C(i, 2) - C(j, 2))^2 \); % neglecting z dimensions
                  %2D-distance
                  if distance_square \( \leq (k \cdot \text{step})^2 \)
                     \( \text{nt}(\text{nn}, \text{kk}) = \text{nt}(\text{nn}, \text{kk}) + 1; \)
                     if (\( C(j, 4) > c \) \& \( C(j, 4) < d \) \| \( C(j, 4) > c1 \) \& \( C(j, 4) < d1 \))
                        \( \text{n}(\text{nn}, \text{kk}) = \text{n}(\text{nn}, \text{kk}) + 1; \)
                     end
                  end
               end
            end
         end
      end
   end
\( \text{s_conc}(\text{nn}, \text{kk}) = \frac{\text{n}(\text{nn}, \text{kk})}{\text{nt}(\text{nn}, \text{kk})}; \)
if \( \text{nt}(\text{nn}, \text{kk}) == 0 \)
   \( \text{s_conc}(\text{nn}, \text{kk}) = 0; \)
end
end
end

% calculating RDF
RDF = zeros(bin, 1); % RDF
RDF_conc = zeros(bin, 1); % concentration of center ions
cc = 0;
total = 0;
for ii = 1:len
if (C(ii, 4) > a & C(ii, 4) < b | C(ii, 4) > a1 & C(ii, 4) < b1)
    cc = cc + 1;
end
end
Overall_Conc = cc / len;

for kk = 1:bin
    for nn = 1:t
        RDF_conc(kk, 1) = RDF_conc(kk, 1) + s_conc(nn, kk);
    end
    RDF(kk, 1) = RDF_conc(kk, 1) / t / Overall_Conc;
    RDF_Sum(kk, 1) = RDF_Sum(kk, 1) + RDF(kk, 1);
end

% plot the data
x = 0.0:step:r−step;
figure;
plot(x, RDF_Sum/layers);
APPENDIX B

Spatial Resolution of APT Analysis of 2D Layered Materials

The spatial resolution of APT analysis of 2D layered materials can be evaluated by comparing experimental and simulated spatial distribution maps (SDMs). This appendix uses the \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\) data from Chapter 5 as an example to illustrate evaluation of the spatial resolution.

The experimental Bi–Bi is shown in Figure B.1a, where the background is 0.5 and the half maximum full width (HMFW) is 0.5 nm. We used simulations of ion positions to determine what level of randomness in ion position can result a similar SDM. Figure B.1b shows a SDM calculated in IVAS for the perfect crystal (zero uncertainty). We note that every atomic plane is disguisable. We then added a random displacement to the coordinates of every atom, where the displacement follows a Gaussian distribution of specified width. When the added uncertainty is 0.25 nm, the generated SDM (Figure B.1c) resembles the experimental SDM, which implies that the spatial resolution in the Z direction is approximately 0.25 nm. On this basis, we can claim sub-nm spatial resolution of individual layers.

The code below generates the pos file with Ag atoms randomly substituting Pb or Bi atoms in \((\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_3\) (Ag concentration \(\sim 4\%\)). The code can also be used to simulate Ag–Ag RDFs.
Figure B.1. (a) Experimental Bi–Bi SDM. (b) Simulated Bi–Bi SDM with no uncertainty in the position of any atom. (c) Simulated Bi–Bi SDM with a Gaussian uncertainty of 0.25 nm added to the position of each atom.

\begin{verbatim}
a=1.598; b=0.419; c=2.147; beta=97.48/180*pi; % monoclinic crystal structure, unit: nm
A=[a,0,0]; B=[0,b,0]; C=[-c*sin(beta-pi/2),0,c*cos(beta-pi/2)]; % unit cell vectors
N=15; M=60; L=10; % unit cell expansion
 t=50; % atoms in a unit cell
SS=cell(N,M,L,t,2); % simulated structure; N,M,L for unit cell labels
% initialization Bi 1–12 Pb 13–22 Se 23–50
for ii=1:N
  for jj=1:M
    for kk=1:L
      for ww=1:12

\end{verbatim}
SS\{ii , jj , kk, ww, 2\} = 209;
end
for ww=13:22
SS\{ii , jj , kk, ww, 2\} = 208;
end
for ww=23:50
SS\{ii , jj , kk, ww, 2\} = 80;
end
end
end
end
end

% The X, Y, Z coordinates of atoms in (PbSe)5(Bi2Se3)3 is stored in 'Pure-X.txt', 'Pure-Y.txt', 'Pure-Z.txt'.

formatSpec = '%f';
fileID = fopen('Pure-X.txt', 'r');
X = fscanf(fileID, formatSpec);
fclose(fileID);

fileID = fopen('Pure-Y.txt', 'r');
Y = fscanf(fileID, formatSpec);
fclose(fileID);

fileID = fopen('Pure-Z.txt', 'r');
Z = fscanf(fileID, formatSpec);
fclose(fileID);

% initialization
for ww=1:50
SS\{1, 1, 1, ww, 1\} = X(ww)*A + Y(ww)*B + Z(ww)*C;
end

% volume construction
for ii = 1:N
  for jj = 1:M
    for kk = 1:L
      for ww = 1:t
        SS\{ii , jj , kk, ww, 1\} = SS\{1, 1, 1, ww, 1\} + (ii - 1)*A + (jj - 1)*B + (kk - 1)*C;
        SS\{ii , jj , kk, ww, 2\} = SS\{1, 1, 1, ww, 2\};
      end
    end
  end
end

% Ag randomization
for ii = 1:N
  for jj = 1:M
    for kk = 1:L
for ww=1:22
    if rand() <= (1/11)
        SS{ii,jj, kk, ww, 2} = 109;
    end
end
end
end
end
end
end

% errors with Gaussian distribution of selected FWHM = 2.35 * Sigma. FWHM = 0.25; % for the case where the position of every atom is accurately determined, FWHM = 0.
sigma = FWHM / 2.35;

% file output
fileID = fopen(’FWHM03–DR05–random–Ag–0.2M–10.pos’, ’w’);
% expansion
for ii = 1:N
    for jj = 1:M
        for kk = 1:L
            for ww = 1:t
                if (rand() - 0.5) >= 0 % detection rate is 0.5
                    x = SS{ii, jj, kk, ww, 1}{1} + normrnd(0, sigma);
                    y = SS{ii, jj, kk, ww, 1}{2} + normrnd(0, sigma);
                    z = SS{ii, jj, kk, ww, 1}{3} + normrnd(0, sigma);
                    mass = SS{ii, jj, kk, ww, 2}{1};

                    fwrite(fileID, x, ’float32’, ’b’);
                    fwrite(fileID, y, ’float32’, ’b’);
                    fwrite(fileID, z, ’float32’, ’b’);
                    fwrite(fileID, mass, ’float32’, ’b’);
                end
            end
        end
    end
end
fclose(fileID);