# Effect of Dimensionality and Pd-Doping on the Microstructure of $SnO_2$

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**Abstract**

The need for high-performance, solid-state $H_2$ gas sensors is one research effort aimed at enabling the future hydrogen economy. Improving the gas-sensing properties of semiconducting oxide materials such as tin oxide, zinc oxide, etc., necessitates the control microstructure and composition. This study compares the effect of dimensionality with the effect of Pd-doping on the grain size of tin (IV) oxide. If tin oxide is fabricated as a line instead of a thin film, it is expected that the average grain size can be significantly reduced, independent of Pd-doping effects. Thin-film and line samples of Pd-doped and undoped tin oxide were fabricated using a sol-gel method and soft-electron beam lithography. X-ray photoelectron spectroscopy (XPS) was used to quantify the composition of the deposited tin oxide, and transmission electron microscopy (TEM) was used to image the tin oxide grain morphology. The effect of dimensionality was found to reduce the average tin oxide grain size by about 40% compared with a thin film. On the other hand, 3% doping of Pd reduced the grain size by as much as 30%, even in a thin film. Comparison of doped and undoped lines did not show a difference in the grain size, possibly because the effect is not cumulative. This research supports the potential of hydrogen gas sensors made from Pd-doped tin oxide lines, which could have enhanced gas-sensing performance due to their reduced grain size.

## Introduction

Ongoing research on hydrogen as a fuel material is important because hydrogen is renewable and abundant, and it can generate electricity in a fuel cell cleanly and efficiently.[1] However, hydrogen storage is still a major challenge, in part because hydrogen can be an explosive gas at room temperature when there is more than 4% of hydrogen in the air. Safely storing hydrogen will require high-performance gas-sensing materials that not only detect hydrogen, but also operate near room temperature and with optimal sensitivity, selectivity, and response/relaxation time. Current research efforts on solid-state gas sensors attempt to improve the gas-sensing performance of semiconducting oxides such as tin oxide by tuning their microstructure and composition.[2–5]

This study compares the effect of dimensionality with the effect of Pd-doping on the microstructure of tin oxide. If the average grain size of tin oxide can be significantly lowered by simply constructing 1-D line structures instead of 2-D thin films, this presents a potential way to improve the performance of tin oxide gas sensors. In order to isolate the effect of dimensionality, both tin oxide thin films and lines were fabricated using the sol-gel method. Transmission electron microscopy (TEM) was performed to find the average grain size in each sample. Pd-doped tin oxide thin films and lines were also created and characterized to complete the grain size analysis.

## Background

A clear trend in the literature shows that gas-sensing properties improve as grain size decreases, potentially because of the increased surface area-to-volume ratio.[6,7] One strategy to lower grain size is to dope the ceramic with another material that might slow grain growth. Pd-doping is attractive because, in addition to its catalytic affinity for hydrogen, it already has been shown to decrease the grain size of tin oxide thin films.[8]

Another approach for decreasing the tin oxide grain size and potentially improving the $H_2$ sensing properties is decreasing the dimensionality of the system.[5,9] The literature suggests that during 2-D nucleation of crystalline material from an amorphous matrix, the crystallization rate is reduced not only by impingement with adjacent grains, but also by additional contact with a free surface.[9] Nucleation in a 1-D system might show an even more reduced crystallization rate. Another reason why dimensionality might affect the grain size is because of the volume shrinkage commonly observed in ceramics fabricated using the sol-gel method.[9] Volume shrinkage creates strain energy, which acts as a barrier to nucleation. Strain energy tends to be relieved at free surfaces, and since the free-surface area-to-volume ratio increases for lower-dimensional structures, one would expect lower-dimensional structures to have a higher nucleation density (#nuclei/vol).[9] If a structure has a decreased crystallization rate and an increased nucleation density, the result is smaller average grain size. The goal of this research is to experimentally demonstrate the effect of dimensionality on the grain size of tin oxide and compare this with the effect that Pd-doping has on the grain size.

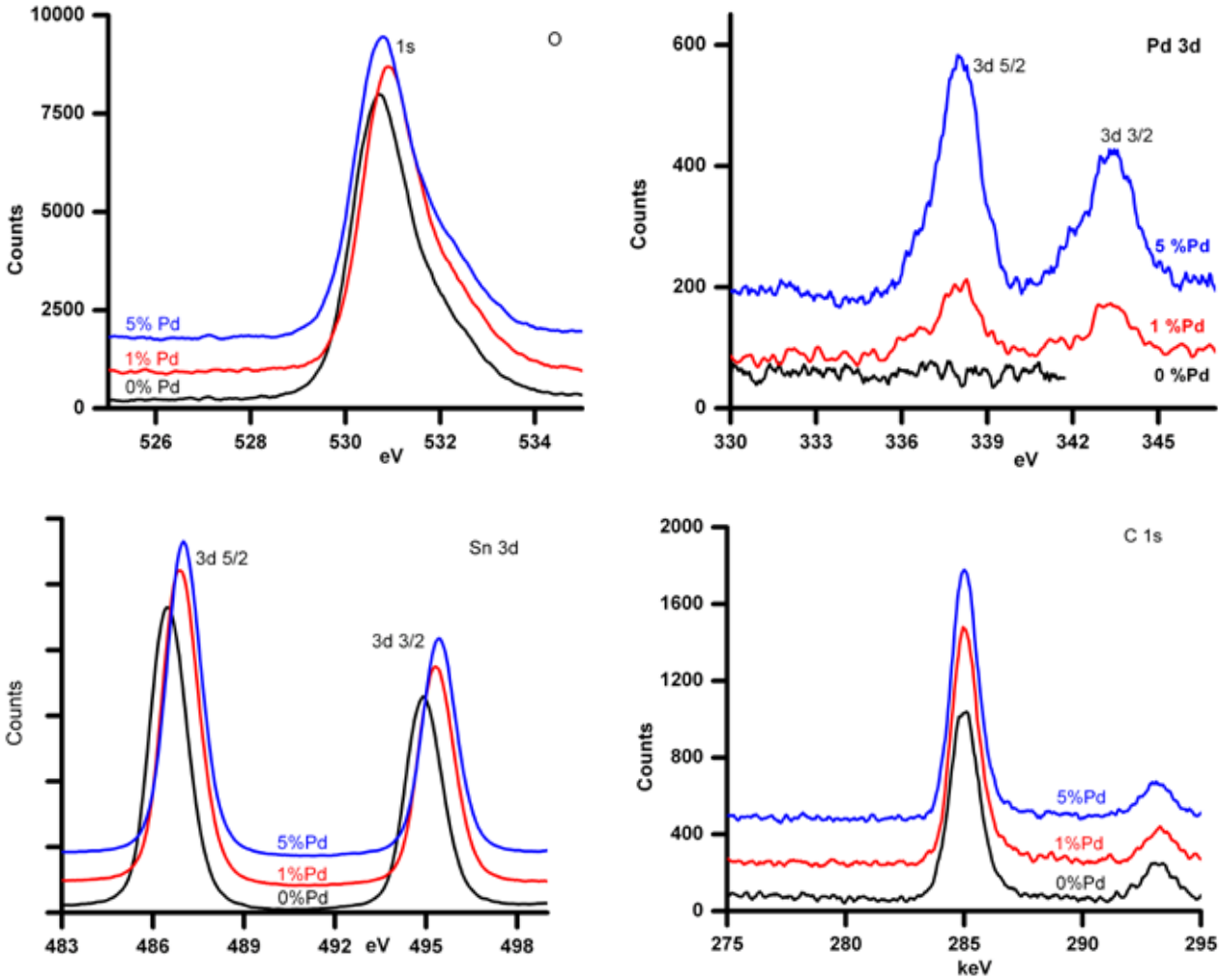



**Figure 1. XPS plots used to verify the O/Sn and Pd/Sn ratios of the thin-film tin oxide samples. Peaks corresponding to oxygen (top left), Pd (top right), Sn (bottom left), and C (bottom right) are displayed, and each plot shows one curve for each Pd concentration.**

## Approach

*Sol-Gel Ceramic Precursor*
The sol-gel method is a "wet chemistry" approach to making ceramic materials. A sol is a colloidal mixture of solid particles dissolved in a solvent. After a stable sol is prepared with the desired composition, this ceramic precursor solution can be easily deposited onto a surface and spin-coated to make a thin film. The film is then heated over a hot plate (150° C) to drive the formation of a gel. Subsequent high-temperature annealing (700° C) removes organic residues and makes solid ceramic film denser.

*Sol Preparation*
The sol used to make undoped tin oxide begins by combining Sn(IV) acetate powder, 2-methoxy ethanol as a solvent, and ethanol amine as a chelating agent. Doping can be achieved by simply including additional metallo-organic powders, such as Pd(II) acetate for palladium doping. While this mixture is heated at 60° C, the metalloorganic compounds first hydrolyze and then condense together to form small solid particles containing tin-oxygen-carbon network.

*Advantages of Sol-Gel*
Unlike other high-energy methods of thin-film deposition, the sol-gel method is a low-cost technique. Sol-gel offers great compositional control because there is a wide variety of metal oxide sols that can be created, and each can be doped and concentrated as desired. In addition, the porosity often associated with materials fabricated from sol-gel is actually advantageous for gas-sensing, since it increases the surface area-to-volume ratio.

*Soft-electron beam lithography (soft-eBL)*
The soft-*e*BL technique combines the advantages of sol-gel with the advantages of electron beam lithography to create ceramic nanostructures - in this case, tin oxide lines. *e*BL works by first exposing a pattern area in a PMMA (poly[methyl methacrylate]) resist and then selectively dissolving away the exposed polymer area. The desired sol is deposited in the PMMA "trenches" and transitions to a gel while in contact with the substrate. Dissolving away the PMMA and the excess sol leaves only the ceramic gel that previously settled in the "trenches." Essentially, the soft-*e*BL method creates a temporary high-spatial-resolution mold that can position the sol-gel in order to create ceramic nanostructures. This technique overcomes the traditional limitations of synthesizing ceramic nanostructures by a top-down method (cutting, melting or etching).

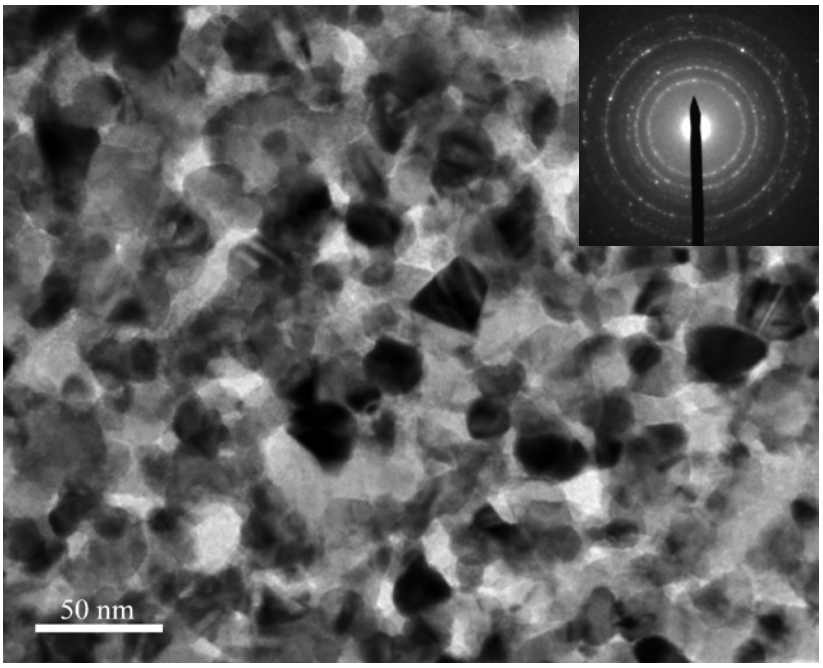
*TEM sample preparation*
TEM is a characterization tool capable of imaging nanoscale microstructural features and analyzing chemical composition. However, TEM requires samples thin enough to be electron transparent. One traditional way of preparing a TEM sample of a thin film on substrate is to "back-grind" the substrate and ultimately create a hole whose edges are electron transparent. This is accomplished by polishing, dimple-grinding, and ion-milling. As the sample becomes thinner, it also becomes more fragile and harder to manipulate. A different approach to making TEM samples, used in this project for making soft-*e*BL tin oxide lines, involves commercially available "membrane" substrates, whose centers are factory-etched to be electron transparent.[10] Such samples require only one day of preparation, compared with the several days needed for other TEM sample preparation techniques.

## Results

*X-ray Photoelectron Spectroscopy (XPS)*
XPS was performed on Pd-doped and undoped $SnO_2$ thin films in order to verify the chemical composition of the deposited materials. To calibrate the XPS spectra and account for charging effects, the value of the carbon peak was taken as a reference, and the spectra were shifted to position each carbon peak at the same energy value. The ratio of Pd-to-Sn and O-to-Sn for each sample was calculated by taking the ratio of the products of each element's peak area and sensitivity factor. Each sample showed an O-to-Sn ratio of 1.4:1, indicating nonstochiometric composition ($SnO_x$ $x \neq 2$). Also, the Pd-to-Sn ratios were found to be 0 %, 0.9%, and 2.8%. The XPS spectra are shown in Figure 1.

*TEM Grain Size Analysis*
Bright-field (BF) TEM images of the tin oxide microstructure were obtained for thin film and line samples, each with and without 3% Pd-doping (Figures 2–5). Diffraction contrast makes the tin oxide grains appear in various shades of gray. There is also significant porosity, which appears white in these samples. The grain-size distribution of each sample was calculated by measuring the grain diameters. Indexed diffraction patterns (Figure 6) confirm the tetragonal crystal structure of tin oxide.

The TEM images of tin oxide lines show two long, dark regions running parallel to the line direction. Atomic force microscopy (Figure 7) suggests that these features are present due to uneven thickness across



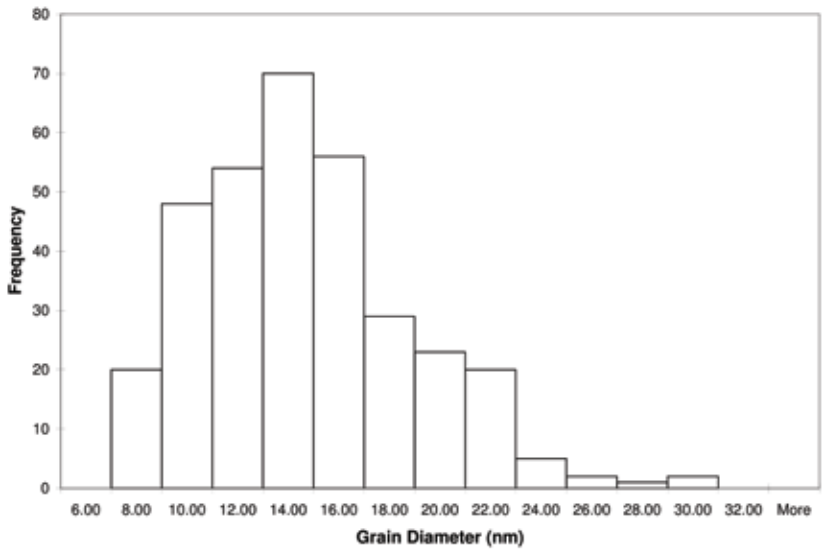




**Figure 2. BF TEM image of 0% Pd-$SnO_2$ thin film (80 nm thick) and histogram (~300 grains measured). Tin oxide grains (dark regions) as well as some porosity (white regions) are clearly visible.**

the line's width. Uneven thickness may be a result of the capillary effect at the edges of the PMMA trenches.

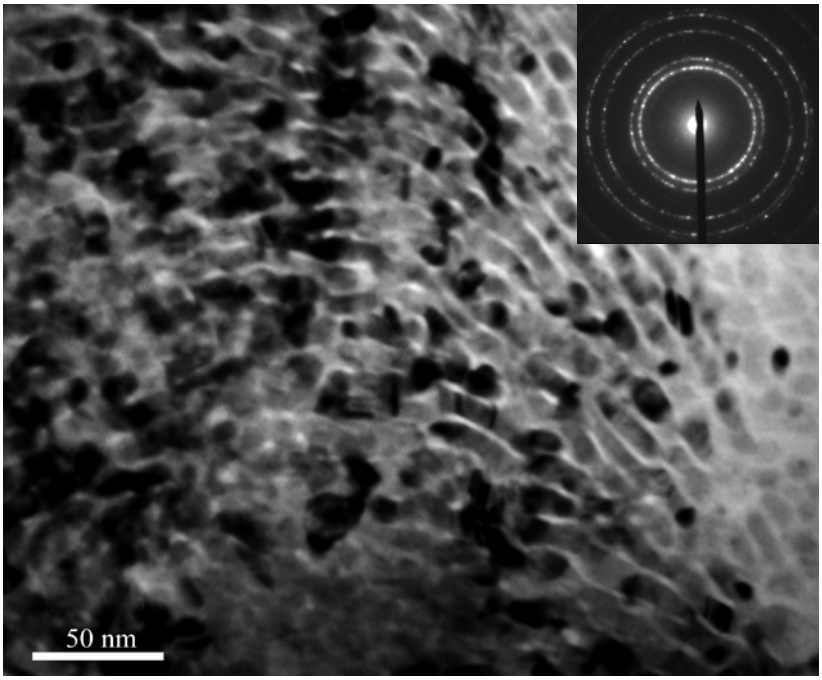
*Effects of Pd-Doping and Dimensionality*
For thin-film samples (Figures 2 and 3), the Pd-doping reduced the average grain size from 14 ± 4 nm to 8 ± 3 nm, but for line samples (Figures 4 and 5), the Pd-doping had negligible effect on the average grain size (5.8 nm 6 ± 1 nm for doped compared to 6 ± 2 nm for undoped).

A significant difference in average grain size (over 40%) was recorded between the 0% Pd-$SnO_2$ thin film and the 0% Pd-$SnO_2$ line samples (Figures 2 and 4). A similar effect was observed for the 3% Pd-doped $SnO_2$ thin films and the 3% Pd-doped lines (Figures 3 and 5), but to a reduced degree.

**Discussion**

The aim of this project was to see the effect of dimensionality on the grain size of tin oxide in comparison with the effect of Pd-doping. It was expected that tin oxide lines would have a smaller grain size than tin oxide thin films, independent of Pd-doping. The result summary (Figure 8) confirms this hypothesis and thus suggests the potential of $SnO_2$ lines for high- performance gas-sensing.

One way to qualitatively analyze the effect of dimensionality and the effect of Pd-doping on the grain size of tin oxide is to consider the thermodynamics and kinetics of grain growth. Upon nucleation of a crystalline material within an amorphous matrix, atoms continuously diffuse onto the growing nuclei. In a 3-D bulk sample, only impingement between growing crystalline nuclei interrupts grain growth by reducing the flux of matrix atoms onto the nuclei. In 2-D and



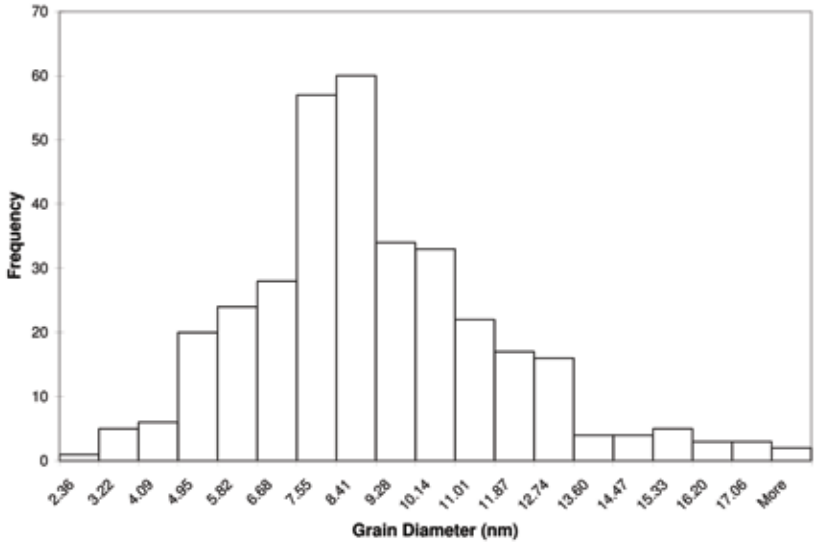




**Figure 3. BF TEM image of 5% Pd-$SnO_2$ thin film (80 nm thick) and histogram (~300 grains measured). Tin oxide grains (dark regions) as well as some porosity (white regions) are clearly visible.**

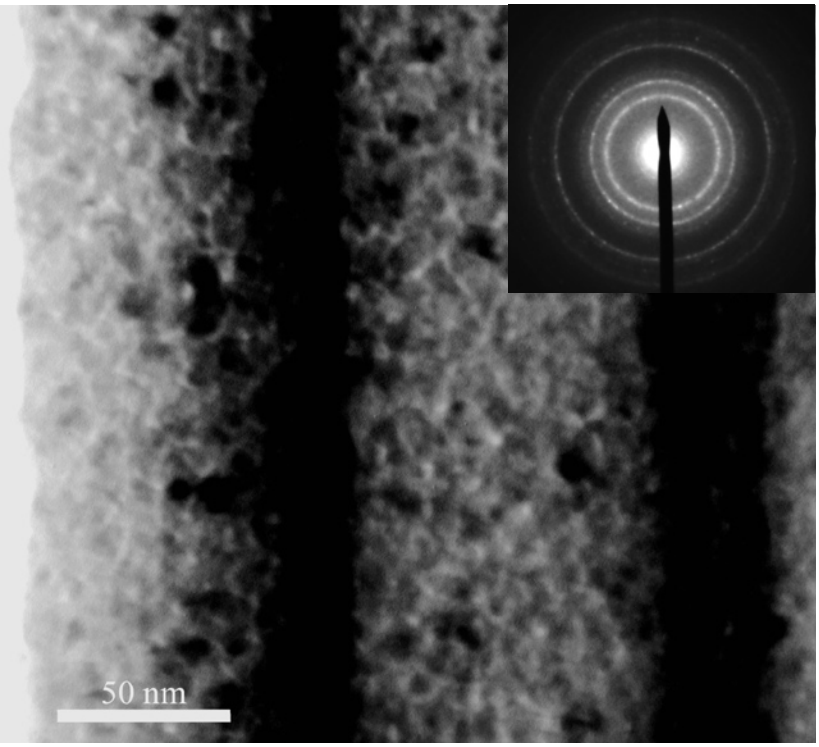
1-D samples, there is a higher free-surface area-to-volume ratio that further decreases the flux of matrix atoms to the nuclei. A decreased growth rate decreases the average grain size. Pd-doping can also reduce the grain size, possibly due to Pd segregation to the grain boundaries. At the grain boundaries, the Pd may be creating an energy barrier to grain growth, but further analysis (EDS elemental mapping) is necessary to support this mechanism.

### Conclusion

A bottom-up, sol-gel approach was used to fabricate Pd-doped and undoped tin oxide thin films. Tin oxide lines were also created using the soft-*e*BL method. This experimental approach allowed each sample's microstructure to be compared, since the same heating and sol-gel processing conditions were used. Of interest was the effect of dimensionality and Pd-doping on the tin oxide microstructure.

Based on the grain size distributions determined from bright field TEM images, there was a significant change in the average grain size in tin oxide lines compared with tin oxide thin films. A similar but smaller effect on the average grain size was observed between doped and undoped tin oxide thin films. The doping effect on the grain size was not as large as the dimensionality effect. In fact, no significant Pd-doping effect on grain size was observed for the line samples.

Having confirmed the microstructural effect of dimensionality, the next research question is to see how much of an effect the smaller grain size has on the gas-sensing properties of tin oxide. Such experiments are being carried out.



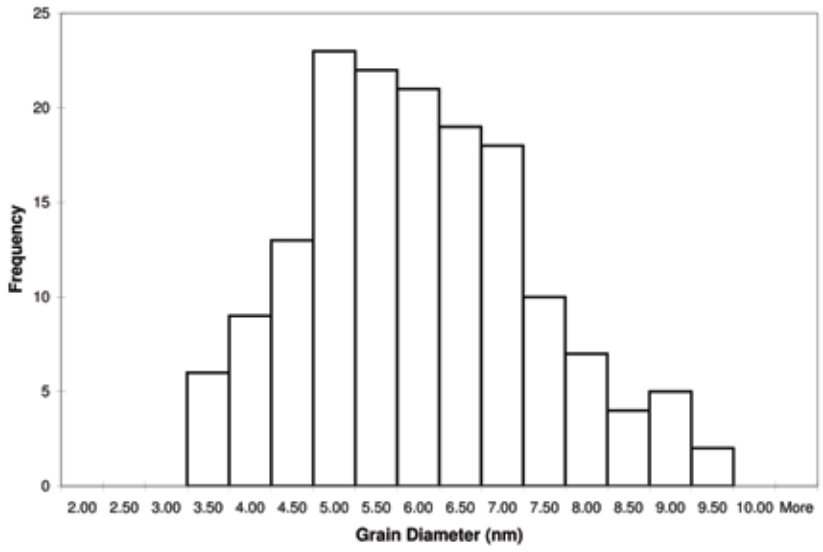
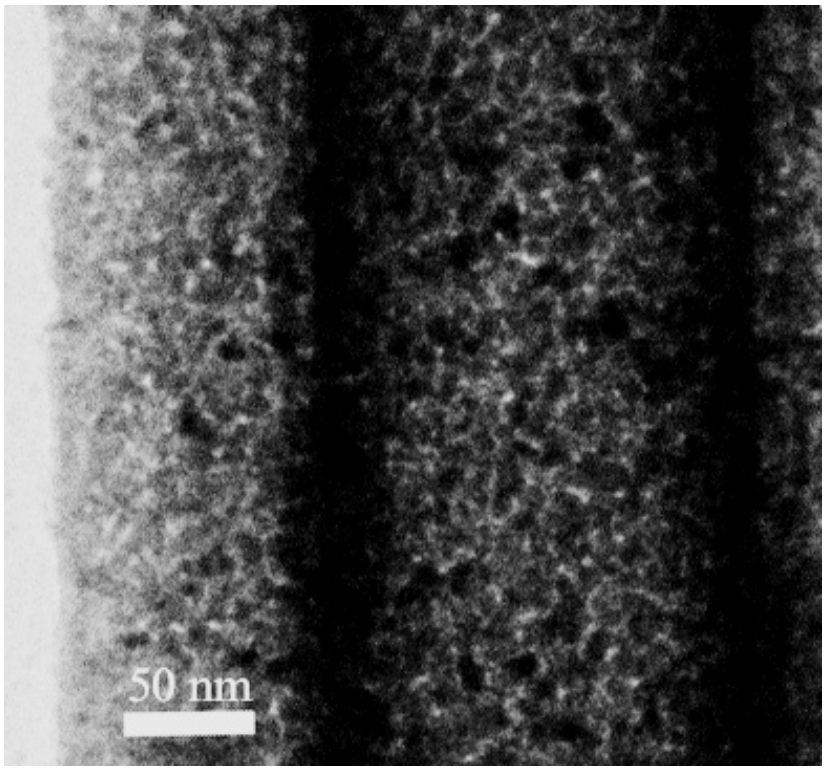




**Figure 4. BF TEM image of 0% Pd-$SnO_2$ lines (300 nm width) and histogram (~150 grains measured). Tin oxide grains (dark regions) as well as some porosity (white regions) are clearly visible.**



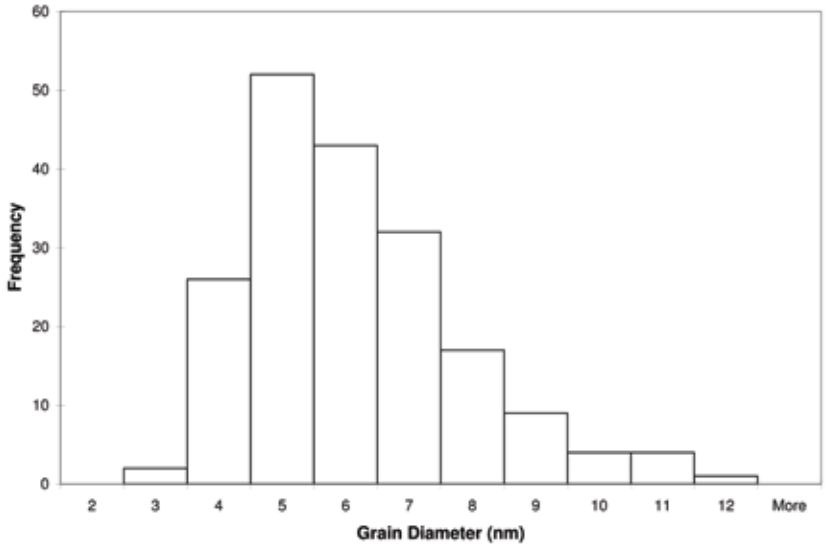




**Figure 5. BF TEM image of 5% Pd-$SnO_2$ lines (300 nm width) and histogram (~150 grains measured). Tin oxide grains (dark regions) as well as some porosity (white regions) are clearly visible.**

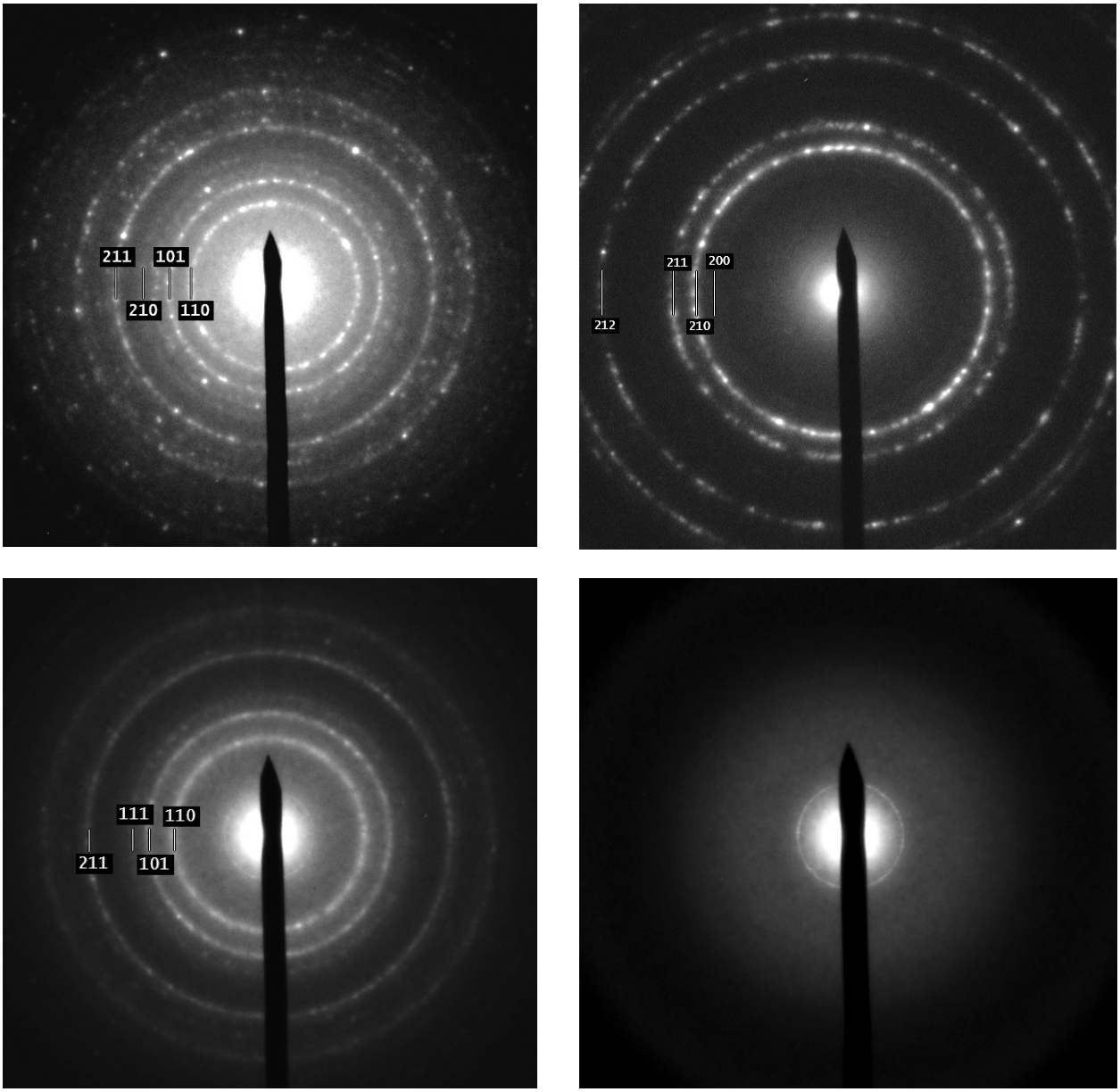



**Figure 6. Electron diffraction patterns of 0% Pd tin oxide thin film (top left), 5% Pd tin oxide thin film (top right), 0% Pd tin oxide line (bottom left), and SiN membrane substrate (bottom right).**

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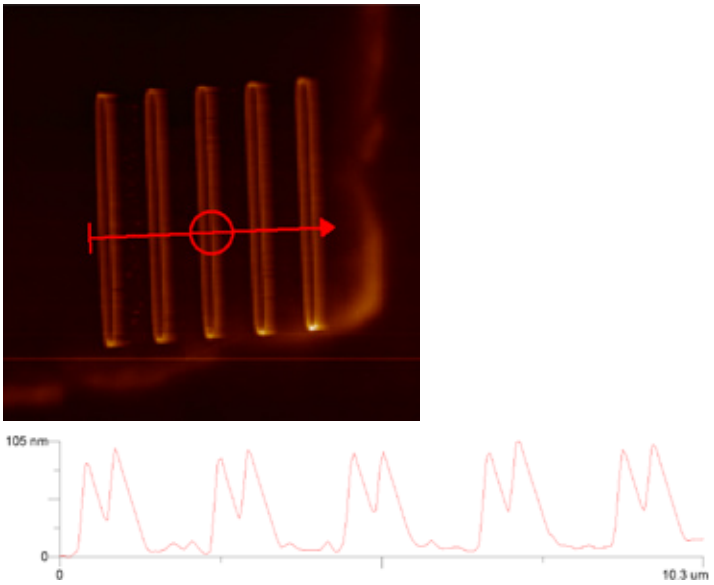


**Figure 7. AFM topography image showing uneven tin oxide line thickness (top); AFM height profile (bottom).**

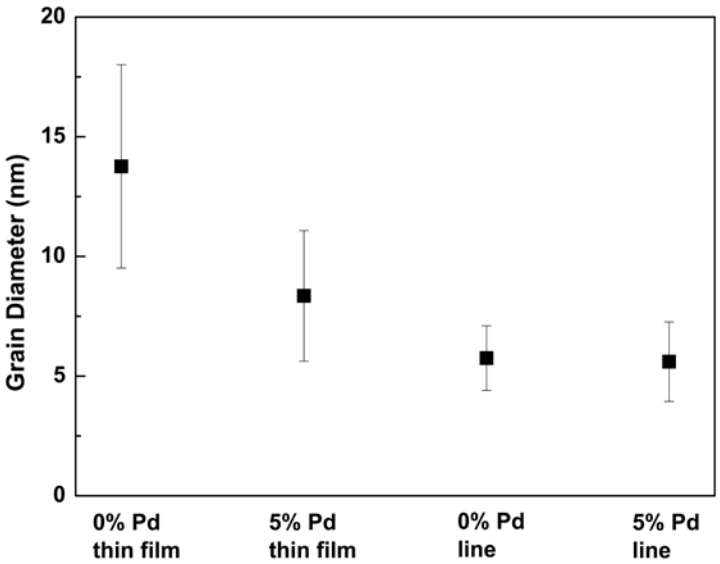


**Figure 8. Grain diameter summary chart for the different dimensionality and Pd-doping experiments. (Each error bar length is two standard deviations long.)**