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ZnO Thin Films Generated by Ex-Situ Thermal Oxidation of Metallic Zn for Photovoltaic Applications

Abstract

ZnO thin films that function as either transparent conducting oxides in solid-state photovoltaic cells or as nanocrystalline dye-absorbers in dye-sensitized solar cells have the potential to reduce the cost of producing electricity from solar energy. Although there exist many methods to produce ZnO thin films, the most economical and practical method may be oxidation of metallic Zn thin films. This research examined the utility of ex-situ thermal oxidation of DC magnetron sputtered Zn thin films in generating useful ZnO thin films for these photovoltaic applications. We annealed Zn thin films in air at 570° C in order to produce ZnO thin films. We monitored the film's resistance and ZnO:Zn composition ratio using relative peak intensities from X-ray diffraction spectra as a function of anneal time. We found that DC magnetron sputtered Zn films that are converted to ZnO by thermal oxidation in air are several orders of magnitude too resistant to be used as transparent conducting oxides in solid-state photovoltaic cells, but that this method of production may provide ZnO films that can be used as a dye absorbing semiconductors in dye-sensitized solar cells.

Keywords

ZnO thin film, Ex-Situ Thermal Oxidation, Dye-Sensitized Solar Cell, Gratzel Cell, Photovoltaic Applications

Cover Page Footnote

Thank you to Professor Jim Doyle for allowing me to work with him on this research. Also thank you to Jeff Thole and Ken Moffat for technical assistance throughout my research.

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ABSTRACT - ZnO thin films that function as either transparent conducting oxides in solid-state photovoltaic cells or as nanocrystalline dye-absorbers in dye-sensitized solar cells have the potential to reduce the cost of producing electricity from solar energy. Although there exist many methods to produce ZnO thin films, the most economical and practical method may be oxidation of metallic Zn thin films. This research examined the utility of ex-situ thermal oxidation of DC magnetron sputtered Zn thin films in generating useful ZnO thin films for these photovoltaic applications. We annealed Zn thin films in air at 570° C in order to produce ZnO thin films. We monitored the film's resistance and ZnO:Zn composition ratio using relative peak intensities from X-ray diffraction spectra as a function of anneal time. We found that DC magnetron sputtered Zn films that are converted to ZnO by thermal oxidation in air are several orders of magnitude too resistant to be used as transparent conducting oxides in solid-state photovoltaic cells, but that this method of production may provide ZnO films that can be used as a dye absorbing semiconductors in dye-sensitized solar cells.

Introduction

Zinc oxide (ZnO) is a semiconductor with a wide band-gap (3.37 eV) and a high transmission coefficient in the visible electromagnetic spectrum that is often degenerately doped as an n-type semiconductor for applications that require conducting oxide layers [1,2]. These characteristics of ZnO have lead to investigations for its use in a wide range of applications that include photovoltaic cells, flat panel displays, gas sensors, transparent thin film transistors, and light emitting diodes [3,4]. ZnO doped with Al, In, or Ga is often used as the transparent conducting oxide (TCO) layer in amorphous silicon, microcrystalline silicon, HIT-silicon, and copper indium gallium selenide (CIGS) photovoltaic cells [2,5]. Another potential application of ZnO thin films to solar cell technology is as a dye absorbing semiconducting layer in dye-sensitized solar cells (DSSC) [6], although the typical materials currently used in DSSCs are titanium dioxide, tin dioxide, and indium oxide [5].

Of the wide variety of methods for ZnO thin film production, the most conventional is DC/RF magnetron sputtering of a ZnO target or sputtering of a Zn target in an oxygenated atmosphere. This research, however, focused on the utility of an alternative method of ZnO production by ex-situ thermal oxidation of DC magnetron sputtered metallic Zn thin films for application as either a TCO or as a dye-absorbing semiconductor for a DSSC. Often cited explanations for photovoltaic cells' lack of popularity as a source of clean and renewable energy are the high costs of the materials necessary to manufacture efficient solar cell devices. The motivation for attempting this particular alternative method of ZnO production is that it could prove to be a relatively simple and inexpensive process for producing ZnO thin films on an industrial scale for their use in photovoltaic devices.

The focus of this research is to investigate this research question: is it possible to produce ZnO thin films through ex-situ thermal oxidation of metallic Zn thin films for application to either solid-state photovoltaic cells or dye-sensitized solar cells? To answer this question we deposited ZnO thin films by DC magnetron sputtering a Zn target at room temperature (RT) and introducing them to a series of high temperature anneals in order to catalyze oxidation, producing a ZnO thin film. We monitored the films' resistance and ZnO:Zn composition ratio while incrementally increasing the anneal time of each film. We found that the ZnO films produced by this method were not suitable for use as TCOs because of their low optical transmittance (~60%) and because they exhibit resistances that are several orders of magnitude higher than the industry standard. Despite failure in our attempt to create a useful TCO, scanning electron microscope (SEM) images of the microstructure of the ZnO thin films provide qualitative evidence that these films could function as a dye-absorbing semiconductor layer in DSSCs.

Methodology & Procedure

We used DC magnetron sputtering to deposit Zn thin films at RT onto four 1" x 1" glass substrates for 20 minutes and for 10 minutes from a 98%:2% Zn:Al target. We measured the films' resistance using a four-point resistivity probe then cut the films with a glass-cutting saw to produce eight 0.5" x 0.5" Zn thin films that were sputtered for 20 minutes, and eight 0.5" x 0.5" Zn thin films that were sputtered for 10 minutes. Seven films from the 20 minute sputter deposition batch (Batch 1) and seven films from the 10 minute sputter deposition batch (Batch 2) were annealed in a horizontal tube furnace in air for either 30, 50, 70, 130, 145, 165, or 200

minutes, while one film from each batch was left as-deposited. Once each film completed its anneal we measured the film's resistance with a four-point resistivity probe. We imaged the films using both an optical microscope and a scanning electron microscope. Finally, we conducted X-ray diffraction (XRD) analyses on each of the thin films in the KECK Lab at Macalester College.

Results & Discussion

Figure 1 shows an XRD analysis that is characteristic of the as-deposited metallic Zn films. As expected, the peaks present in the XRD spectra for this film are the Zn (002), Zn (100), Zn (101), and the Zn (102) as identified in the Mineral Powder Diffraction File [7]. The one large peak of approximately 20,000 counts at $2\theta \approx 37.5^\circ$ indicates that the as-deposited Zn films are highly oriented along the (002) crystallographic plane.

Figures 2 and 3 show XRD analyses that characterize the dataset as we exposed the as-deposited Zn films to annealing at 570°C for varying time increments. The XRD spectra shown in Figure 2 is for a Zn film annealed for 70 minutes. After a relatively short anneal time this spectra shows a mix of both characteristic Zn peaks and characteristic ZnO peaks. The four Zn peaks that were present from the as-deposited spectra still appear, while the ZnO (100), ZnO (002), ZnO (101), ZnO (102), ZnO (110), ZnO (103), and ZnO (112) peaks are also present. The presence of characteristic peaks of both Zn and ZnO indicate that the films are beginning to transition from a pure Zn composition to a composition of pure ZnO. We also see that the highest intensity peak is only registering approximately 5,000 counts, which indicates that the films are deteriorating from the original highly oriented structure present in the as-deposited films.

Figure 3 shows a characteristic XRD spectra for a Zn thin film that has been sufficiently annealed such that it has completely converted to a ZnO thin film. Only characteristic ZnO peaks are present, while the characteristic Zn peaks are not present in the XRD spectra. The highest intensity peaks in Figure 3 register approximately 2,000 counts, which further indicates that the films become more randomly oriented as they are exposed to a longer time annealing at high temperature.

Figures 4 and 5 summarize the entire data set for the annealing process for both Batch 1 and Batch 2. The plots show both the film's resistance and the ZnO:Zn composition ratio as generated from the relative intensities of certain peaks from the XRD spectra. We calculated the ZnO:Zn composition ratio by selecting two characteristic peaks that represent ZnO and two characteristic peaks that represent Zn. Using the relative intensities of these four characteristic peaks we calculated four separate composition ratios and a mean composition ratio of the form $\frac{I_{ZnO}}{(I_{ZnO} + I_{Zn})}$, where I_{ZnO} represents the relative intensity of one of the characteristic ZnO peaks and I_{Zn} represents the relative intensity of one of the characteristic Zn peaks

Figures 4 and 5 provide three important results. The first result we drew from these plots is that both the 20 minute sputter deposition films and the 10 minute sputter deposition films reached 100% ZnO composition in the range of 130-145 minutes annealing at 570 °C. The 20 minute sputter deposition films experienced a rapid increase in ZnO composition, jumping from ~60% ZnO composition to 100% ZnO composition in a short time interval, whereas the 10 minute sputter deposition films reached 100% ZnO composition more gradually. The second interesting result from these plots is that the resistance of the thin films plotted on a logarithmic scale tracks the ZnO:Zn composition ratio relatively well. This is demonstrated explicitly in

Figure 6 which displays the resistance of the films as a function of the mean ZnO:Zn composition ratio. The third, and most pertinent, conclusion we made from these plots is that once the thin films reached 100% ZnO composition their resistances are on the order of 1 M Ω . This result is significant because in order for these ZnO films to be useful as TCOs in solid-state photovoltaic cells they should exhibit a resistance on the order of 10 Ω . Due to the ZnO films' high resistance we can conclude that producing ZnO thin films through ex-situ thermal oxidation of metallic Zn thin films is not a practical method of producing useful thin films for solid-state photovoltaic devices.

Another characteristic of the ZnO thin films we produced that renders them impractical for use as TCOs is their lack of transparency. Figure 7 compares the transparency a ZnO thin film produced through thermal oxidation to that of a ZnO thin film deposited as ZnO that would be considered the industry standard TCO for application to solid-state photovoltaic cells. The most transparent film we produced through oxidation has a transparency of only 60% in the visible electromagnetic spectrum whereas the industry standard film has an optical transmittance of 87%. Our films' low transparency appears to be due to the rough microstructure of the films' surfaces which scatters the light incident on the film.

This hypothesis for the films' rough microstructures is supported by the comparison between the XRD spectra of the as-deposited films and the annealed films and by SEM images of the films' surface morphologies (Figure 8). The SEM photomicrographs show that the as-deposited Zn films are composed of roughly spherical particles with diameters of 200-500 nm, while the ZnO films demonstrate a more randomly oriented globular morphology. The photomicrographs of the ZnO film also show the presence of ZnO nanorods, which Liu et al.

(2007) have identified in ZnO synthesized from oxidation of granular Zn films. Visual qualitative analyses of the ZnO films we produced through thermal oxidation indicate that there is a potential for these ZnO films to have utility as a dye-absorbing wide-band gap semiconductor for use in the DSSC. DSSCs require a nanocrystalline, mesoporous, and highly textured semiconductor material to provide a large surface area for the photosensitive dye to adhere to. If our ZnO thin films prove to have a sufficiently rough morphology then they might be applicable to DSSCs, however further quantitative analyses using atomic force microscopy (AFM) and other techniques are necessary to fully determine if ZnO can be applied to DSSC technology.

Conclusion & Future Work

We produced ZnO thin films through ex-situ thermal oxidation of metallic Zn films deposited by DC magnetron sputtering at RT. The motivation for this research was to determine if these ZnO thin films could be applied as TCOs in traditional solid-state photovoltaic devices or as dye-absorbing semiconductors in dye-sensitized solar cells. We monitored the films' resistances and ZnO:Zn composition ratio as a function of anneal time and examined the films' microstructure on a scanning electron microscope. We found that this alternative method of ZnO production generates ZnO films that have a high resistance ($\sim 1 \text{ M}\Omega$), low optical transmittance ($\sim 60\%$), and a globular microstructure containing ZnO nanorods. Considering the ZnO films' high resistance and low transparency we unequivocally conclude that ex-situ thermal oxidation of metallic Zn is not a practical method for ZnO thin film production for application as TCOs in solid-state photovoltaic cells. Despite this, visual qualitative analyses of SEM photomicrographs

of the ZnO thin films indicate that ZnO thin films produced through this alternative method have the potential to be used as a dye-absorbing layer in DSSCs. Further quantitative analysis of the film's microstructures and further experimentation on the controls of the film's microstructures are necessary to fully determine the films' utility in DSSC technology.

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Figures

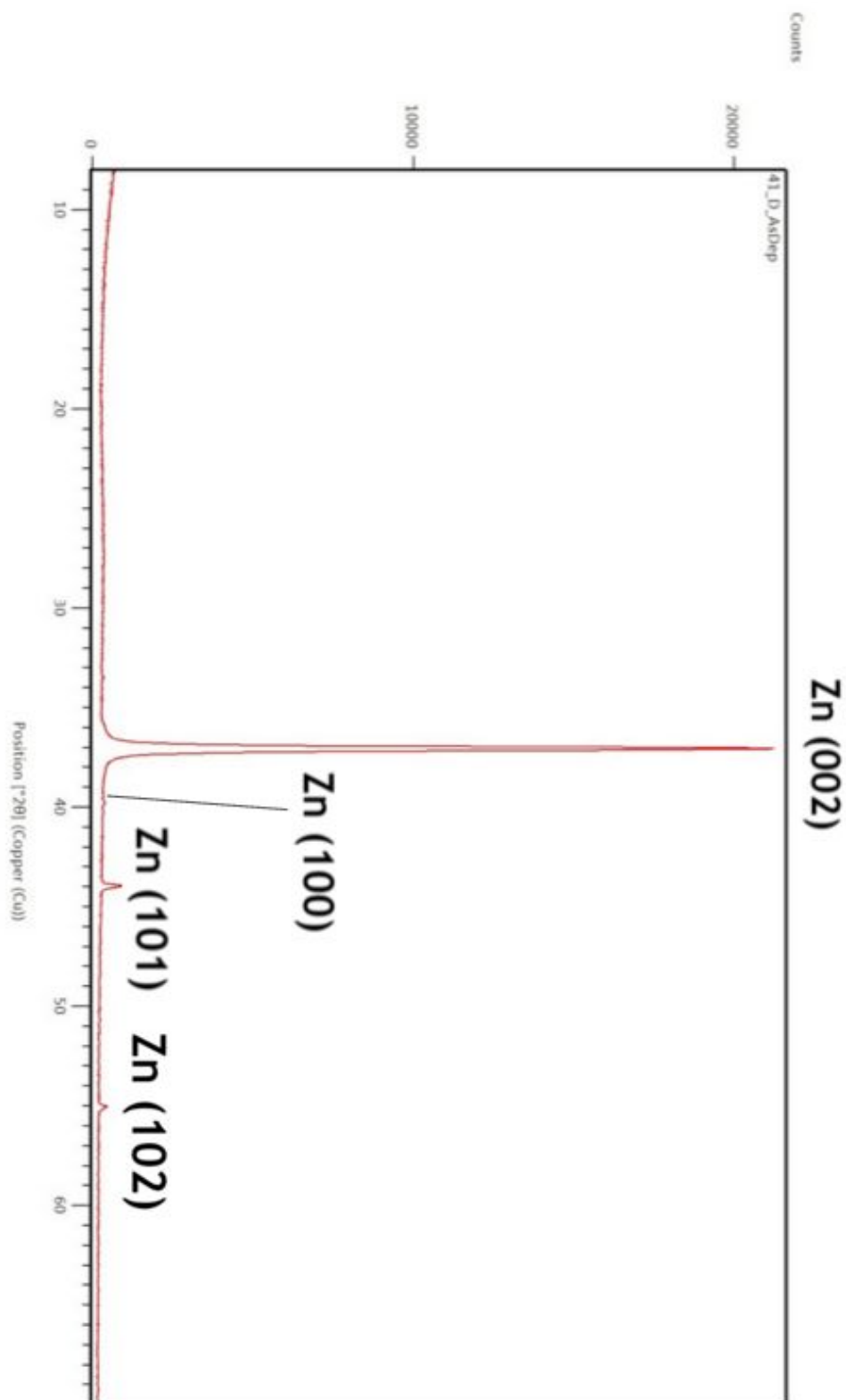


Figure 1. Characteristic XRD spectra for an as-deposited Zn film.

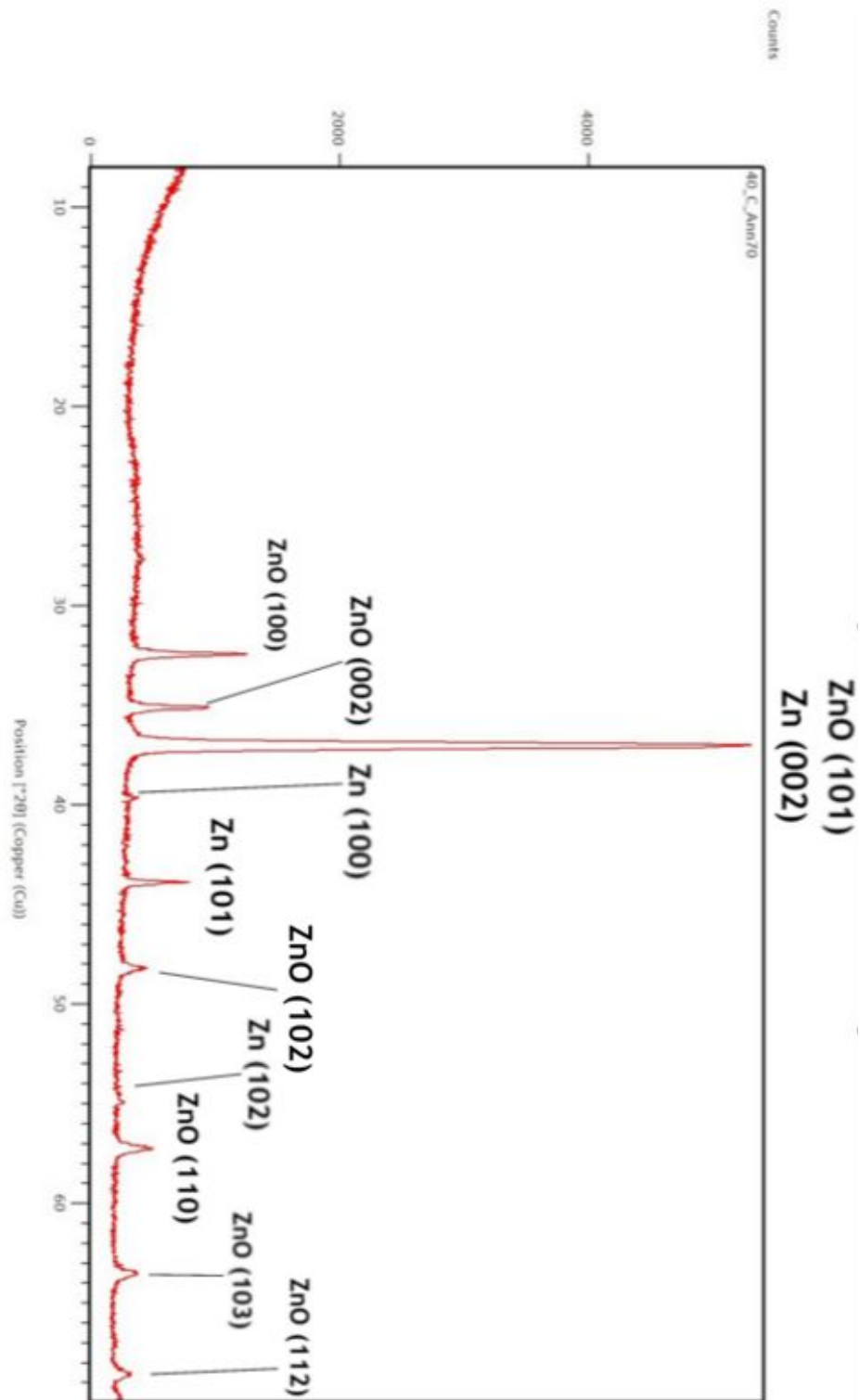


Figure 2. Characteristic XRD Spectra for a Zn thin film annealed for 70 minutes at 570°C.

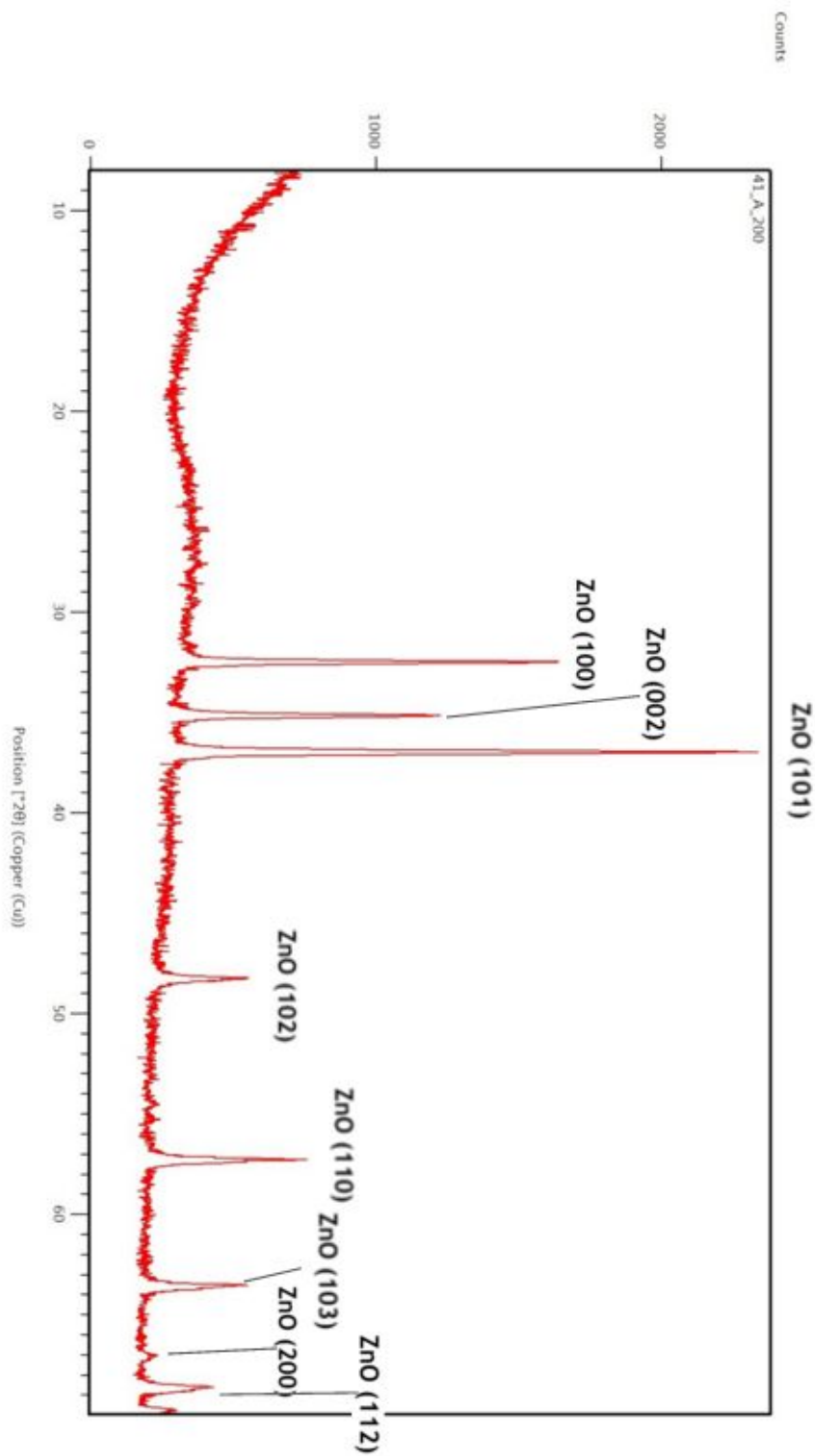


Figure 3. Zn thin film annealed for 200 minutes at 570 °C that has been completely converted to a thin film of ZnO composition.

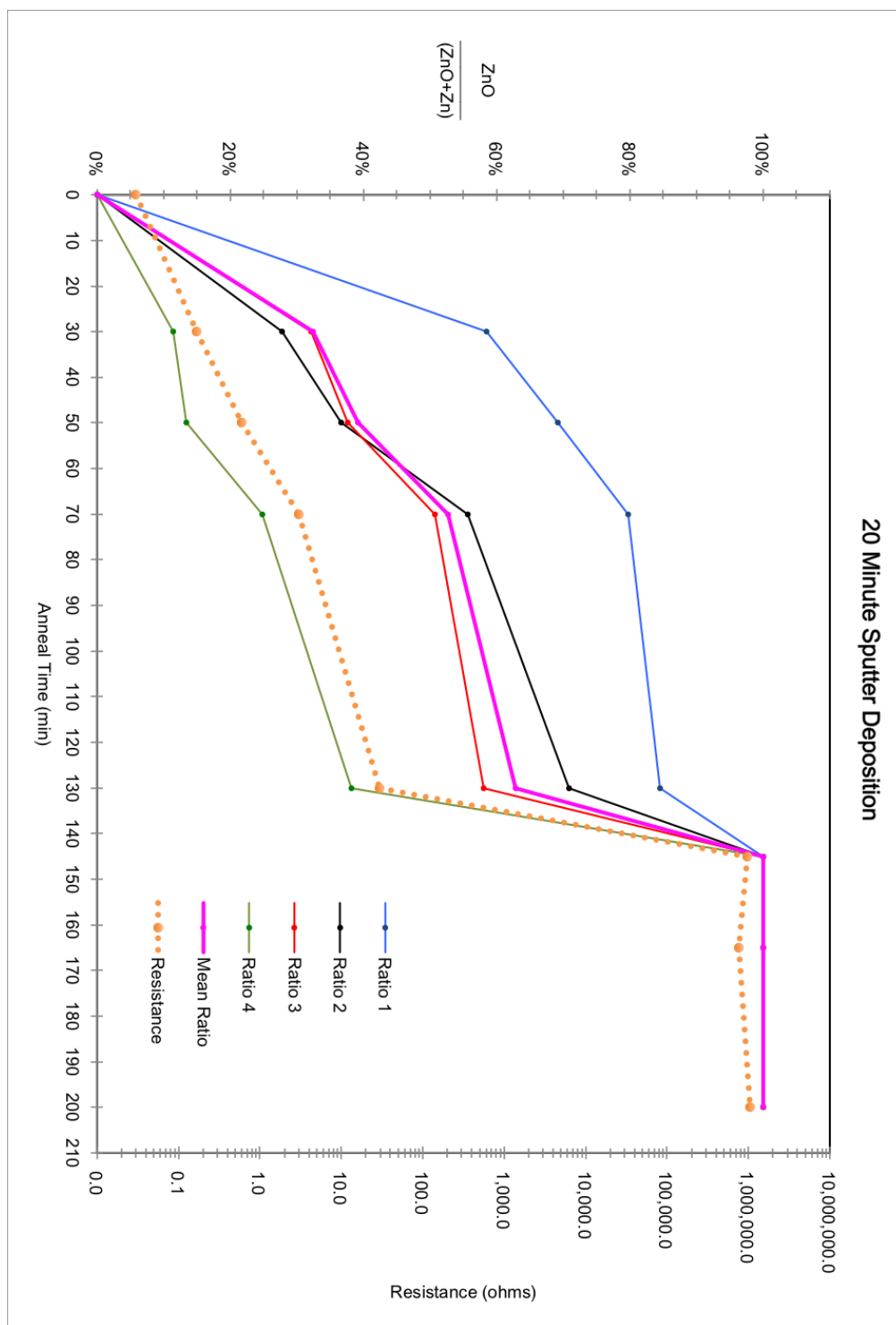


Figure 4. Summary of the dataset for the annealing process of the 20 minute DC magnetron sputtered Zn films. The left vertical axis is the ZnO : (ZnO + Zn) composition ratio as discussed in the text, the right vertical axis is the resistance plotted on a logarithmic scale. The horizontal axis is the time spent annealing at 570°C. The thick pink line is the mean of the four composition ratio and the dotted orange line is the plot of the resistance.

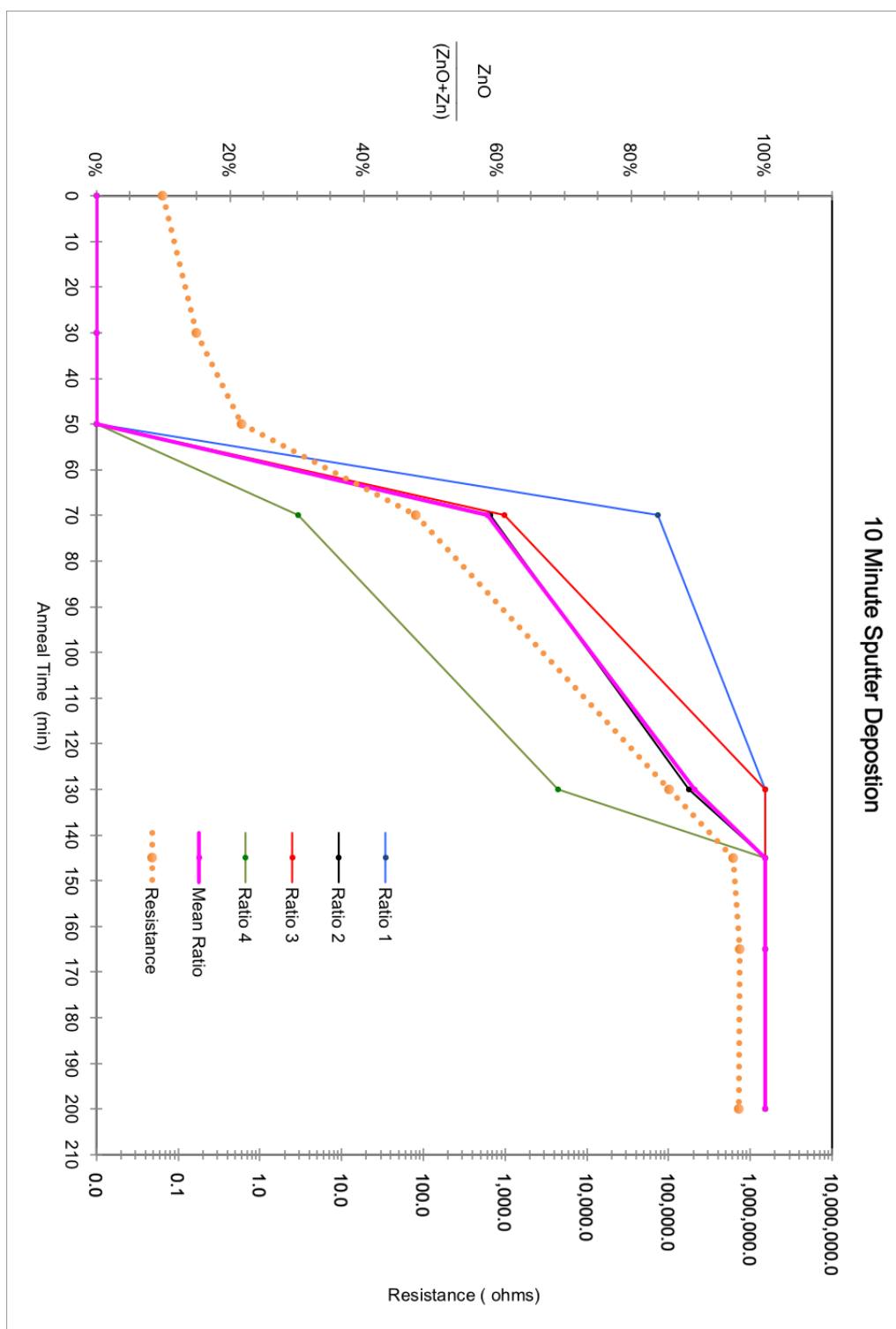


Figure 5. Summary of the dataset for the annealing process of the 10 minute DC magnetron sputtered Zn films. The left vertical axis is the ZnO : (ZnO + Zn) composition ratio as discussed in the text, the right vertical axis is the resistance plotted on a logarithmic scale. The horizontal axis is the time spent annealing at 570°C. The thick pink line is the mean of the four composition ratio and the dotted orange line is the plot of the resistance.

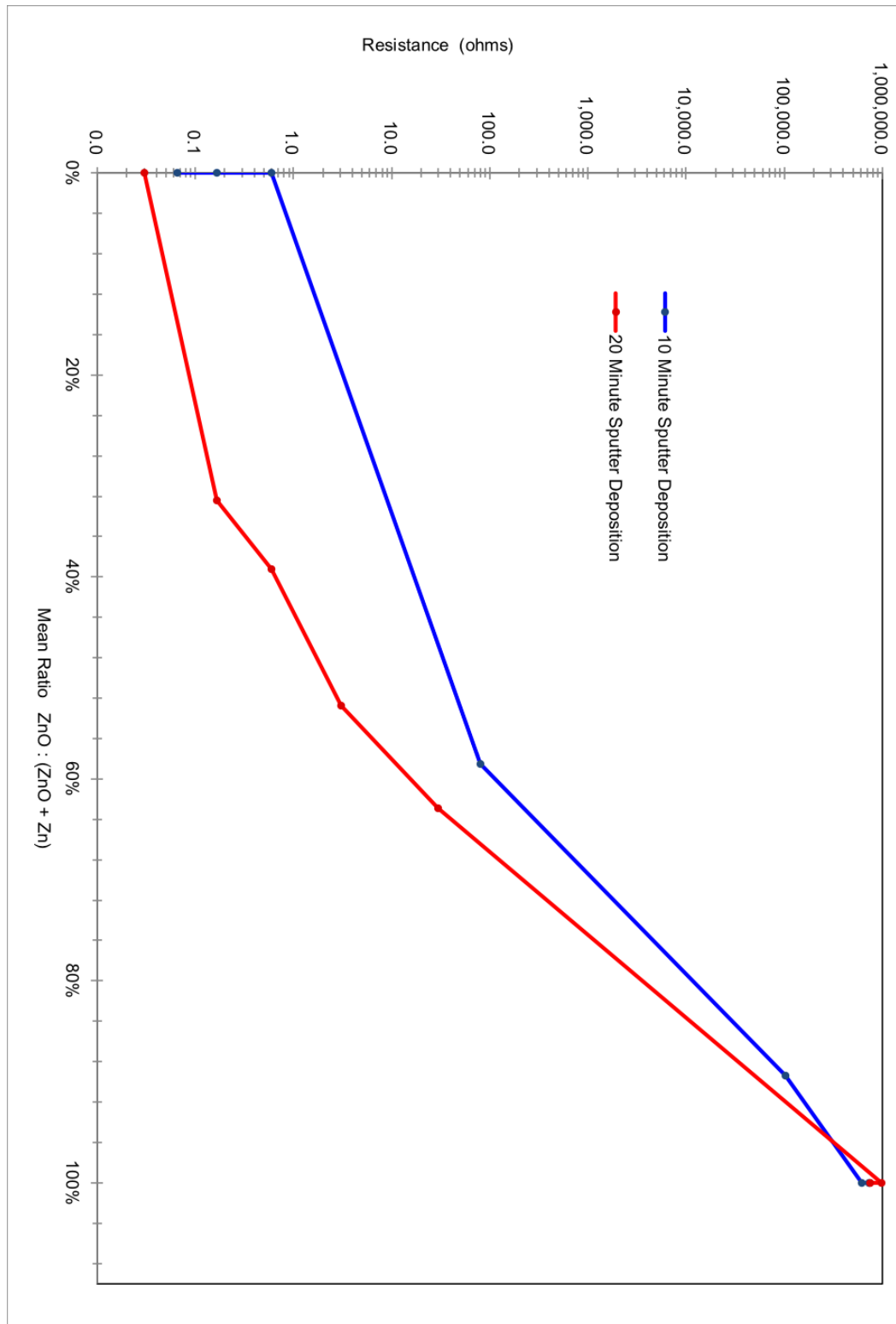


Figure 6. Plot of the resistance as a function of the ZnO:Zn composition ratio for both the 20 minute deposition films and the 10 minute deposition films.

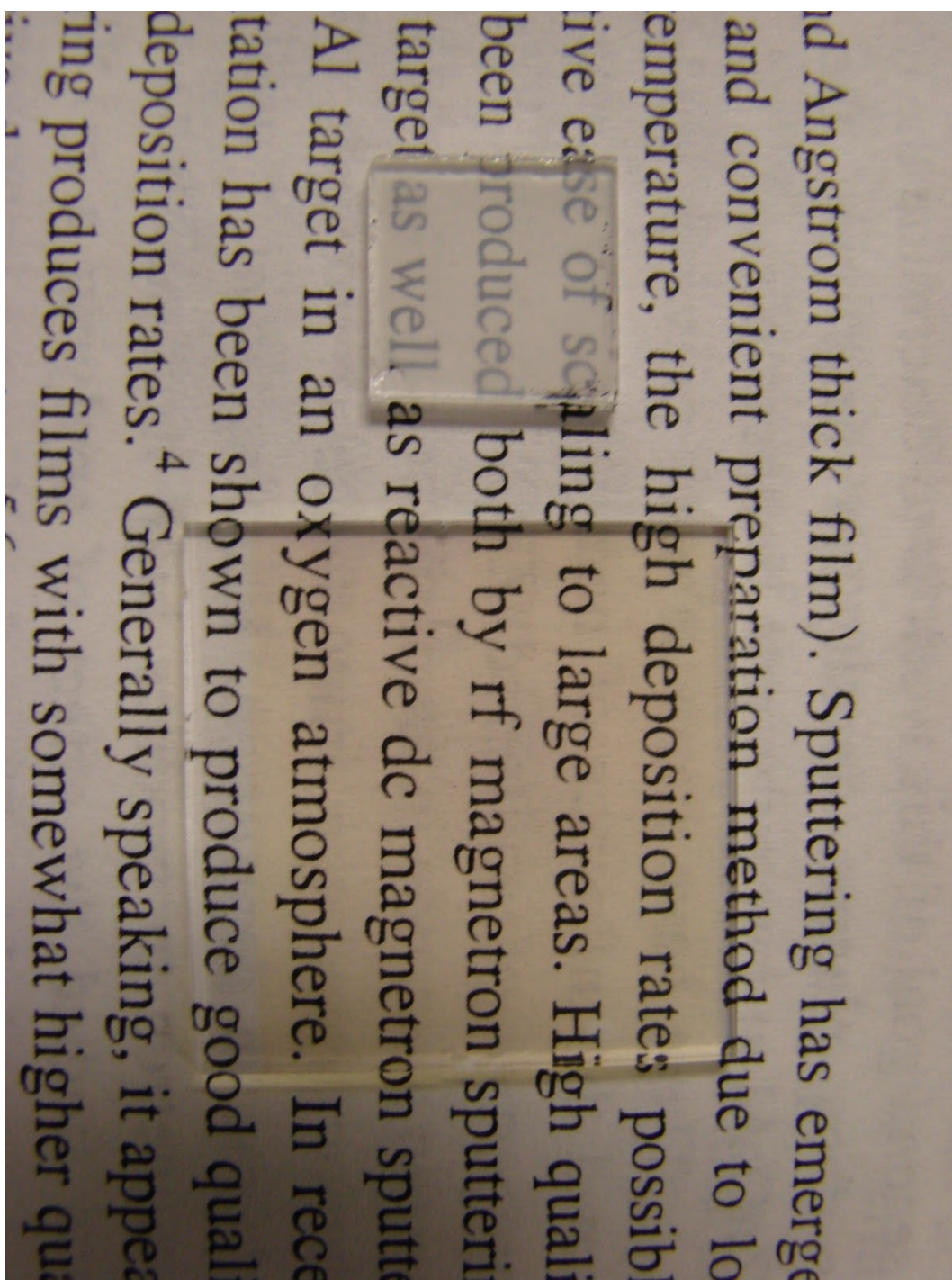


Figure 7. Visual comparison of ZnO thin film produced through ex-situ thermal oxidation and a ZnO thin film deposited as ZnO. The top film is the most transparent ZnO thin film we were able to produce using the oxidation technique, it exhibits an optical transmittance of 60%. The bottom film is representative of the industry standard ZnO thin film used in TCOs, it exhibits an optical transmittance of 87%.

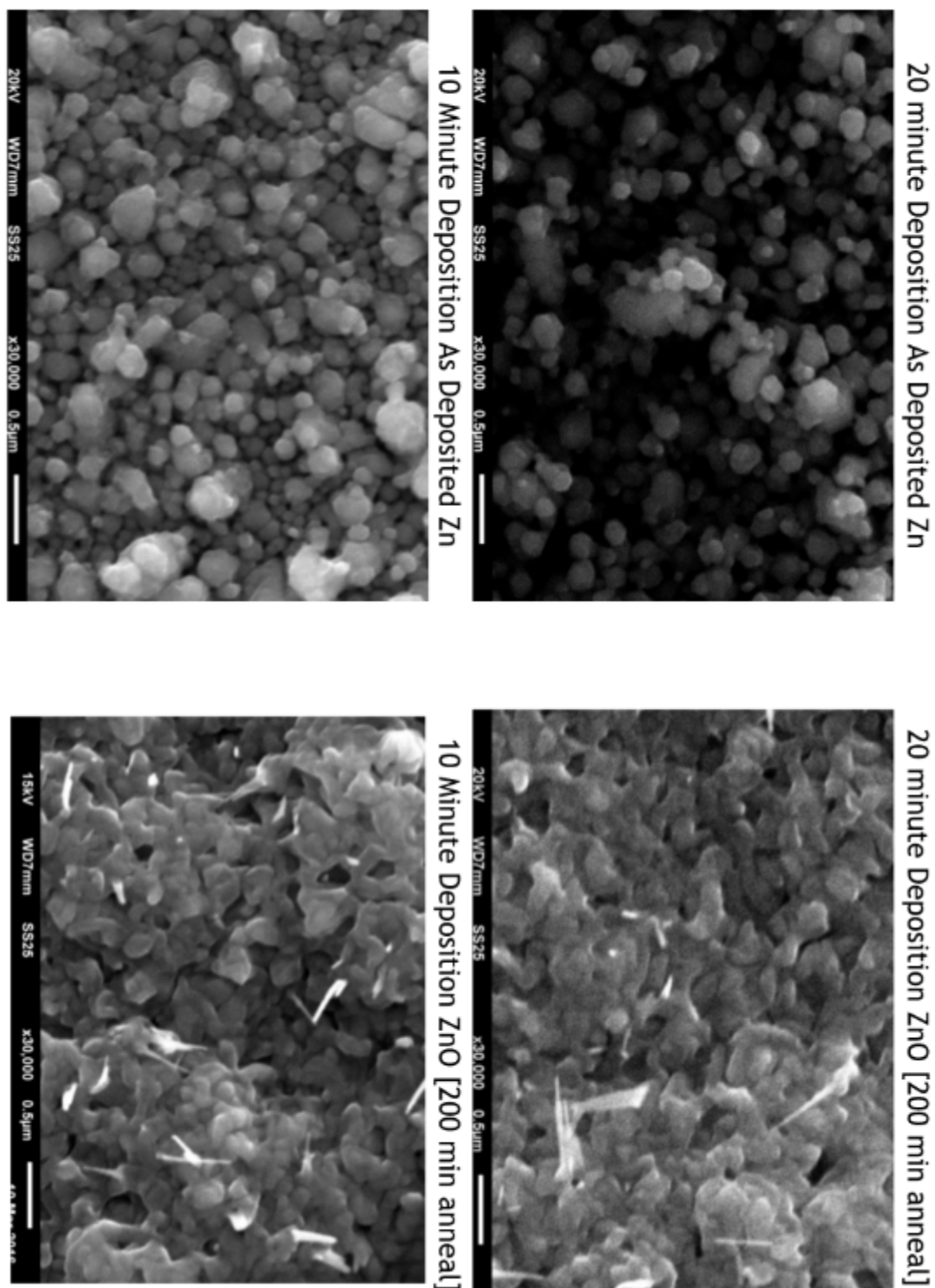


Figure 8. SEM photomicrographs of the As-Deposited Zn thin films (top) and the ZnO films produced after 200 minutes of annealing at high temperature (bottom) showing the films' microstructure. 30,000x magnification, scale bar is 500 nm.