Effects of Post-Deposition Annealing on Zinc Oxide

Abstract

This study focuses on thin film deposition of ZnO onto a glass slide using magnetron sputtering. The study focuses on understanding the effects of post-deposition annealing temperatures. The goal is to optimize crystal quality, conductivity, and transparency. The results attempt to answer the effects of room temperature deposition and changes in film properties once annealed. Annealing temperatures ranged from 100°C to 400°C with an annealing time of 30 minutes. This found an ideal temperature of 250°C for post-deposition annealing, resulting in approximately 3.86 times more conductivity with little to no decrease in transparency. However crystal quality did not conclusively improve at any temperature range. While providing increased parameters for conductivity and transparency, industry standards find post-deposition annealed films to be 5 times more resistive.

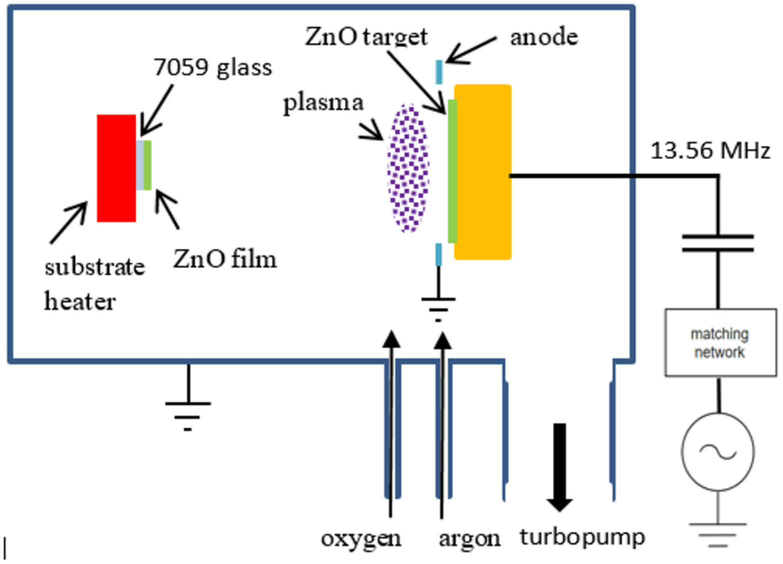
Keywords: Magnetron Sputtering, Transparent Conducting Film, Zinc Oxide, Anneal

1 Introduction

The development of solar cells relies on a conductive layer that can transport charges around the cell. These layers provide the conductivity and charge-carrying capabilities of a solar cell. This is commonly accomplished by thin conducting films such as Zinc Oxide (ZnO) and Indium Tin Oxide (ITO). ITO is an industry-leading thin conducting film favored for its high conductivity and transparency. The issue with ITO is indium’s cost as a rare metal. An inexpensive alternative is ZnO, an earth-abundant metal that can be deposited as a thin film.

This study focuses on thin film deposition of ZnO onto a glass slide using magnetron sputtering. The study focuses on understanding the effects of post-deposition annealing temperatures. The goal is to optimize crystal quality, conductivity, and transparency. Deposition is accomplished through magnetron sputtering which is a process that involves a near-vacuum environment where ZnO can be ionized and deposited onto a substrate. In this case, the substrate is a glass slide. Magnetron sputtering entails a Radio Frequency, RF, machine that produces a plasma that ionizes a ZnO target. The ionized molecules are kept in place with magnetic fields, allowing them to deposit onto the glass slide uniformly. Figure 1 depicts the magnetron sputtering schematic. Industry-leading thin films use a substrate heater to heat the substrate during deposition. This study focuses on the effects of room temperature deposition and changes in film properties once annealed.

Figure 1: Magnetron Sputtering Schematic



2 Methods

A. Deposition

The glass slide is first prepared for deposition. All dust is removed from the front and back with an air duster and then placed into the substrate holder. Held in place by screws, a film name is scratched onto the back of each slide. To initiate the magnetron sputtering process, the chamber is vacuumed down to $\sim 1.7 \times 10^{-7}$Torr, measured using the ion gauge. The device is shut off to prevent high-pressure damage to the filament. The load lock is pumped out until it reaches below 200 mTorr. The substrate holder containing the glass slide is loaded into the main chamber and then sealed off. Argon gas is pumped in at a steady flow of ~34 sccm. Once flowing with gas, the pressure in the chamber is ~4.5 mTorr. Water cooling to the target is turned on to prevent cracking. The power supply is set to 150 W and is turned on producing a plasma. In the event a plasma does not form, the vacuum can be throttled to increase the pressure, allowing the plasma to set and the pressure can be throttled back to ~4.5 mTorr. The first 10 minutes of deposition is considered a pre-sputter where the shutter guard is closed so no deposition occurs on the glass slide. This is to stabilize the system and prime the target. After 10 minutes, the shutter is lifted and deposition occurs for 30 minutes. After 30 minutes, the power supply is shut off and the substrate holder is removed by reversing all previous steps.

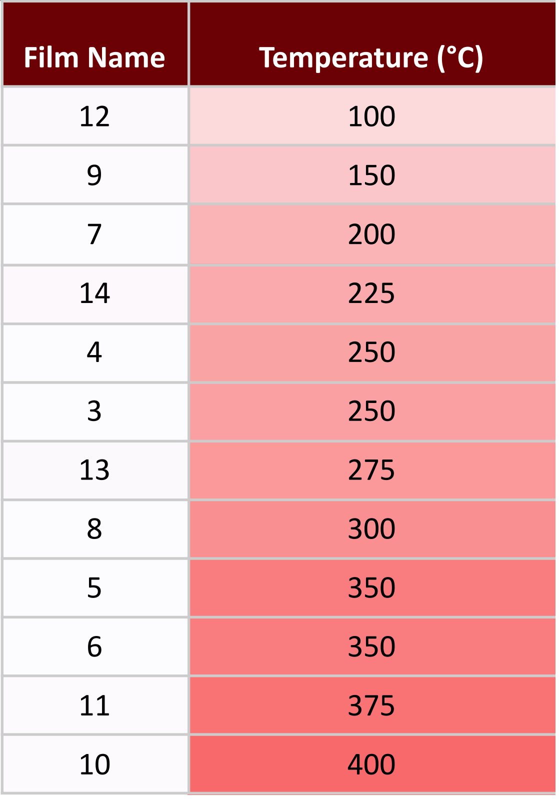
B. Measurement

Once the substrate holder is removed from the chamber, the glass slide is collected to have pre-anneal measurements taken. First, the conductivity is measured by applying a 1 mA current to the deposited side of the glass slide and measuring the resulting voltage, allowing us to determine changes in resistivity before and after annealing. A transmittance measurement is done at a range of 200 nm to 1100 nm. Finally, an x-ray diffraction measurement is taken from 0° to 90°. After these measurements, the film slide is annealed.

C. Anneal

Annealing occurs in a tube furnace at the set temperature for each film. Annealing is a process of heating a substance over a period of time and cooling it down to change its structure. The temperatures chosen and their corresponding names are seen in Figure 2. Each film is annealed for 30 minutes while pumped with nitrogen to prevent oxidation. Once annealed, the film is pulled out and allowed to cool down to room temperature before post-anneal measurements are taken.

Figure 2: Range of Temperatures Annealed for Each Film



Film Name	Temperature (°C)
12	100
9	150
7	200
14	225
4	250
3	250
13	275
8	300
5	350
6	350
11	375
10	400

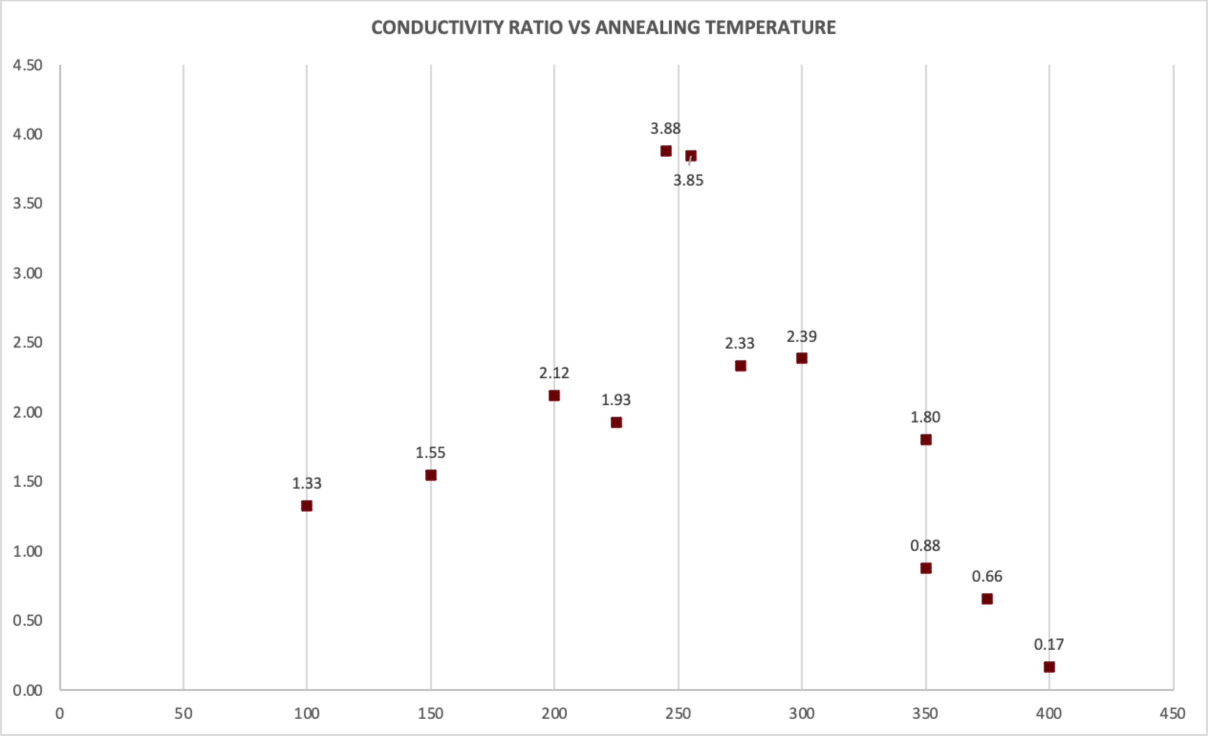
D. Measurement

Final measurements for conductivity, optical, and x-ray diffraction are taken from the post-annealed sample. The methods and ranges for each measurement are repeated as in step A.

3 Results

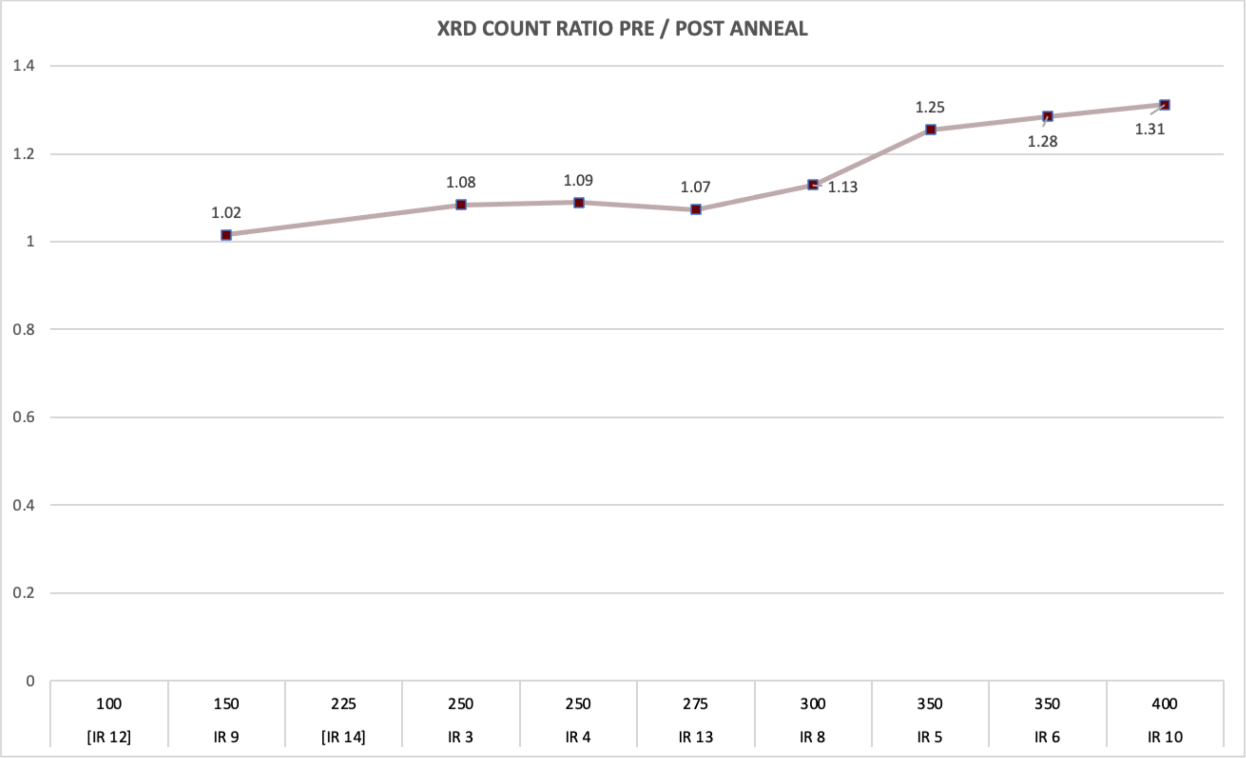
The conductivity ratio results are shown in Figure 3 where the peak conductivity is seen at 250°C at a ratio of 3.88 and 3.85 for the two samples annealed. This implies that the ZnO film is approximately 3.86 times more conductive post-anneal compared to pre-anneal. The conductivity ratios follow an increase until 250° and drop steadily after 250°.

Figure 3: Ratio of Conductivity Pre and Post Anneal



To compare X-ray diffraction measurements, a peak count ratio was taken for pre and post-annealed films. All peaks were found at approximately 34°. The XRD measurements depict an inconclusive slight upward trend from 150° to 400°. Figure 4 plots the ratios ranging from 1.02 to 1.31 as the temperature increases. Missing data points for films IR14 and IR12 are due to malfunctions with the XRD machine preventing measurements.

Figure 4: X-Ray Diffraction Peak Ratios Pre and Post-Anneal



The transmittance data is compared by taking an average percent transmittance after the first peak which accounts for changes in band gap absorption. The averaging for each film begins around 500 - 600 nm and until 1100 nm. The averages are taken for both pre and post-anneal films and the difference between averages determines an increase or decrease in transparency. Figure 5 shows the average % transmittance for each film and their differences. Figure 6 shows the raw optical data where the two peaks and variability per film can be observed.

Figure 5: Average % Transmittance Pre and Post Anneal

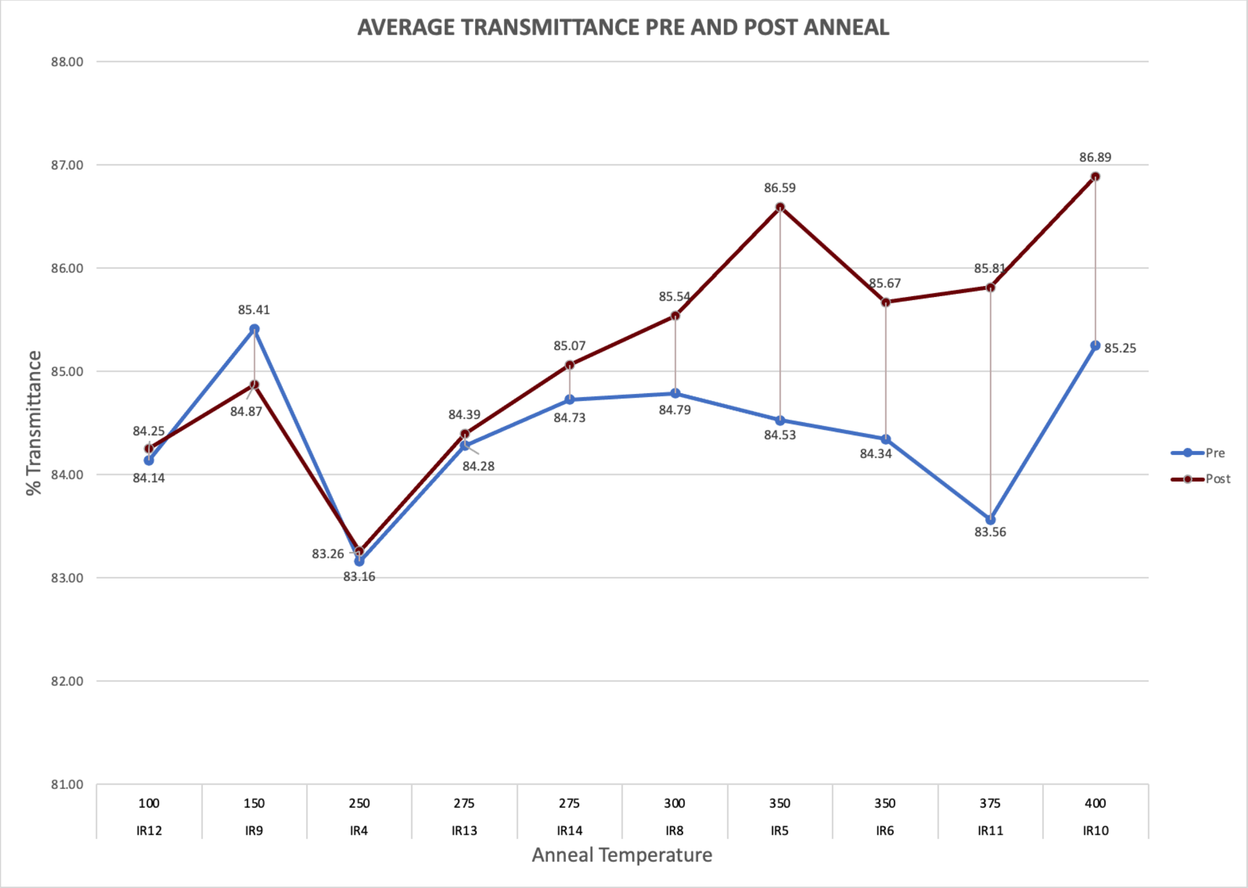
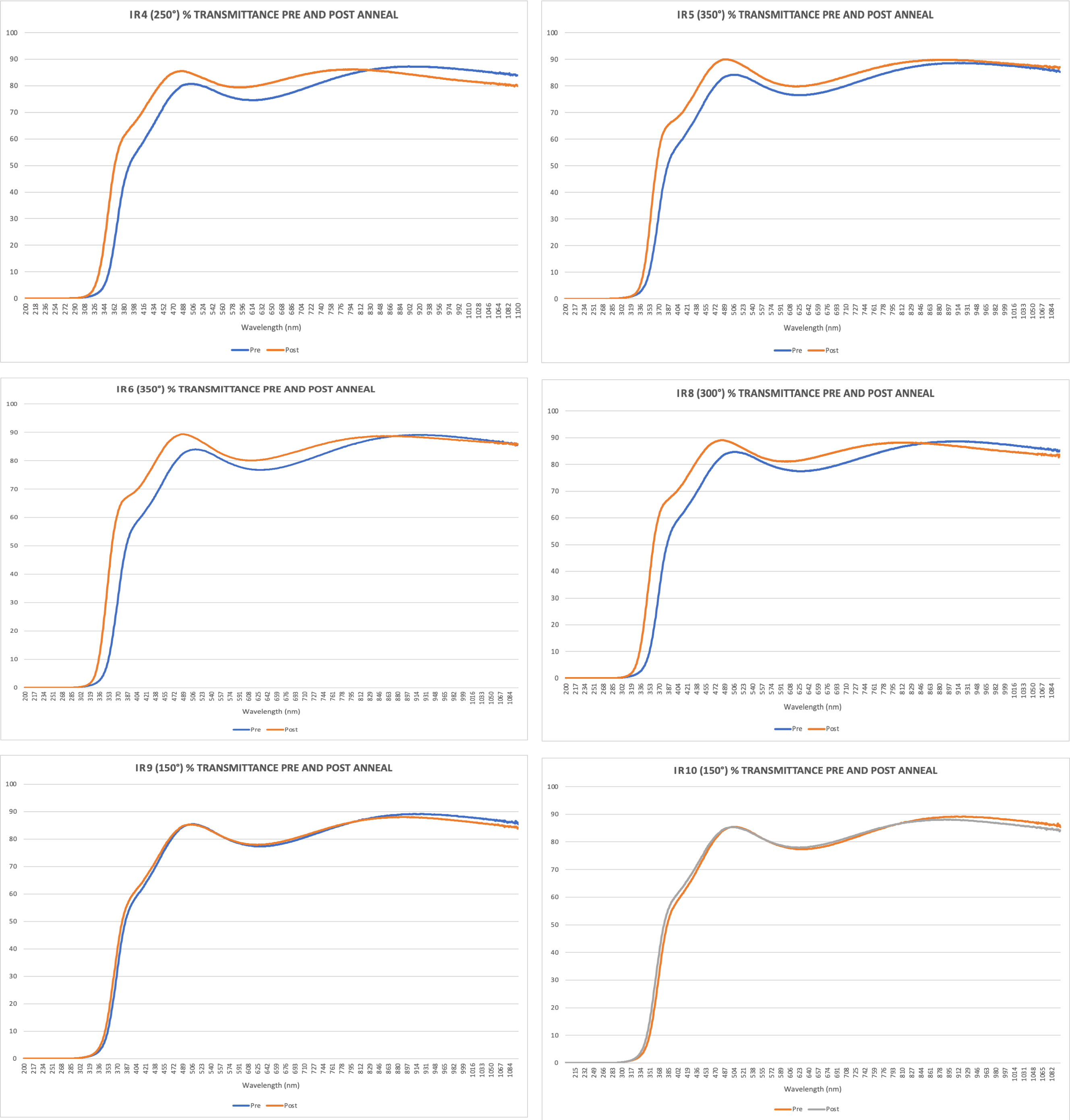


Figure 6: % Transmittance per Wavelength



IR4 (250°) % TRANSMITTANCE PRE AND POST ANNEAL

IR5 (350°) % TRANSMITTANCE PRE AND POST ANNEAL

IR6 (350°) % TRANSMITTANCE PRE AND POST ANNEAL

IR8 (300°) % TRANSMITTANCE PRE AND POST ANNEAL

IR9 (150°) % TRANSMITTANCE PRE AND POST ANNEAL

IR10 (150°) % TRANSMITTANCE PRE AND POST ANNEAL

4 Discussion

The conductivity and optical measurements were the most conclusive and provided insight into conductivity behaviors and molecular structure. Conductivity ratios peak at 250°C, synonymous with an increasing positive difference in transparency. Films did not see any increase in transparency until they were annealed at temperatures greater than 250°C. This can be attributed to an oxidation of Zinc and Aluminum dopants as the temperature increases. At higher annealing temperatures, free Zinc and Aluminum atoms bond more easily with present oxygen around the film. Once bonded, Zn and Al become transparent, increasing the average transmittance for films annealed at higher temperatures. This, in turn, decreases conductivity since excess Zn and Al provide free electrons to carry current pre-anneal. Increased free electrons allow for higher current carrying capacity, while a decrease lowers current carrying capacity.

The X-ray diffraction data shows little to no conclusive increase in counts for ZnO. The greatest count increase was 1.31 times its pre-anneal count. The lack of a conclusive trend implies there was no significant increase in crystal quality for these films. A higher count ratio would imply a higher presence of ZnO thus better molecular structure. The films in this research conclude no increase in quality, but a peak temperature for conductivity and transparency.

5 Conclusion

This study of post-deposition annealing of ZnO concluded a strong bias for temperature when developing ideal films. The goal of the study was to observe changes in crystal quality, conductivity, and transparency at different annealing temperatures. ZnO is primarily used as an n-type semiconductor for solar cells, thus it is used for annealing temperatures that result in increased crystal quality, conductivity, and transparency.

The study shows 250°C as the ideal post-deposition annealing temperature to increase conductivity and prevent oxidation. To increase transparency, a temperature higher than 250°C is preferred at the cost of higher conductivity. Higher quality films developed in the industry tend to anneal at temperatures ranging from 200°C to 300°C, aligning with this study's ideal temperature of 250°C. Other studies that use substrate heaters found 100°C as the ideal temperature to produce higher crystal quality and reduction in peak width. [1] Although the temperature is consistent, higher-quality films tend to be approximately 10 times more conductive. The films in this study did not reach this increase in conductivity which can be attributed to various factors. Higher-quality films are usually deposited onto a substrate attached to a substrate heater which will heat the film as deposition occurs. This method could increase crystal quality thus increasing conductivity [2].

One of the possible reasons for decreased conductivity at temperatures greater than 250°C is the usage of a tube furnace for annealing. Although nitrogen was pumped into the furnace to prevent oxidation, it is not airtight and oxidation can occur at this stage. Oxidation would decrease conductivity by removing free electrons from carrying current. A possible future consideration would be to anneal using a different device allowing for airtight annealing. This would prevent oxidation and allow for a stricter demonstration of post-deposition annealing. Further research could be done on longer annealing times than 30 minutes which could reveal a bias towards other temperatures. Similar studies have also depended on film thickness instead of deposition time as their control which could be another factor to address. [3] Due to difficulties with the XRD machine, many films had to be excluded due to mismatched baselines and counts which could be attributed to varying film thickness.

References

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