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The goal of this work is study the mechanism of ZnO thin film deposition by rf magnetron sputtering with an argon plasma. This research will help understand the growth kinetics of the ZnO layer in relation to the growth conditions for solar cell application. We study the rate of growth, the electrical properties, the optical transmission and the zinc to oxygen ratio of each sample as a function of growth temperature. We conclude that Zn evaporation competes with incorporation into the film by combining with an arriving O atom.

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Growth Kinetics of ZnO by Magnetron Sputtering for Solar Cell Application

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Abstract
The goal of this work is study the mechanism of ZnO thin film deposition by rf magnetron sputtering with an argon plasma. This research will help understand the growth kinetics of the ZnO layer in relation to the growth conditions for solar cell application. We study the rate of growth, the electrical properties, the optical transmission and the zinc to oxygen ratio of each sample as a function of growth temperature. We conclude that Zn evaporation competes with incorporation into the film by combining with an arriving O atom.
Introduction

Zinc Oxide (ZnO) is a Transparent-Conducting Oxide (TCO) that has been found to be very useful for a number of applications including solar cells due to its economically effective growth process, unique optical and electrical properties, reproducibility, wide availability, and non-toxic nature [1]. ZnO can be used as the top contact layer of the cell. The properties of ZnO depend on the conditions of growth of the films [2]. For solar cell applications we are especially interested in two of these properties: transparency and electrical conductivity [3]. The films need to be as transparent as possible in order for the active layer of the cell to receive the maximum amount of sunlight, while being sufficiently conductive to make good electrical contact. They can be grown by several methods, including using a thermal electron or molecular beam evaporator, a pulsed laser, sputtering system, or spin coating system.

Understanding the growth mechanism of ZnO, that is, how the deposition of zinc and oxygen atoms onto the substrate happens, is key to being able to optimize its properties and produce good quality cells. Yet, little work has been done to understand the behaviour of zinc and oxygen atoms during the deposition of ZnO thin films. Magnetron sputtering is one of the most common and cost-effective ways to deposit thin films onto solar cells. Thus, the goal of this research was to study the relationship between the growth conditions and the properties of the thin film and develop a plausible model describing the formation of the ZnO layer by magnetron sputtering in order to fully optimize the films for applications. To do so, in this work we deposited the ZnO thin films on glass and silicon samples at varying
temperatures and analysed the properties of each film as a function of the growth temperature.

**Experimental Procedure**

ZnO thin films were grown on 2.54 cm x 2.54 cm square glass substrates by rf magnetron sputtering with a voltage of 200 V using an aluminium-doped ZnO (AZO) target (2.5 at. %). Doping ZnO with Al increases the donor-like defects in the film. This means that the material contains more electron traps shortening the distances electrons have to move to combine with another hole. This allows electron to move more easily, making the film more conductive [4]. Rf magnetron sputtering involves creating a plasma from argon gas using radio frequency (13.56 Hz) power of 100 W. Figure 1 illustrates the deposition process. The distance between the substrate and the target was 10 cm. The deposition time was 20 mins with 5 mins pre-sputter during which the substrate was covered by a shutter. The substrates were heated to different temperatures ranging from room temperature to 300 °C, the maximum attainable temperature in the system. The base pressure in the vacuum chamber was $1 \times 10^{-7}$ Torr. The argon pressure during deposition was 8 mTorr. Some of the films were grown with 1mTorr of O₂ gas to the plasma in addition to the argon.

**Results**

Several measurements were conducted to characterize each film, including conductivity measurements, thickness measurements, optical transmission measurements, and Zn to O ratio measurements using energy dispersive
spectroscopy (EDS). These are basic, commonly used technics of film characterisation for thin films.

The conductivity measurements were made using a four-point probe. In this method, four probes are aligned and equally spaced on the sample by a distance $r$. The resistivity $\rho$ of the film is determined by equation (1) where $I$ is the current between the two outer probes and $V$ is the voltage between two other [5].

$$\rho = 2\pi r \frac{V}{I} \tag{1}$$

The conductivity $\sigma$ is the inverse of the resistivity.

$$\sigma = \frac{1}{\rho} \tag{2}$$

This measurement is important because these ZnO thin films are intended for solar cell application, and it is important to ensure high enough conductivity so that the solar cells are optimized. Figure 2 shows low resistivity for all films grown with no systematic temperature dependence. There may be a slight overall increase as shown by the fit, but the scatter in the data was high so we do not see any real trend. The average resistivity of our films was of the order of $10^{-3} \, \Omega \cdot cm$ and studies have shown films with resistivities lower than $10^{-3} \, \Omega \cdot cm$ are of acceptable conductivity level for photovoltaic solar cell application. The film with the lowest resistivity of $1.05 \times 10^{-3} \, \Omega \cdot cm$ was grown at $130^\circ C$.

The thicknesses of the films were measured using a Tencor AlphaStep 200 model stylus profilometer. This apparatus measures the drop of a needle dragged across the edge of the films, giving the difference in height between the thin film and the glass substrate the film is on. The average thicknesses ranged from 2626.9 Å at
220°C to 4243.8 Å at 50°C. We found that the deposition rate decreased linearly with increasing temperature as shown in Figure 3.

A Beckman diode array spectrometer was used to take transmission measurements as a function of wavelength. For solar cell application, we want the films to be as transparent as possible in the visible part of the spectrum in order to maximize the light absorption in the absorber layer of the cell. Figure 4 shows examples of transmission graphs for a few films. For thin films grown above 100°C, the variation in the average transmission is subtle, but the transmission in the visible, between 400 nm and 700 nm, show a systematic increase in transparency with substrate temperature (Figure 5), indicating approach to stoichiometric (Zn:O = 1:1).

Finally, the zinc to oxygen ratio was determined by a scanning electron microscope (SEM) with an energy dispersive spectrometer attachment. This technique uses a beam of electrons that interact with an electrically conductive sample to detect the features of its topography as well as its composition by means of the x-rays emitted. The x-ray measurement was calibrated with a sample that we grew with an overpressure of O₂ at high temperature and assumed to be stoichiometric. Figure 6 shows the results of these measurements for thin films grown at 8 mTorr of argon only and for films grown with 1 mTorr of O₂ added. A perfect ZnO crystal would have a 1:1 ratio [6]. The results for both growth pressures indicate that the Zn to O ratio converges to 1 at high temperatures but is always greater than 1. This means that there are always more zinc atoms than oxygen atoms and this is consistent with the average transmission data, since
stoichiometric ZnO has a band gap of 3.3 eV and should be perfectly transparent in the visible (except for film interference effect). In the discussion section below we will present a simple model that accounts for the deposition rate and Zn/O ratio dependence on substrate temperature.

**Discussion**

We observed that the films were thinner when grown at higher substrate temperature. Figure 3 shows that there is about 600 Å of difference between films grown at 300°C and those grown at room temperature. A possible explanation of this behaviour seems to be linked to evaporation of the adsorbed zinc atoms. At higher temperatures, the zinc atoms evaporate from the substrate at increasing rate, and this limits the growth rate. This is supported by the higher Zn/O ratio at low temperatures, indicating that the Zn spends more time on the substrate before evaporating, increasing its probability to combine with an O atom, and thus incorporate into the film. Furthermore, the average Zn to O ratio of the films grown at higher O₂ pressure is closer to 1:1. This result agrees with the evaporation model: with the augmentation of the O concentration in the chamber, the chances of bonding before the surface Zn evaporates are higher. Figure 5 supports the fact that there is less Zn in the sample as the temperature is increased because the Zn renders the film less transparent and we noticed that the transmission decreased at lower temperatures.

Figure 6 illustrates a simple growth mechanism of the ZnO thin film during deposition. In step (1), the Ar atom from the plasma hits the AZO target. The
collision frees a Zn or an O atom, which then lands on the substrate surface. Once a Zn atom reaches the substrate, there are two possibilities: either the Zn atom bonds with an O atom (2) and is adsorbed into the film; or it evaporates off of the substrate (3).

The composition of the films is explained schematically in equations (3) and (4), showing the development between gaseous Zn, adsorbed Zn, oxygen, and solid ZnO:

\[
\text{Zn} \ (g) \rightleftharpoons \text{Zn} \ (\text{ad}) \tag{3}
\]

\[
\text{Zn} \ (\text{ad}) + \text{O} \ (g) \rightarrow \text{ZnO} \ (s) \tag{4}
\]

During the deposition, Zn in its gas form is converted to adsorbed Zn (on the substrate). As shown in Figure 7, this Zn (ad) can evaporate as Zn (g) or pair with O to form ZnO (s), which is incorporated to the film. When the temperature increases, Zn (ad) converts back into Zn (g) at a faster rate therefore there is less Zn (ad) to react with the O and create ZnO (s), resulting in a thinner ZnO layer on the substrate.

Additional recent research from the same lab, done as a continuation of the project, has provided more evidence for this behaviour. Zn-only films were grown using a pure Zn target as a function of substrate temperature. Instead of the film thickness, the deposition rate was evaluated using atomic absorption spectrometry because the films were too rough to measure using the stylus profilometer. The results are shown in Figure 8. Indeed, with no O, it is more difficult for the Zn to adhere to the substrate, resulting in a decrease in deposition rate with increasing substrate temperature.
Conclusion

By studying the effects of substrate temperature during deposition on the optical and electrical properties, we have developed a simple model that helps explain the growth kinetics of ZnO thin film by rf magnetron sputtering. The resistivities measurements helped ensure that the films had good electrical conductivity for solar cell application. The deposition rate, determined by the thickness measurements, established that the films were thinner when grown at higher temperatures. The transmission measurements also ensured that the films were transparent enough for solar cell application. The transmission measurements and the Zn/O ratio of the films showed that the percentage of Zn decreased when the substrate temperature was increased. It is proposed that several factors influence the growth mechanism of a ZnO thin film: the amount of Zn adsorbed onto the surface of the substrate, the amount of surface Zn evaporating from the substrate, and amount of O incident on the surface combining with the surface Zn to produce ZnO. As the temperature increases, there is less Zn (ad) for the O to react with, resulting in both a thinner film as well as a lower Zn to O ratio.

This is a study of one variable that affects the growth of the ZnO layer: the substrate temperature. For a more comprehensive and in-depth analysis of the growth mechanism, several other factors need to be considered, such as pressure of doping. Therefore, future work may include a study of the effect of additional O₂ pressure to get a more stoichiometric sample. It would also be interesting to look at the effect of argon pressure in the chamber on the deposition rate. Although the Al
doping concentration is very low, it might be informative to compare films grown using a pure ZnO target and those growth with an Al-doped ZnO target.

**Acknowledgements**

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References


**Figure Captions**

Figure 1. Sketch of vacuum chamber during deposition. The error bars represent the standard deviation of the mean.

Figure 2. Graph of average resistivity as a function of substrate temperature. The error bars represent the standard deviation of the mean.

Figure 3. Graph of average thickness as a function of substrate temperature

Figure 4. Transmission graphs for films grown at 50 °C, 130°C, 220°C, and 260°C

Figure 5. Graph of average transmission for wavelengths from 400 nm to 700 nm as a function of substrate temperature

Figure 6. Graph of Zn/O ratio as a function of substrate temperature

Figure 7. Sketch of model of ZnO thin film growth kinetics (explained in the discussion)

Figure 8. Graph of Zn-only deposition as a function of substrate temperature
Resistivity as a function of substrate temperature

Figure 2.
Figure 3.
Figure 4.
Average transmission as a function of substrate temperature

Figure 5.
Figure 6.
Figure 7.
Figure 8.