Zinc Oxide Deposition Methods for Opto-Electronic Applications

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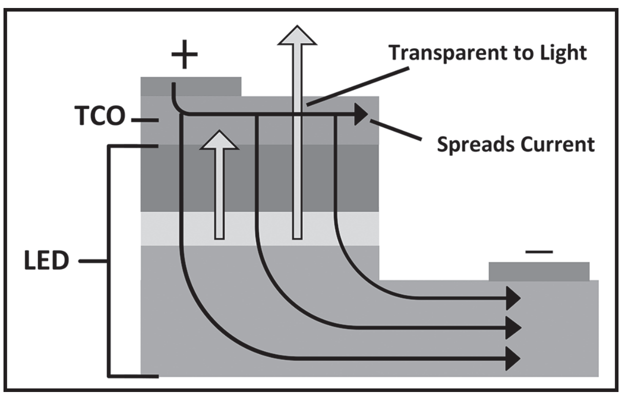
Abstract:

The purpose of this study is to investigate the feasibility of combining the atomic layer deposition (ALD) and hydrothermal deposition methods for growing zinc oxide (ZnO) thin films for opto-electronic applications. The main application considered throughout this study is the transparent conductive oxide (TCO) layer in gallium nitride (GaN) LEDs. The focus of this research was to maximize the optical transparency and minimize electrical resistivity of the grown ZnO films. A resistivity value as low as 2.75 milli-ohm centimeters (mΩ·cm) was obtained for ZnO, which is comparable to the measured resistivity of ITO, 1.09 mΩ·cm. Optical transmission measurements showed that a ZnO film with a thickness of 1.34 micrometer (µm) stays within around 10% of an ITO film with a thickness of 0.33 µm. Despite already yielding values comparable with ITO, the ZnO film performance can probably still improve since further optimizations can be made to the hydrothermal deposition process.



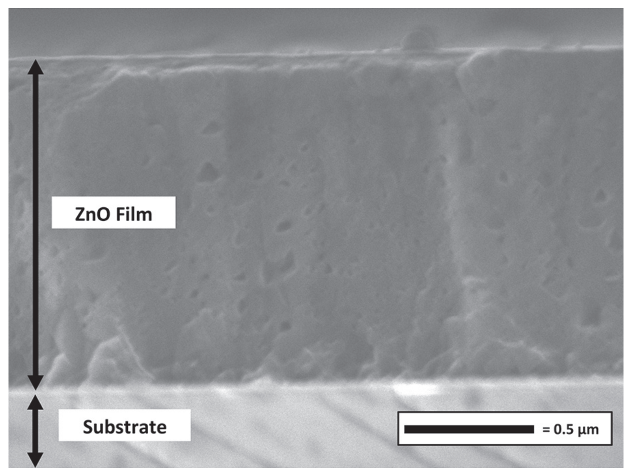


Figure 1, above: *Basic diagram of LED with TCO layer.*
Figure 2, right: *SEM image of ZnO film.*

Introduction:

Due to its relatively low cost, ZnO is receiving attention as a viable alternative to the current industry standard, indium tin oxide (ITO), for use as the TCO material [1]. The TCO layer is an essential component of opto-electronic devices because of its ability to spread current while also being transparent to light. Figure 1 shows a basic diagram of the TCO layer on an LED.

Numerous methods exist for depositing a thin film of ZnO onto a substrate, but several of these methods require expensive machinery and very controlled environments. Hydrothermal deposition, however, is a relatively simple method because it does not have these requirements [2]. The only prerequisite is a thin seed layer on which to grow the hydrothermal film, which is precisely grown using ALD. The main goal of the research this summer was to observe the electrical and optical performance of the ZnO films grown specifically using ALD and hydrothermal deposition. Figure 2 shows a scanning electron microscope (SEM) image of the ZnO thin film.

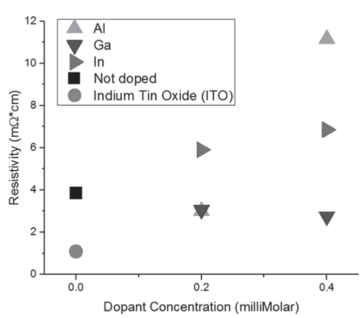
Process:

ZnO thin films were deposited on Al_2O_3 (sapphire) substrates in four steps: 1) ALD seed layer, 2) anneal treatment, 3) hydrothermal layer, and 4) final anneal treatment.

In the ALD seed layer step, diethylzinc was used as the zinc precursor, or source, and we found that using H_2O as the oxygen precursor, while running the process at 300°C, gave the highest quality seed layer structure with the highest conductivity. The standard number of cycles was chosen to be 25, which yielded a thickness of around 4 nanometers (nm). The self-limiting nature of ALD means that each cycle produces only single layers of a certain thickness; this makes ALD an excellent method for growing the seed layer.

The annealing (heat treatment) step had the best results when done at 700°C for 30 minutes in the presence of nitrogen gas. The hydrothermal deposition process was carried out in an aqueous solution heated to and held at 90°C for two hours. The standard solution used consisted of 1.3 milli-liters (mL) of NH_4OH, 25mL of 5 milli-molar (mM) $ZnNO_3$ and 5 mM of Na-Citrate. To help increase conductivity, the solution was also doped with aluminum (Al), gallium (Ga), and indium (In) before the hydrothermal process began. The amounts of dopants used ranged from 0.1 mM to 4 mM.

The main mechanism behind hydrothermal deposition is that as the temperature and pH level increases, the solubility of the aqueous solution decreases, and ZnO becomes more likely to form. First, the ionized zinc and



Material	Dopant (mM)	Resistivity (mΩ·cm)
ITO	**N/A**	**1.089**
Ga-ZnO	**0.4**	**2.75**
Al-ZnO	0.2	3.01
ZnO	N/A	3.86
In-ZnO	0.2	3.92

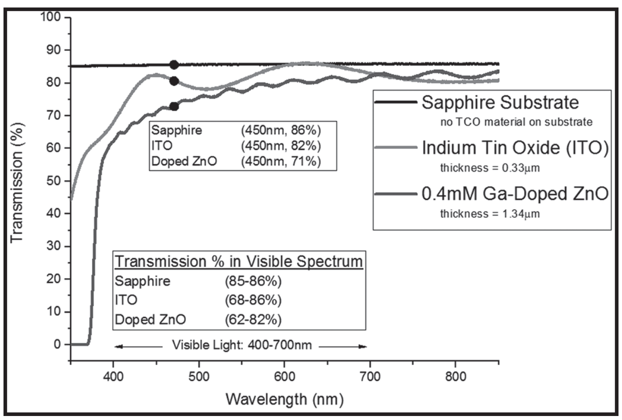


Figure 3, top: Left; Resistivity values vs. Dopant Concentration (lower resistivity means higher conductivity). Right; Table of lowest resistivity values for comparison.

Figure 4, bottom: Optical Transmission vs. Wavelength for the sapphire substrate alone, ITO, and doped ZnO.

hydroxide particles will form zinc hydroxide, and then the zinc hydroxide will dehydrate into zinc oxide and water.

Data:

Some of the best results recorded are shown in Figures 3 and 4. Figure 3 shows the different resistivity values of doped and undoped ZnO films compared to the measured resistivity of ITO. While ITO has the lowest resistivity at 1.089 mΩ.cm, one of the best results obtained for ZnO was with a 0.4 mM Ga-doped film. Other dopants and amounts seemed to increase the resistivity relative to the undoped ZnO film, which had a resistivity of 3.86 mΩ·cm.

Figure 4 shows the difference in transmission between a sapphire substrate without a film, ITO, and doped ZnO. Without any film, the substrate transmits around 85%. With a 0.33 micrometer (μm) thick ITO film, the transmission ranges between 68-86% in the visible spectrum. Despite being thicker, the 1.33 μm film of ZnO remains within 10% of the ITO film throughout most of the visible spectrum.

Conclusions:

This research confirmed that using the combination of ALD and hydrothermal deposition is a feasible method for growing ZnO, yielding optical and electrical performance comparable to the industry standard, ITO. However, there is still room for improvement. The hydrothermal deposition method needs to be investigated further to obtain a film with more transparency and a more controlled thickness. In addition, attenuation coefficients need to be obtained so optical performance can be accurately quantified independently of film thicknesses. Finally, LEDs need to processed to assess the actual light quality and efficiency.

Acknowledgements:

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