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High Vacuum PVD Technique for Enhancing ZnO Thin Films: Optical and Electrical Characterization

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ABSTRACT

This study explores the fabrication of high-quality zinc oxide (ZnO) thin films using a high-vacuum deposition process. ZnO, a material of significant interest due to its extensive applications, necessitates reliable deposition techniques. The research is segmented into three stages: sample preparation and cleaning, fabrication, and characterization. Soda lime glass (SLG) substrates were utilized, with metallic Zn deposited via physical vapor deposition (PVD) using electron beam deposition (e-Beam). Post-deposition, the Zn films were annealed at various temperatures to induce oxidation into ZnO. The resultant films were analyzed through UV-VIS spectrophotometry and Hall Effect measurements to assess their optical and electrical properties. The primary aim was to develop ZnO thin films using e-Beam technology in a high vacuum environment (1×10^{-5} Torr), with a novel focus on reducing annealing time for ZnO thin films at elevated temperatures under atmospheric pressure. Additionally, the study provides an in-depth understanding of the relationship between deposition parameters and film qualities, enabling precise tuning of ZnO thin film characteristics. This research holds significant potential for enhancing the performance of optoelectronic devices, such as solar cells and LEDs. The controlled deposition method established here can be commercialized, facilitating the mass production of high-quality ZnO thin films with tailored properties to meet the growing industrial demand.

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Keywords: Zinc Oxide (ZnO); High-Vacuum Deposition; Electron Beam Deposition (e-Beam); Optical and Electrical Properties; Physical Vapor Deposition (PVD)

INTRODUCTION

Nanostructured materials have attracted great interest due to their properties and versatile applications in various fields such as materials science, electronics, optics, catalysis, and medicine. Among these materials, zinc oxide (ZnO) is particularly characterized by its flexibility and cost-effectiveness. It is used in semiconductor components and LCD cameras. Nanostructured materials have attracted great interest due to their properties and versatile applications in various fields such as materials science, electronics, optics, catalysis, and medicine. Among these materials, zinc oxide (ZnO) is particularly characterized by its flexibility and cost-effectiveness. It is used in semiconductor devices, LCD coatings, zinc-air battery anodes, cosmetics and more. Recently, the scientific community has recognized ZnO as the material of the future due to its low cost compared to other alternatives [1].

ZnO is an n-type semiconductor with a band gap energy of 3.37 eV, a remarkable exciton binding energy of 60 MeV and a high optical transparency at room temperature, typically in the range of 20 to 27 °C [2]. In addition, ZnO exhibits strong electrochemical stability, high thermal stability, and good stability in hydrogen plasma. Previous studies have emphasized the stability of ZnO thin films, which makes them extremely attractive for various applications [1, 3].

The aim of this study is to evaluate the optical and electrical properties of ZnO thin films fabricated using Physical Vapor Deposition (PVD) in a high vacuum environment. Ultraviolet-visible (UV-Vis) spectroscopy is used to extensively analyse the optical properties of the ZnO thin films. This technique enables the measurement of the optical bandgap energy, dispersion parameters, and complex dielectric constants related to the composition and bonding state of the material. Hall Effect measurement technique is employed to characterize the electrical properties of ZnO, offering valuable information about carrier mobility, carrier concentration, Hall coefficient, resistivity, magnetoresistance, and conductivity type. By conducting this research, the aim is to manipulate and improve the material properties of ZnO, particularly its optical and electrical characteristics.

The advancement of several technical disciplines, such as electronics, optics, and renewable energy, relies heavily on the development of thin films that are high-performing, cost-effective, and ecologically friendly. ZnO, due to its distinctive optical and electrical properties, shows great potential for applications in solar cells, gas sensors, and transparent conductive electrodes. However, fabricating high-quality ZnO thin films with optimal performance characteristics remains a challenge. Conventional fabrication methods often encounter issues such as low material utilization efficiency, poor film uniformity, and environmental concerns [4].

Physical vapour deposition (PVD) in a high vacuum system has proven to be a promising technique to overcome these challenges as it allows precise control over the thickness and composition of the film [5]. This enables the production of films with high purity and exceptional properties. Due to its numerous desirable properties for practical use, there has been a strong focus on the synthesis of ZnO thin films in recent decades. To date, ZnO thin films have been produced using various methods such as pulsed laser deposition (PLD), magnetron sputtering, molecular beam epitaxy and chemical vapour deposition. However, the reactive e-beam evaporation technique has received less attention in the study of ZnO thin films, although it offers significant potential to produce ZnO in a high vacuum environment. This technique allows precise energy control and a high rate of material deposition, which can lead to a significant improvement in the quality and uniformity of the films [6]. Nevertheless, the application of e-beam PVD for ZnO thin films has not yet been fully explored, especially regarding optimising the deposition parameters for improved optical and electrical properties.

METHODOLOGY

Substrate Preparation

In this study, a 30 mm × 30 mm soda lime glass (SLG) was utilized as the substrate for ZnO. The SLG substrates underwent an initial rinsing with distilled water to remove any oil residue left by the factory, thereby preventing contamination. Subsequently, the SLG was immersed in methanol within a beaker, ensuring complete coverage. The beaker was then placed in an ultrasonic bath maintained at a temperature of 35°C for a duration of 15 minutes, facilitating thorough cleaning. Following ultrasonic treatment, the methanol residue on the substrate was removed by rinsing with distilled water. Finally, the substrates were dried using a stream of nitrogen gas.

Fabrication Process

The cleaned glass substrates from the previous process were inserted into the e-beam chamber. High-purity Zinc pellets (99.99%) were carefully placed inside the graphite crucible, while the glass substrates mounted on the substrate holder inside the chamber. The chamber door was then securely closed to commence the vacuum process. This continued until the pressure inside the chamber reached 1.1×10^{-5} Torr. At this point, the fabrication process began with the voltage set to 7kV and the current set to 1mA. The current was gradually increased until it reached 2mA. Additionally, the rotation speed of the substrate holder was set to 8 rpm. An electric current and magnetic fields were applied to the electron gun, which produced kinetic energy for the electron beam to target the zinc. The zinc was heated and evaporated inside the chamber. This caused the vaporized Zn particles to coat the surface of the substrate when the thermal energy was less than 1 eV and the distance between the substrate and the material ranged from 0.3 m to 1 m. The Thermal Evaporating System, model LES-100 by LAT Co. Ltd, was used for the e-beam process. Prior to operation, the chiller was activated to prevent the machine from overheating, ensuring the stability and reliability of the deposition process.

Annealing Process

Recent studies have investigated the effects of heat treatment on ZnO thin films. Annealing in air generally improves crystallinity, increases grain size, and enhances optical properties [7]. For this study, the annealing process took place in a rapid thermal annealing. The ZnO thin film were annealed at various temperatures ranging from 200°C to 600°C. The ramp rate to reach the desired annealing temperatures varied for each target temperature: 25°C/min to 300°C (12 minutes), 26.7°C/min to 400°C (15 minutes), 29.4°C/min to 500°C (17 minutes), and 30°C/min to 600°C (20 minutes). All samples were subsequently annealed at their respective temperatures for 60 minutes. Afterward, the sample was cooled down for 10 minutes before the sample was taken out to be characterized.

Characterization

The optical properties of the ZnO thin film, including its transmission spectrum and energy band gap, were investigated using Perkin Elmer Lambda 1050+ UV-VIS spectrophotometer in the 250-800 nm range, which covers the visible light spectrum. Prior to the measurements, the spectrometer was calibrated using SLG as the reference, commonly known as the 'blank sample.' To ensure the accuracy of the results, the glass substrate underwent thorough cleaning to eliminate any potential impurities.

The electrical properties of the ZnO thin film were examined using the Ecopia HMS-3000 Hall-effect Measurement System. The ZnO thin films were cut into 1 cm × 1 cm samples using a diamond cutter due to space constraints. The samples were then cleaned, and silver paste was applied to each corner. The Hall voltage, carrier mobility, resistivity, and other relevant parameters of the ZnO thin films were recorded using specialized software. To validate the accuracy of the measurements, the magnetic field was periodically reversed, and any changes in the voltage readings were noted. Multiple measurements were conducted to ensure the reliability and precision of the results.

For the morphology study, The Energy Dispersive X-Ray Spectroscopy (EDX) technique was employed to investigate the elements composition of the ZnO thin film. The Tescan Vega 3 scanning electron microscope (SEM) has been utilized for this work to provide a comprehensive list of elements along with their corresponding atomic weight percentages for thin films.

RESULTS AND DISCUSSION

UV-VIS Spectrometer

The optical transmissions of ZnO thin film have been studied using UV-VIS spectrophotometer. Figure 1 presents a comparative graph showing the transmittance (%) of Zinc Oxide (ZnO) films with a wavelength range of 300 nm to 800 nm after annealing at 200°C, 300°C, 400°C and 500°C, alongside reference data for standard low iron soda-lime glass (SLG). The SLG line, represented in gray, remains relatively high and stable above 90% across the entire wavelength range, serving as a benchmark for evaluating the transmittance of the ZnO films.

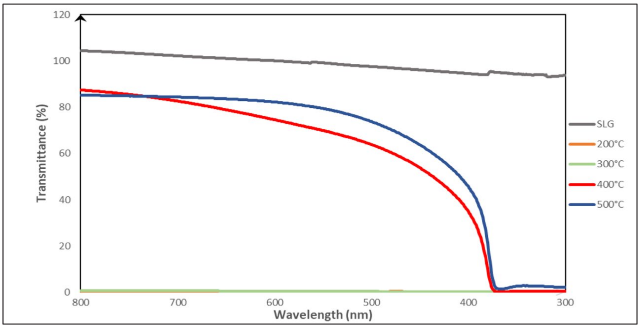

Figure 1: Transmittance spectra of ZnO thin films annealed at 200, 300, 400 and 500°C

At 200°C, depicted by the orange line, the transmittance of the ZnO film is very low, remaining close to zero across the entire wavelength range. This indicates that the film is highly opaque at this annealing temperature, suggesting poor crystallinity and a high density of defects. Similarly, at 300°C, represented by the green line, the transmittance remains very low, indicating that the film continues to be opaque. Although there is a slight increase compared to 200°C, it is not significant enough to impact the optical properties, indicating only minimal structural changes.

A notable improvement is observed at 400°C, shown by the red line.

Here, the transmittance starts higher in the visible range (around 800 nm) and decreases as the wavelength shortens, with a significant drop around 400 nm. This indicates a substantial improvement in transparency in the visible range, suggesting better crystallization and fewer defects in the ZnO film [8, 9]. The trend continues at 500°C, represented by the blue line, where the transmittance follows a similar pattern to 400°C but with overall higher transmittance across the visible spectrum. This suggests further enhancement in film quality, with better crystallinity and reduced defect density [9]. The results obtained from this measurement indicates that ZnO thin films annealed at higher temperatures (400°C and 500°C) show higher transmittance in the visible range compared to lower annealing temperatures (200°C and 300°C) [9, 10].

The physical appearance of the ZnO films at different annealing temperatures, as shown in Figure 2, further support the findings from the UV-VIS measurements. The visual changes observed in the films with increasing temperature align with the improvements in optical and electrical properties. At lower temperatures, the films appear opaquer and less uniform, while higher temperatures result in clearer and more homogeneous films. These visual observations provide tangible evidence of the effect of annealing temperature on film morphology, supporting the quantitative measurements obtained from UV-VIS spectroscopy.

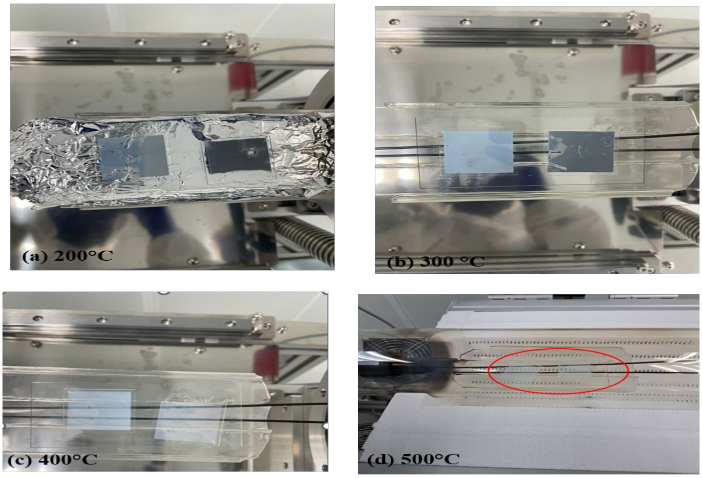

Figure 2: Physical appearance of the ZnO films at temperature of (a) 200°C, (b) 300°C, (c) 400°C and (d) 500°C

Hall Effect Measurement

The electrical parameters of ZnO films annealed at varying temperatures (200°C, 400°C, and 500°C) as determined by the Hall Effect method are presented in Table 1. The parameters consist of resistivity, conductivity, and mobility.

At an annealing temperature of 200°C, the ZnO film exhibits an extremely low resistivity of 8.22×10^{-5} Ω·cm, indicating a highly conductive film. Whereas the value of conductivity is high at 1.22×10^{4} 1/Ω·cm, suggesting efficient electron transport within the film, which can be attributed to the material's inherent n-type semiconductor behaviour and the formation of a high-quality crystalline structure with minimal defects. Furthermore, the very high carrier mobility of 9.25×10^{3} cm²/V·s points to minimal scattering of charge carriers, further supporting the notion of a high-quality crystalline structure with few defects [11].

Table 1: Electrical Parameters of ZnO Thin Films at Different Temperatures. The parameters include resistivity, conductivity, and mobility

Label	Hall Effect Measurement		
	Resistivity (Ω cm)	Conductivity (1/Ω cm)	Mobility (cm^2/Vs)
Zn 200	8.22×10^{-5}	1.22×10^{4}	9.25×10^{3}
Zn 400	6.62×10^{2}	1.51×10^{-3}	1.42×10^{1}
Zn 500	1.00×10^{2}	9.98×10^{-3}	4.06×10^{-1}

Interestingly, as the annealing temperature is increased to 400°C, a significant change occurs in the film's properties [12]. The ZnO film annealed at 400°C exhibits a significantly higher resistivity of 6.62×10^{2} Ω·cm, indicating a reduction in conductivity. The lower conductivity of 1.51×10^{-3} 1/Ω·cm suggests that the film's electron transport efficiency has decreased, possibly due to structural changes or an increased defect density at this higher annealing temperature. Additionally, the mobility drops drastically to 1.42×10^{1} cm²/V·s, implying increased scattering of charge carriers, possibly due to structural changes or a higher defect density at this temperature.

The ZnO film annealed at 500°C shows a lower resistivity of 1.00 x 10^2 Ω·cm compared to the 400°C sample, but it is still significantly higher than the 200°C sample. As for the conductivity, its value improves to 9.98 x 10^{-3} 1/Ω·cm, suggesting a recovery in electron transport efficiency. However, the mobility of 4.06 x 10^{-1} $cm^2/V\cdot s$, while higher than the 400°C sample, remains much lower than the 200°C sample, indicating moderate carrier scattering and a less-than-optimal crystalline structure [13].

Energy Dispersive X-Ray Spectroscopy (EDX)

Table 2 presents data from Energy Dispersive X-ray (EDX) spectroscopy for ZnO thin films annealed at temperatures of 300°C, 400°C, and 500°C. The key elements of interest are Zinc (Zn) and Oxygen (O), as they form the ZnO thin film.

Table 2: The normalized atomic (%) for ZnO thin films at temperature of 300°C, 400°C and 500°C extracted from EDX analysis

Element	300°C	400°C	500°C
	Atomic (%)	Atomic (%)	Atomic (%)
O	68.26	77.54	87.58
Zn	31.74	22.46	12.42

At 300°C, the atomic percentage of oxygen is 45.83%, suggesting the film has a significant amount of oxygen but might not be fully optimized for ZnO formation, potentially indicating incomplete oxidation or the presence of other phases [13, 14]. Zinc is present at an atomic percentage of 21.31%. This indicates that there is a considerable amount of zinc in the film, which, combined with the oxygen content, suggests the formation of ZnO, but possibly with some deficiencies or excess zinc leading to defects [15]. The atomic percentage of oxygen increases to 53.95% at 400°C. This rise indicates better incorporation of oxygen into the film, likely improving the ZnO stoichiometry and suggesting enhanced oxidation and reduced defects compared to the 300°C sample [16]. Zinc's atomic percentage decreases to 15.63% at this temperature. This reduction, in conjunction with the increased oxygen content, suggests a more stoichiometrically balanced ZnO film, implying improved film quality with fewer excess zinc atoms and better crystallinity. At 500°C, the oxygen content further increases to 57.49%, indicating an even more optimized ZnO structure, with ample oxygen to bond with zinc and form a high-quality film with fewer oxygen deficiencies. The zinc atomic percentage drops significantly to 8.15%. This substantial decrease is indicative of a well-formed ZnO film where most of the zinc has bonded with oxygen. The high oxygen content and lower zinc percentage suggest that the film at this temperature has the best stoichiometry and is likely the most crystalline and defect-free of the three samples.

The EDX spectroscopy data reveals a clear trend in the composition of the ZnO thin films with increasing annealing temperature. At 300°C, the film has a moderate amount of oxygen and a high amount of zinc, indicating potential deficiencies in the oxide structure. As the temperature increases to 400°C, the oxygen content rises and zinc content decreases, suggesting improved film quality with better stoichiometry. By 500°C, the film exhibits the highest oxygen content and the lowest zinc content, indicating an optimal ZnO formation with reduced defects and better crystallinity. These changes in elemental composition with temperature correlate well with the improvements observed in the optical and electrical properties of the ZnO films, as discussed in previous sections. The higher oxygen content and reduced zinc percentage at elevated temperatures suggest enhanced film quality, making the ZnO thin films annealed at 500°C the most suitable for applications requiring high transparency and good electrical properties [17].

There is a significant trade-off between transparency and conductivity in ZnO thin film to qualify as good transparent conductive oxide (TCO). Increasing the carrier concentration to improve conductivity could affect transparency. However, it can be mitigated by optimizing the doping concentration during the fabrication process [18].

CONSLUCIONS

The ZnO thin films were successfully fabricated on the entire glass substrate using the PVD technique in a high vacuum system, followed by an annealing process to activate oxidation. This study focused on investigating the optical and electrical properties of thin films. Optical characterization by UV-Vis spectroscopy revealed that the ZnO thin films exhibit high transmittance in the visible wavelength range, making them an excellent choice for transparent conductive oxides. Electrical parameters obtained from Hall effect measurements indicate that the ZnO thin films have a favorable resistivity, which can be tuned by the controlled conditions during deposition. The observed variations in electrical properties can be attributed to the interplay between crystal structure, defect density and the influence of annealing temperature on the ZnO thin films. These properties are decisive for ZnO being a good semiconductor material for the integration of thin films in electronic devices. In summary, this research highlights the effectiveness of the high vacuum PVD method in producing high quality ZnO thin films with desirable optical and electrical parameters. These results improve our understanding of ZnO thin film deposition and can serve as a reference for future work, such as doping ZnO with different elements to tailor its properties and improve performance for specific applications. The application of ZnO thin films also has the potential to expand knowledge in the field of advanced technology and nanomaterials.

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