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Electrical and Optical Properties of Boron Doped Zinc Oxide Thin-film Deposited by Metal-organic Chemical Vapour Deposition for Photovoltaic Application

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Authors' contributions

This work was carried out in collaboration between the two authors. Both authors contributed equally in this study, read and approved the final manuscript.

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ABSTRACT

Globally, there is a high demand for clean, sustainable and renewable energy for domestic and industrial use. Conventional photovoltaic cell technology relies heavily on crystalline silicon wafers which render silicon-based solar cells expensive due to the initial cost of production and required complex deposition methods. Due to these challenges, great research interest is now directed towards thin-film solar cells. In this work, the metal-organic chemical vapour deposition (*CVD*) method was chosen in the preparation of boron-doped zinc oxide (ZnO: B) thin film onto a glass slide substrate. The prepared ZnO: B thin films were characterized and optimized as a window

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layer for solar light trapping. The transmittance of the ZnO: B films varied between 70% and 81% for boron concentration ranging from 0.0 M to 0.06 M. With the increase in boron concentration, bandgap and resistivity of the ZnO: B varied from 2.96 to 3.72 eV and 120 Ω-cm to 58 Ω-cm, respectively. Based on the results obtained, we believe that ZnO: B is suitable as a window layer for solar light trapping in the fabrication of a photovoltaic cell.

Keywords: Metal-organic chemical vapour deposition; ZnO: B; optical properties; electrical properties; photovoltaic cell.

1. INTRODUCTION

Solar energy is the principal source of energy due to its abundance. However, in most cases, it goes to waste. The solar energy can be harnessed using a photovoltaic cell to produce reliable power for domestic use [1]. The photovoltaic cell is a transducer that converts light energy into electric energy by photoelectric effect [2]. A working photovoltaic cell was developed by utilizing a semiconductor of aluminium with a gold window layer to obtain a *p-n* junction [3]. By 1956 the cell enhanced effectiveness in terms of power conversion efficiency had improved to about 1% [4]. Since then, a lot of effort has been directed to research on thin films and as a result, different thin-film innovations undergoing development today are majorly targeted at decreasing the material's size for light absorption, subsequently lowering processing costs.

Among the wide range of photovoltaic cells, boron-doped zinc oxide ZnO: B cells have been broadly examined [5]. However, efficiencies are still very low [6]. The ZnO is small in size and light in weight, they are also easily fabricated [7]. Also, the ZnO has a wide range of applications in electronic circuits such as radiation detectors and solar cells hence, researchers have focused on the improvement of its electrical properties [8], optical properties of undoped [9] and doped [10] ZnO films to deliver photovoltaic cells with high efficiency. Mostly, the ZnO thin films are preferred as a window layer in the fabrication of solar cell because of their high transparency and wide bandgap [11]. Sulphur vacancies cause changes from stoichiometry amid its development, consequently, the quality of the surface relies upon the technique utilized and the films must be free from defects [12].

Different deposition methods such as metal-organic chemical vapour deposition (*CVD*), vacuum evaporation, splash techniques among others have been used to get quality photovoltaic cells [13]. Notably, every strategy has some limitations. For instance, stoichiometric ZnO is hard to get through the thermal evaporation method while high temperatures are required in spray deposition. Boric acid as a source of a dopant in ZnO was investigated using metal-organic chemical vapour deposition (*CVD*) [14]. The resistivity of the ZnO: B films decreased substantially showing a minimum value of about 0.02 Ωm and an improved transmittance within the visible region (380nm-780nm). In another work, ZnO/Cu_xS thin-film photovoltaic was deposited using the chemical spray method. It was observed that the thickness of the film, grain size, spectral responses, structure, photovoltaic response, and current-voltage (*I-V*) characteristics depended on preparation techniques [15]. Vacuum evaporation procedure was also in another study to deposit ZnO on a glass substrate [16]. From the deposited ZnO thin film, the resistivity at 200^oC was 1.5 Ωm with a $1x10^{21}$ m^{-3} carrier concentrations and 6×10^{-4} m^2 v^{-1} s^{-1} mobility. Additionally, high vacuum deposition technique was utilized to deposit ZnO: Cl films in which a combination of ZnO and $CdCl_2$ powders with different concentrations of the dopant at room temperature were used [17]. The films showed that the chlorine doping and annealing improved the electrical properties.

From the above reports, it is evident that limited studies exist on ZnO: B thin film deposited by metal-organic chemical vapour deposition (*CVD*) for photovoltaic application. In this work, therefore, the optical and electrical properties of the ZnO: B deposited by metal-organic chemical vapour deposition (*CVD*) will be investigated and characterized for photovoltaic applications.

2. MATERIALS AND METHODS

Metal-organic chemical vapour deposition (CVD) technique was used for the deposition of ZnO: B. Ammonium hydroxide (NH_4OH)served both as a complexation agent, as well as providing the alkalinity required of the required solution (Hu et al. 1992). The complexing agent and alkalinity of the solution are provided by the solution of ammonium hydroxide as illustrated by equation Eq. (1).

$$NH_3 + H_2O \rightarrow NH_4 + OH^- \quad (1)$$

2.1 Cleaning of Substrate

Glass slides were used as a substrate for the deposition of thin films. Before deposition, the glass slides were cleaned by a liquid detergent before being dipped in ethanol for 10 minutes to remove grease. Afterwards, the glass slides were soaked in 100^{o}C hydrochloric acid for nucleation centres to be created. Finally, the glass slides were cleaned with distilled water for around 15 minutes and then dried at a temperature of 200^{0}C.

2.2 Deposition of Zno: B Thin Films

Solutions of 0.038 M $Cd(NO_3)_2$, 0.076 M NH_4OH and 0.076 M urea were prepared and mixed. 15 ml of each solution was taken into different measuring glass beakers, and distilled water was added to top the volume to 100 ml. This mixture was heated to a temperature of 78^{o}C. Using a burette, 29% NH_4OH was added slowly until a pH of 9 was reached, which was maintained throughout for each film deposited. Then, 10 ml boric acid (H_3BO_3) of varying concentrations (0.0, 0.02, 0.04, 0.06, 0.08 to 0.1 M) was added to the 100 ml solution to vary boron as a dopant for each film prepared. The deposition temperature was maintained at 82^{0}C for 55 minutes under continuous stirring. The films were characterized after annealing at a temperature between 200^0 C and 300^{0}C.

2.3 Optical and Electrical Characterization of the ZnO: B Thin Films

Once the thin films were prepared, their optical properties within the 380 nm-780 nm range of wavelengths were measured using UV-NIR VIS spectrophotometer 3700 DUV and recorded. Simulation of transmittance data was done to obtain optical constants such as refractive index (n) and bandgap energy (E_g). The E_g was calculated from the allowed direct transition given by Eq. (2) [18].

$$\alpha h\nu = \left(h\nu - E_g\right)^{\frac{1}{2}} \quad (2)$$

where α is the absorption coefficient, *h* the Planck's constant, v the photon frequency and E_g the bandgap energy.

Also, the electrical resistance of the ZnO: B at boron concentration ranging from 0.0 M to 0.1 M, were analysed. The sheet resistivity (ρ) was experimentally determined by utilizing a four-point probe (Fig. 1). The current was set through the external probes 1 and 4 and instigates a voltage in the internal voltage probes 2 and 3.Using the current and voltage readings from the probe, sheet resistivity, ρ was calculated using Eq. (3).

$$\rho = \frac{\pi}{\ln(2)}\left(\frac{V}{I}\right)t \quad (3)$$

Where,

$\frac{\pi}{\ln 2} = 4.532\,t$ is sample thickness.

3. RESULTS AND DISCUSSION

3.1 Optical Properties of the ZnO: B Thin Film

3.1.1 Transmittance

The optical transmittance of the ZnO: B thin films increased as boron concentrations increased (Fig. 2). The increase is attributed to an

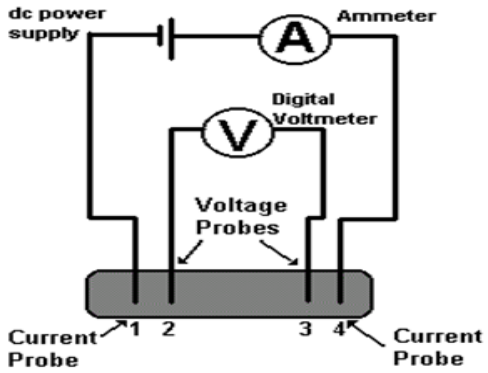

Fig. 1. Four-point probe sheet resistivity measurement apparatus

improvement in film homogeneity [19]. Therefore, doping ZnO with boron the transparency of the deposited film. The transmittance values obtained in this work are in agreement with a previous study [14] in which the values were around 80%. Lower transmittance was also obtained in the wavelength above 450nm in another previous study [20]. At a wavelength of about 600 nm transmittance starts to decrease as a result of the uneven surface of the thin films [21].

The average transmittance curve of ZnO: B samples within the visible region (380-780 nm) obtained is shown in Fig. 3. It was observed that the highest average percentage transmittance within the visible region of the deposited film was 81.38 **±** 0.41 %. Transmittance varied with an increase in boron concentration and had its maximum value at 0.06 M. This was due to the reduction of voids within the ZnO sample as well as improvement of the crystallinity and homogeneity of the films. Above the 0.06M boron concentration, the average transmittance decreased probably due to decreases in film crystallinity [22].

3.1.2 Reflectance

The ZnO: B thin films prepared with a boron concentration of 0.02 M had the highest reflectance at around 450 nm and decreased sharply above 500 nm (Fig. 4). Also, it was observed that reflectance increased for the wavelength range of 0-400nm. Boron ions in ZnO lowered reflectance values of ZnO films. This may be attributed to the formation of ZnO nanocrystals [23]. [24] carried a similar study on ZnO for the wavelength ra nge of 400-1000 nm and obtained reflectance below 55% which is in agreement with this work.

3.1.3 The bandgap of ZnO: B

The bandgap (E_g) energy was obtained by extrapolating the linear part of the curve $(\alpha h\nu)^2$ which intercepts the energy axis, as described in Tauc-Laurentz relation (Eq. (3)). In this work, E_g ranging from 2.96 - 3.72 eV was obtained (Table 1). Also, the simulation was done using scouts' software of transmittance normalized data and the E_g values ranging between 3.01 and 3.69 eV were also obtained which are similar to those obtained by Tauc-Laurentz relation. It was observed that the E_g increased with an increase in boron concentration in the ZnO, up to 0.06 M. This increase in band gap is attributed to the Burstein- Moss effect. As boron concentrations increases, the fermi-level is shifted into the conduction band. The dopant B^{2+} ions cause an increase in free carrier concentration; this lifts Fermi level up into the conduction band leading to an increase in the [12]. Beyond the 0.06 M, the bandgap decreased which can be attributed to the formation of defects as a result of too much dopant. Earlier measurements were done on ZnO yields E_g of 2.5 - 2.7 eV which agrees with our results [25]. Also, E_g of 2.5 - 3.0 eV were obtained under the same deposition condition as in our study [20]

3.1.4 Refractive Index (*n*)

The average refractive index (*n*) reduced to a minimum value of 1.44 when boron concentration was 0.06 M (Fig. 5). The presence of a boron dopant enhances the transparency of the films and it was optimum at 0.06 M. After the 0.06 M, the *n* increased. This was as a result of a decrease in transparency of the deposited films. It is also observed that the values of *n* reduce as the boron concentration increases up to the optimum concentration of 0.06 M and then increases (Fig. 5). Boron concentration enhances the transparency of the deposited thin films [25].

3.1.5 Electrical properties of Zno: B thin film

The resistivity of ZnO: B thin film decreased with an increase in boron ions to a minimum resistivity of 58±0.5 Ω-cm obtained at 0.06 M boron concentration (Fig. 6). Boron substitutions in ZnO improved its crystallinity [15]. After the 0.06 M boron concentration, the resistivity increased due to a reduction in both carrier concentration and carrier mobility [26]. In our work, the ranges of electrical resistivity observed were 70.0 Ω-cm to 120 Ω-cm. Using a spray pyrolysis method, a resistivity of 10^3 Ω-cm was reported [27]. The huge difference can be attributed to the low purity of the chemicals used.

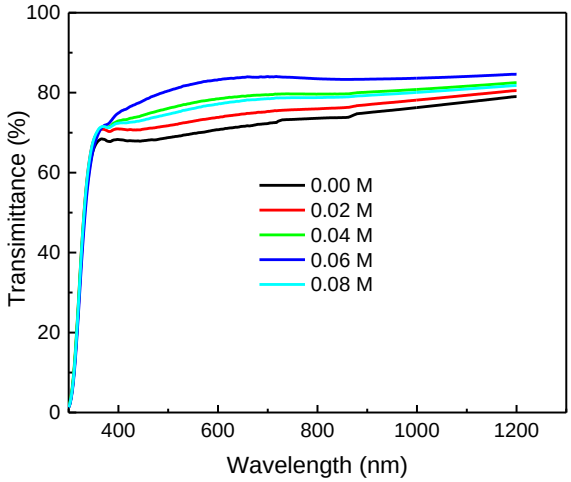

Fig. 2. A graph of transmittance against wavelength for ZnO: B films deposited at different boron concentrations

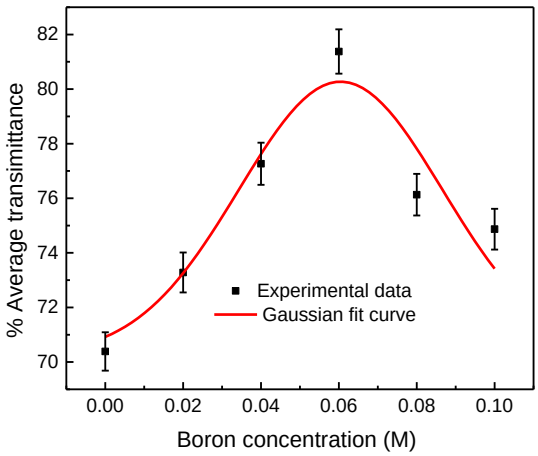

Fig. 3. Graph of average transmittance (%) against boron concentration (mol/l)

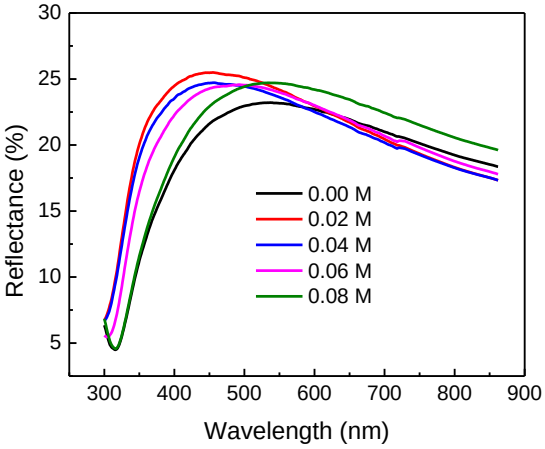

Fig. 4. Graph of reflectance against wavelength for ZnO: B films deposited at different boron concentrations

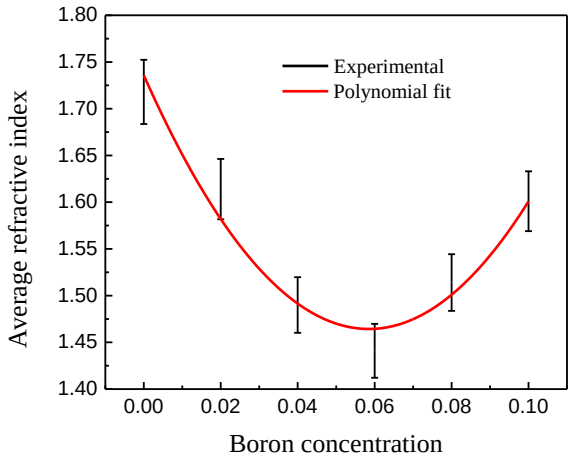

Fig. 5. A graph of the average refractive index against boron conc. (mol/l)

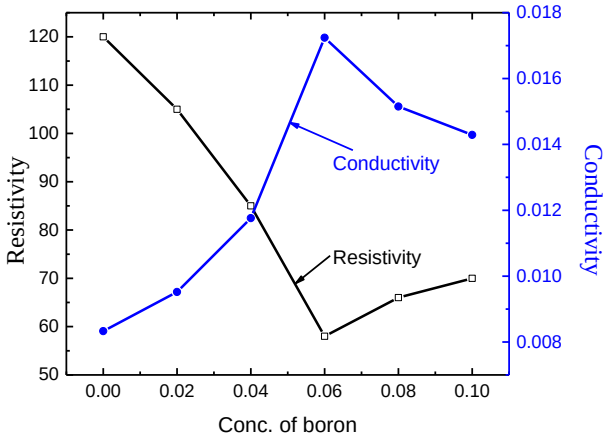

Fig. 6. Plot of conductivity and resistivity against the concentration of boron ions

Table 1. Energy band gaps at different boron concentration (mol/l)

The concentration of Boron in ZnO (mol/l)	E_g (eV) Tauc L.R	E_g (eV) Simulation
0.00	2.96 ±0.04	3.01 ±0.09
0.02	3.29 ±0.03	3.31 ±0.04
0.04	3.52 ±0.02	3.48 ±0.06
0.06	3.72 ±0.02	3.69 ±0.04
0.08	3.50 ±0.02	3.46 ±0.04
0.10	3.05 ±0.01	2.91 ±0.07

4. CONCLUSIONS

Metal-organic chemical vapour method was successfully used to deposit ZnO: B thin films. Electrical and optical properties of the deposited ZnO: B thin films were investigated for photovoltaic applications. The ZnO: B thin films had an average transmittance of 70-81% within the visible region. The E_g was found to between 2.96-3.72 eV. Electrical conductivity increased from $8.33x10^{-2}$ -$1.72x10^{-1}$ $[\Omega\text{-cm}]^{-1}$ as concentration of boron increased from 0.0-0.06 M. Presence of borons substitutions in ZnO improved the homogeneity of the thin films. The results of this work indicate that ZnO: B thin films can be used as a window layer in the fabrication of photovoltaic cell.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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