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Investigation of Optical Parameters of Different Rates Al doped ZnO by Electrochemical Deposition

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In this study, pure ZnO and Al-doped ZnO thin films with different doping ratios were fabricated using the electrochemical deposition method, and their fundamental optical parameters were examined in detail. The Al doping ratios were set to 2.5%, 5%, 7.5% and 10%. The wavelength range selected for optical analysis was 300–700 nm. Accordingly, all Al-doped ZnO thin films exhibited higher absorption compared to the pure ZnO film, with the maximum absorption observed for the 2.5% Al-doped ZnO thin film. As the doping ratio increased, the absorption decreased. The incorporation of Al reduced the transmittance of the ZnO thin films. The average transmittance values of ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films were 95%, 79%, 82%, 83% and 83%, respectively. The optical band gap (Eg) of the Al-doped ZnO thin films was higher than that of the pure ZnO thin film. The Eg values for ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO and 10% Al-doped ZnO thin films were 3.51, 4.01, 4.00, 3.99 and 3.98 eV, respectively. The highest extinction coefficient (k) for all films was observed at 300 nm. While the k value of the pure ZnO film at 300 nm was 0.004, the corresponding values for 2.5%, 5%, 7.5% and 10% Al-doped ZnO thin films were 0.046, 0.039, 0.039, 0.041 and 0.043, indicating that k increased nearly tenfold with Al doping. For all thin films, the maximum refractive index (n) was also observed at 300 nm, and the n values decreased with increasing wavelength. At 300 nm, the refractive index of the pure ZnO film was 1.124, while the values for 2.5%, 5%, 7.5% and 10% Al-doped ZnO films were 1.338, 1.322, 1.328 and 1.333, respectively. Additionally, the optical conductivity (σ), real dielectric constant (ϵr), imaginary dielectric constant (ϵi), and dielectric loss (ϵi/ϵr) of the films were determined. All these parameters decreased with increasing wavelength but increased compared to the pure ZnO film. The maximum values were obtained for the 2.5% Al-doped ZnO thin film.

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1. Introduction

Zinc oxide (ZnO), a transparent metal oxide that has attracted significant attention in recent years, is a promising semiconductor material [1-4]. At room temperature, ZnO exhibits a wide band gap along with a large exciton binding energy of about 60 meV.[5]. Its band structure and optical properties closely resemble those of GaN, which is well known as a suitable material for optical device fabrication. These similarities indicate that ZnO is one of the promising candidates for such applications [6]. Due to their extensive electrical and optical properties, ZnO thin films have gained considerable importance in a wide range of technological applications. It has been demonstrated that pure ZnO and Al-doped ZnO thin films exhibit high optical transmittance and electrical conductivity in the UV, VIS, and NIR regions [7]. A number of approaches, including the sol–gel method, have been reported for the preparation of Al-doped ZnO thin films [8, 9], pulsed laser deposition [10], spin coating [11], RF sputtering [12], sub-molecule doping [13], and chemical vapor deposition[14]. However, the equipment and processing steps required for these techniques tend to be relatively complex and are generally not suitable for producing large-area films. Electrodeposition, on the other hand, is a highly versatile and practical technique for the growth of one-dimensional ZnO nanorod arrays owing to its simple setup, ease of implementation, low cost, capability for large-area deposition, strong adhesion, and ability to achieve high-quality synthesis at comparatively low temperatures [15]. Therefore, in this study, Al-doped ZnO thin films with various doping ratios were prepared on ITO substrates using the electrodeposition method, and their optical properties were comprehensively investigated.

2. Materials & Methods

In this study, ZnO and Al-doped ZnO thin films with various doping ratios were synthesized in a single step using the electrochemical deposition method. A Metrohm Autolab PGSTAT128N system was employed for all electrochemical experiments. For the deposition of pure ZnO thin films, an electrolyte consisting of 5 mM $ZnCl_2$ and a supporting solution of 250 mM LiCl was used. For the Al-doped ZnO thin films, 5 mM $Al(NO_3)_2 \cdot 9H_2O$ was introduced as the aluminum source. The aluminum doping ratios were adjusted to 2.5%, 5%, 7.5%, and 10% relative to Zn. The applied potential, deposition time, and temperature for the reaction were set to –0.9 V, 3600 s, and 70 °C, respectively. An ITO-coated glass substrate served as the working electrode, while an Ag/AgCl electrode and a platinum plate were used as the reference and counter electrodes, respectively. Optical characterization was performed using a Hach DR600 UV–Vis spectrophotometer. The wavelength range for the measurements was set between 300 and 700 nm.

3. Results

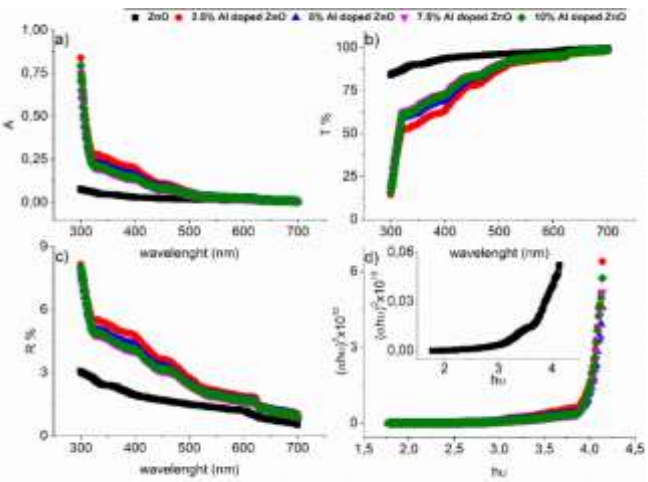

Figure 1: Plots of a) absorption, b) transmittance, c) reflectance versus wavelength of pure ZnO and ZnO thin films doped with Al at different ratios and d) The plot of $(\alpha h\upsilon)^2$ versus photon energy.

Figure 1a shows that Al doping enhances the absorption capacity of the thin films. For all films, the maximum absorption occurs at a wavelength of 300 nm. Although the absorption values increase with Al incorporation into ZnO, the 2.5% Al-doped ZnO thin film exhibits the highest absorption curve across nearly the entire wavelength range. Absorption decreases with increasing wavelength.

Figure 1b presents the transmittance (%) of ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films as a function of wavelength.

The relation between absorbance (A) and transmittance (T) is given by;

$$A = -logT \qquad [1]$$

Assuming that multiple reflections are negligible, the transmittance of the thin film is expressed as [16, 17];

$$T = (1-R)^2 \exp(-A) \qquad [2]$$

where R is the reflectance and can be determined from the measurements of both T and A using Eq. (2) which can be rearranged as follow

$$R = 1 - \left(\frac{T}{\exp(-A)}\right)^{1/2} \qquad [3]$$

For all thin films, The transmittance exhibits an increasing trend with respect to wavelength, with the maximum transmittance observed at 700 nm. The addition of Al reduces the transmittance of ZnO thin films, and among the doped films, the lowest transmittance values are observed for the 2.5% Al-doped ZnO thin film. The average transmittance values of ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films in the 300–700 nm range are 95%, 79%, 82%, 83%, and 83%, respectively. The higher transmittance of the pure ZnO film is attributed to improved grain orientation along the c-axis, which reduces optical scattering [18]. Figure 1c shows the reflectance (%) of ZnO and Al-doped ZnO thin films as a function of wavelength. For all films, the reflectance decreases with increasing wavelength. The lowest reflectance values are observed in the pure ZnO thin film, while the highest reflectance values occur in the 2.5% Al-doped ZnO thin film. The maximum reflectance for all films is recorded at 300 nm, whereas the minimum reflectance is observed at 700 nm.

The optical band gap was estimated from UV–Vis absorption measurements, and the dependence of the absorption coefficient on the band gap energy (E_g) can be described as follows [16]:

$$\alpha(h\upsilon) \approx \left(h\upsilon - E_g\right)^n \qquad [4]$$

where $h\upsilon$ is photon energy and n is ½ for direct allowed transitions. From the plots of $(\alpha h\upsilon)^{\frac{1}{n}}$ versus hυ E_g is obtained by extending the linear region of the plot to the energy axis, where the point of intersection corresponds to the band gap value.

Figure 1d presents the $(\alpha h\nu)^2$ versus hν plots for ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films. The corresponding optical band gap (Eg) values for ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films are 3.51, 4.01, 4.00, 3.99, and 3.98 eV, respectively. With Al incorporation, the band gap of the ZnO thin film increases by approximately 0.5 eV, and the highest Eg value is observed for the 2.5% Al-doped ZnO thin film.

The optical band gap of the Al-doped ZnO thin films is higher than that of the pure ZnO film, which is attributed to substitutional levels arising from Al impurities within the lattice. This effect can be explained by the widening of the band gap energy described by the Burstein–Moss (B–M) theory [19] In Al-doped ZnO thin films, donor levels are introduced near the conduction band. According to the Pauli exclusion principle, a quantum state cannot be occupied by two identical states simultaneously; therefore, electrons require more energy to transition from the valence band to higher empty states in the conduction band. This results in an apparent increase in the band gap energy [12]

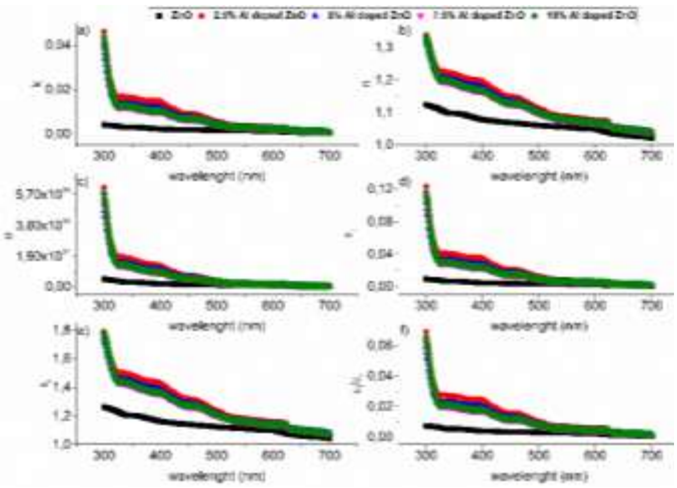

Figure 2: a) extinction coefficient (k), b) refractive index (n), c) optical conductivity (σ), d) imaginary dielectric constants (ε_i), e) real dielectric constants(ε_r), f) dielectric loss ($\varepsilon_i/\varepsilon_r$) of the pure ZnO and ZnO thin films doped with Al at different ratios versus to the wavelength

The relationship between the absorption coefficient (α) and the extinction coefficient (k) can be determined using the expression given below;

$$k = \frac{\lambda \cdot \alpha}{4\pi} \qquad [5]$$

The refractive index (n) is then calculated as follows [17]:

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{1-R^2} - k^2} \qquad [6]$$

Figure 2a presents the extinction coefficient (k) values of ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films as a function of wavelength. The k values of all thin films decrease with increasing wavelength. The highest k value for all films is observed at 300 nm. While the k value of the pure ZnO thin film is 0.004 at 300 nm, the corresponding values for the 2.5%, 5%, 7.5%, and 10% Al-doped ZnO thin films are 0.046, 0.039, 0.039, and 0.041, respectively. Above 326 nm, the k values approach nearly zero as the wavelength increases. The low k values in the 326–700 nm wavelength range indicate that the fabricated films are highly transparent, which is consistent with the transmittance spectra presented in Figure 1b. Figure 2b shows the refractive index (n) values of ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films as a function of wavelength. For all thin films, the maximum n value is observed at 300 nm, and these values decrease with increasing wavelength. At 300 nm, the refractive index of the ZnO thin film is 1.124, while the n values of the 2.5%, 5%, 7.5%, and 10% Al-doped ZnO thin films are 1.338, 1.322, 1.328, and 1.333, respectively. In all thin films, the n values sharply decrease with increasing wavelength up to approximately 324 nm, whereas the decrease becomes more gradual from 325 nm to 700 nm. This behavior can be attributed to the increase and subsequent decrease in optical absorption within the wavelength ranges of 300–350 nm and 350–900 nm, respectively. Nevertheless, the refractive index systematically decreases with increasing Al doping concentration. It is well established that Al atoms incorporated substitutionally into the ZnO lattice act as shallow n-type donors, thereby generating additional free electrons. As the Al doping level increases, the free carrier concentration in Al-doped ZnO thin films correspondingly increases. This enhancement in carrier density leads to a reduction in the refractive index, primarily due to free-carrier (Drude) effects [13, 20]. At 700 nm, the n values of the ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films are 1.020, 1.041, 1.034, 1.035, and 1.035, respectively.

$$\sigma = \alpha n c / 4\pi \qquad [7]$$

$$\varepsilon_r = n^2 - k^2 \qquad [8]$$

$$\varepsilon_i = 2nk \qquad [9]$$

and

$$dielectiric\ loss = \varepsilon_i / \varepsilon_r \qquad [10]$$

are the optical conductivity, imaginary and real components of the dielectric constant and dielectric loss, respectively [21, 22].

Figure 2c shows the optical conductivity (σ) values of ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped

ZnO, and 10% Al-doped ZnO thin films as a function of wavelength. The maximum σ values for all films are observed at 300 nm. At 300 nm, the σ values for ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films are 4.628×10^{13}, 6.096×10^{14}, 5.091×10^{14}, 5.44×10^{14}, and 5.74×10^{14}, respectively. The σ values decrease with increasing wavelength. At 700 nm, the σ values are 1.118×10^{12}, 4.606×10^{12}, 3.278×10^{12}, 3.406×10^{12}, and 3.418×10^{12}, respectively. Figure 2d presents the imaginary dielectric constant (ε_i) values of ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films as a function of wavelength. The ε_i values reach their maximum at 300 nm for all films. At 300 nm, the ε_i values for the ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films are 0.009, 0.123, 0.103, 0.110, and 0.116, respectively. These values decrease with increasing wavelength, reaching their minimum at 700 nm. At 700 nm, the ε_i values are 5.289×10^{-4}, 0.00218, 0.00155, 0.00161, and 0.00162, respectively. Figure 2e shows the real dielectric constant (ε_r) values of ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films as a function of wavelength. The maximum ε_r values occur at 300 nm, with values of 1.26462, 1.78946, 1.74636, 1.76256, and 1.77558 for the respective films. The ε_r values decrease with increasing wavelength, reaching their lowest value at 700 nm. At 700 nm, the ε_r values are 1.04154, 1.08435, 1.07116, 1.07253, and 1.07266, respectively. Figure 2f presents the dielectric loss ($\varepsilon_i/\varepsilon_r$) values of ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films as a function of wavelength. The maximum dielectric loss is observed at 300 nm. The $\varepsilon_i/\varepsilon_r$ values decrease with increasing wavelength. At 300 nm, the $\varepsilon_i/\varepsilon_r$ values for ZnO, 2.5% Al-doped ZnO, 5% Al-doped ZnO, 7.5% Al-doped ZnO, and 10% Al-doped ZnO thin films are 0.00742, 0.06904, 0.05909, 0.06259, and 0.0656, respectively, while at 700 nm these values are 5.078×10^{-4}, 0.00201, 0.00145, 0.00150, and 0.00151, respectively.

In general, the evaluated optical parameters in the visible spectral range are lower than those obtained in the ultraviolet region and exhibit only a weak dependence on both wavelength and Al doping concentration. Moreover, the dielectric damping factor, together with the real and imaginary components of the complex dielectric function, shows a systematic decrease with increasing Al content. This attenuation of the optical parameters at higher Al doping levels can be attributed to the enhanced free carrier density in Al-doped ZnO thin films, which modifies the optical response through free-carrier absorption and screening effects [20].

6. Conclusion

In this study, pure and Al-doped ZnO thin films were successfully synthesized using the electrochemical deposition method. The Al doping concentrations were set to 2.5%, 5%, 7.5%, and 10%. The fundamental optical parameters of the synthesized pure and Al-doped ZnO thin films—including absorption, transmittance, reflectance, energy band gap, extinction coefficient, refractive index, real and imaginary dielectric constants, optical conductivity, and dielectric loss—were investigated within the wavelength range of 300–700 nm. In doped thin films, the doping concentration is typically kept low; however, in this study, the Al content was increased up to 10% to examine and interpret how high Al incorporation influences the optical properties. It was observed that films with low Al content (2.5%) exhibited increased absorption and, consequently, reduced transmittance. As the Al doping concentration increased, absorption decreased while transmittance increased.

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Author Contributions

F.U: Conceptualization, writing, data acquisition, calculation, editing, writing, conceptualization, data acquisition.

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