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Influence of Time Variation on UV-Sensitive Optical Properties in ZnO/CuO Blend Films

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Abstract:
Recent research focuses on nanomaterials due to their possible applications spanning different fields like optoelectronics, catalysis, and sensing. Of the nanomaterials, metal oxide nanomaterials have proven to be a good substitute for semiconducting materials in optoelectronic applications, given their multiple characteristics. A study of the blend of ZnO/CuO thin films will be beneficial to investigate the optimization of the optical characteristics. Hence, this article examines the influence of time on the optical characteristics of ZnO/CuO blend films. With a chemical bath deposition technique, thin films of ZnO/CuO blend were deposited onto a transparent substrate placed in an aqueous solution comprising 10ml of ZnO and CuO, along with 1ml of Triethanolamine. The films were grown at a constant temperature of 90^o for different durations: 30 minutes, 45 minutes, 60 minutes, and 75 minutes. Optical properties of the films were studied using UV-visible spectroscopy for all the deposited ZnO/CuO films within the wavelength range from 200 – 1000nm. The findings revealed that the films deposited at 45 minutes and 60 minutes exhibited high absorbance, whereas those deposited at 30 minutes and 75 minutes displayed low absorbance. Moreover, the study identified various optical bandgaps of the material, noting that the film deposited at 45 minutes demonstrated the bulk bandgap of ZnO/CuO.

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Authors' Contribution
IOA researched the literature, developed the study and analysed the data. UCU reviewed the manuscript and edited the final version. OEE experimented and wrote the first draft of the manuscript. NOF assist in laboratory experimental works.

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INTRODUCTION

In recent decades, semiconductor nanomaterials have garnered significant attention and research interest due to their potential applications for enabling advanced device functionalities across diverse fields like optronics, catalytic action, and sensors. The unique structural, chemical, optical, and catalytic characteristics of nanomaterials, which differ from those of their counterpart, have been a driving force behind the increasing popularity of nanomaterial research (Dirar *et al.,* 2018). Notably, ZnO and CuO metal oxide nanomaterials, known as n-type and p-type semiconductors, have been recognized for their novel properties, including band gaps of 3.37eV and 1.34eV, respectively. The ongoing research into the blend of ZnO-CuO nanocomposites seeks to understand the mechanisms of these nanoparticles and explore their fascinating properties and advantages (Chang *et al.,* 2012). Studies have demonstrated that ZnO-CuO nanocomposites have emerged as promising candidates, surpassing pure ZnO or CuO in various practical fields due to their unique optical and electrical properties. ZnO is a versatile compound for producing nanostructures suitable for nanotechnology usage, including field emission arrays and nanosensors (AL-khezraji *et al.,* 2021). Conversely, CuO, a p-type semiconductor with a 1.35eV band gap value, exhibits significant promise as an emission source, catalyst, and medium for gas sensor applications (Zainelabdin *et al.*, 2012). However, the ZnO/CuO blend offers outstanding adjustable properties in catalysis, electronics, optics, and magnetism, which renders it highly versatile for numerous uses.

Coupling these semiconducting metal oxides results in an enhanced surface area, providing additional reactive centers, facilitating mass and electron transmission, and preventing photon corrosion (Das and Srivastava, 2018), hence improving the efficiency. The optical results from these studies indicate that ZnO/CuO composites hold great potential for various device applications. Moreover, these composites significantly attract considerable interest from physicists, chemists, and materials scientists because of their practical utility in areas including photo-catalysis, sensing technology, microelectronic processing, piezoelectric transducers, energy conversion devices, and solar cells (Das and Srivastava, 2018). Various methods like spray pyrolysis (AL-Khezraji *et al.,* 2021), co-precipitation (Tupe *et al.,* 2022), thermal decomposition (Arafat *et al.,* 2022), and sol-gel (Bandekar *et al.,* 2020) have been employed in the deposition of ZnO/CuO blend films. Understanding the influence of time on the optical characteristics of ZnO/CuO blend films is crucial. However, this research aims to focus on elucidating how time-dependent processes influence the performance and suitability of these materials and analyze methods for enhancing these properties to ensure optimal performance for optoelectronic applications.

This study will investigate the effect of time on the optical properties of ZnO/CuO blend films using a chemical bath deposition technique. By employing a straightforward synthesis approach to prepare the precursors, the research will examine and evaluate the optical characteristics of the grown films, including absorption, transmission, reflection, extinction coefficient, and bandgap energy, to determine their suitability for optoelectronics applications and contribute valuable insights for the development and optimization of ZnO/CuO blend films for enhanced optoelectronic functionality.

MATERIALS AND METHODS

Substrate Cleaning Procedure

The surface of the glass substrate was meticulously cleaned and activated. The substrates underwent a series of treatments, including immersion in acetone and methanol, rinsing with distilled water, and then subjected to 30 minutes of ultrasonication in an acetone solution. Subsequently, the substrates were rinsed in distilled water and dried in an oven.

Finally, we stored the substrates in an airtight container.

Synthesis of Copper Oxide (CuO)

We synthesized CuO by reacting 0.2g of Copper Chloride ($CuCl_2$) in 50 ml of ethanol. The resulting solution was placed on a Heidolph MR Hei-Standard hot plate at 80ºC and continuously stirred using a magnetic stirrer for 60 minutes. A black precipitate was formed which was oven dried to remove excess ethanol and form the nanoparticles (Asamoah *et al.,* 2020).

Synthesis of Zinc Oxide (ZnO)

We synthesized ZnO by reacting 0.2g of Zinc acetate ($Zn(CH_3COO)_2.2H_2O$) in 100ml of distilled water. The resulting solution was thoroughly stirred on a Heidolph MR Hei-Standard hot plate at 80ºC with a magnetic stirrer to achieve a homogeneous solution. The solution was let for 60 minutes until a white precipitate was formed and was subsequently dried in an oven to form the nanoparticles (Asamoah *et al.,* 2020).

Blending of ZnO and CuO

10 % of CuO and 20 % of ZnO was measured and combined in a 50ml beaker, with 1ml of Triethanolamine added to balance the pH of the reaction. The resulting solution was thoroughly stirred with a magnetic stirrer to ensure homogeneity. The pH of the solution was determined using a digital pH meter and found to be about 8.26.

The deposition of the films employed a chemical bath deposition technique with a constant temperature of 90º to fabricate the films. The substrate was vertically suspended on a substrate holder and immersed in the reaction bath for 30 minutes. After 30 minutes, the substrate was removed from the reaction bath, rinsed in a beaker containing 50ml deionized water, and left to air dry. We maintained the same procedure for different time intervals of 45 minutes, 60 minutes and 75 minutes to deposit the films.

Characterization Studies

The resulting films from the reaction formed thin layers at the front and back sides of the glass substrate. Subsequently, the optical characteristics of the films were studied for each sample utilizing a UV-visible spectrophotometer to obtain the absorbance, along with other properties derived through calculations.

RESULTS AND DISCUSSION

Optical Analysis of ZnO/CuO Blend

The investigation of the optical characteristics of ZnO/CuO grown at different deposition times at the same concentration and pH of 8.26 was analyzed employing a N4S UV-vis spectrophotometer across a wavelength range of 200 - 800nm. Yu et al. (2021) synthesized a variety of greatly porous Zn-Cu and Zn-Co composites featuring a three-dimensionally ordered macropores (3DOM) structure utilizing the colloidal crystal template technique. CuO/ZnO nanocomposite materials films were analyzed using XRD and FTIR, which confirmed the crystalline structure and successful formation of the CuO/ZnO nanocomposite (Patil and Sayyad, 2017).

Absorption Spectra

The absorption spectra of as-deposited ZnO/CuO film are as given in Figure 1. The absorbance values of ZnO/CuO film plotted with wavelength for various time intervals showed the films deposited under the same parametric conditions at room temperature exhibited higher intensity in the ultraviolet region, gradually decreasing in the visible and near-infrared regions, observing a relatively constant value. The film grown for 30 minutes displayed an absorbance value of 0.757, indicating a favourable light harvesting property, while the film grown for 45 minutes showed the highest absorbance at a value of 0.79, signifying more light absorption of the material. Furthermore, the film grown for 60 minutes peaked at 0.781, seemingly more advantageous than the film grown for 30 minutes, whereas the film grown for 75 minutes had the lowest absorbance at 0.684. Peaks at 380 and 460nm indicate the presence of both spherical and spindle-like structures of CuO, with the spindle structure being more prominent at the 45-minute reaction time. Overall, the film's absorbance increases with time, rendering the film grown for 45 minutes and 60 minutes suitable for applications such as solar collectors, sensors and detectors, light-emitting diodes, and laser technology. Rahmat et al. (2022) employed mechanical alloy to synthesize a ZnO-CuO composite. They studied the films' structure and optical characteristics utilizing the XRD technique and the FTIR spectrum. Their findings revealed a reduction in crystalline size upon increasing the milling time because of the dispersion of Zn and Cu atoms, leading to the formation of individual crystal structures.

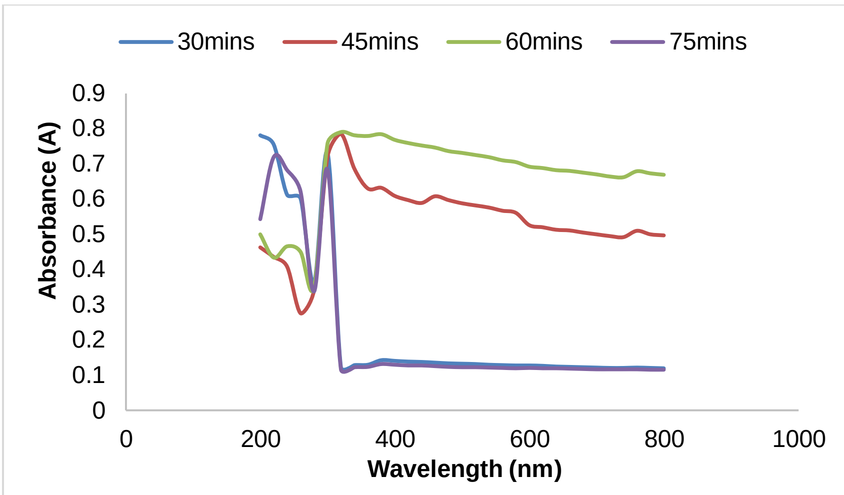

Fig. 1. Plot of Absorbance against wavelength at different time intervals.

Optical Transmission Spectra

Figure 2 depicts the transmission spectra of the as-deposited ZnO/CuO film. The transmittance values plotted against the wavelength for all the deposited films showed an increase in transmittance in the ultraviolet region for the films grown for 75 minutes and 30 minutes, along with a gradual decrease in the visible and near-infrared regions. In contrast, the films grown for 45 minutes and 60 minutes exhibited a reduction in transmittance and sustained across the visible and infrared regions. The low transmittance displayed by the film deposited at 45 minutes and 60 minutes could result from impurities, film thickness, and material properties, which influence the efficiency of transmitting radiant energy and contribute to strong absorption. These characteristics make them suitable for use in the upper layers of solar cells to minimize surface light reflection. Zhu et al. (2006) synthesized ZnO-CuO nanostructures by heating a Cu-Zn alloy (brass) on a hotplate at room temperature. Results revealed a shift in the predominant products from CuO nanowires to ZnO nanflakes on increasing Zn content.

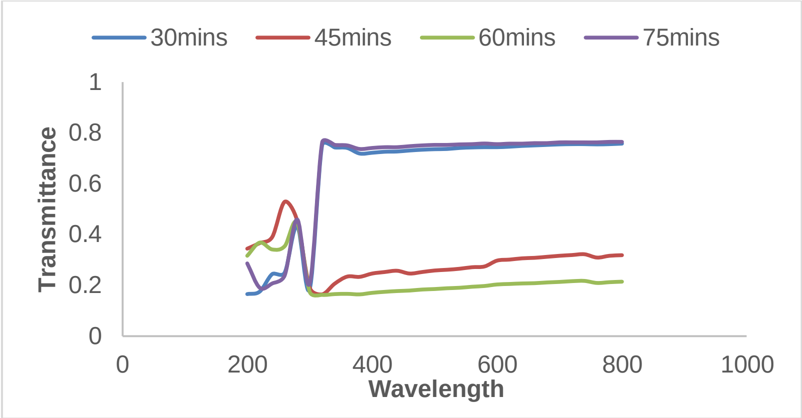

Fig. 2. Plot of Transmittance against wavelength at different time intervals.

Optical Reflection Spectra

Figure 3 presents the reflectance spectra of the deposited films. All the films exhibited low reflectance in the ultraviolet region, reaching a maximum peak value of 20%, decreased drastically with a steady increase in the visible and near-infrared regions, indicating the material's improved visibility and safety in low-light conditions. The film grown for 30 minutes showed a notable decrease in reflectance, followed by the film grown for 75 minutes, which could be result from the wavelength of light, polarization and the angle of incidence. However, this suggests that lower absorbance leads to reduced material reflectivity, as observed in the graphs. Based on these observations, the film grown for 45 minutes has superior reflective material, albeit low, but suitable for use in home insulation. Kamarajan et al. (2022) investigated the influence of various calcining temperatures ranging from 300℃ to 500℃ on the characterization of synthesized nanoparticles. FT-IR results indicated the involvement of biomolecules in zinc ions reduction to ZnO nanoparticles that served as a capping agent for the synthesized ZnO.

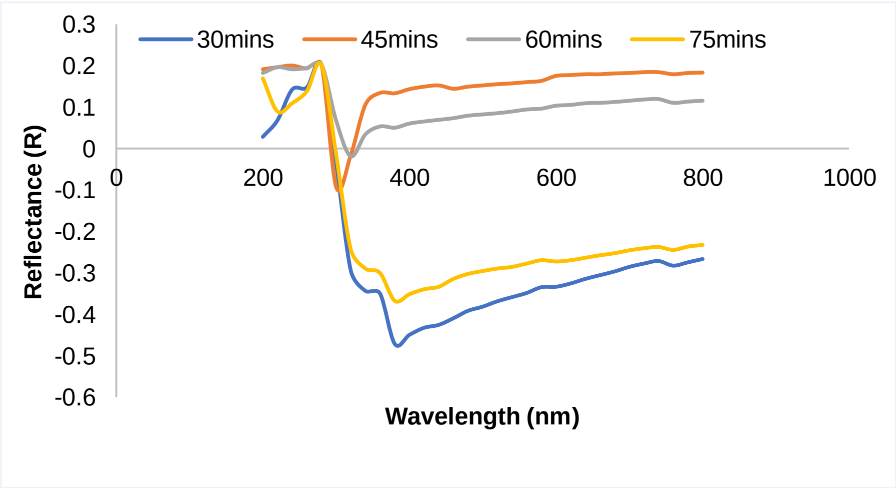

Fig. 3. Plot of Reflectance against wavelength at different time intervals.

Absorption Coefficient Squared versus Photon Energy

Figure 4 depicts the absorption coefficient squared versus photon energy spectra of ZnO/CuO film. In semiconductor materials, the bandgap energy is a crucial parameter, typically determined through the Tauc plot method, which involves plotting the square of the absorption coefficient against Photon Energy. The optical bandgap energy (Eg) is gotten through extrapolating the linear portion of the plot of absorption coefficient squared versus Photon Energy (eV), as shown in Figure 4, indicating a direct transition. The optical bandgap values obtained for the deposited films are 3.87eV, 3.36eV, 2.14eV, and 3.65eV at 30 minutes, 45 minutes, 60 minutes, and 75 minutes. Results revealed that samples with low absorbance exhibited higher bandgap values and vice versa, suggesting a direct bandgap with a high quantum effect. Although the film deposited at 45 minutes had a slightly lower bandgap in contrast to film grown at 30 and 75 minutes, it demonstrated the bulk bandgap of ZnO. Generally, all the films except for 60 minutes had bandgap values within the theoretical bandgap range of ZnO/CuO, making them suitable for applications in photovoltaic cells. Bandekar et al. (2020) utilized the sol-gel deposition technique to synthesize nanocomposite of Cu and Zn. They observed that the grown ZnO-CuO particles revealed antibacterial characteristics against gram-positive and gram-negative bacteria.

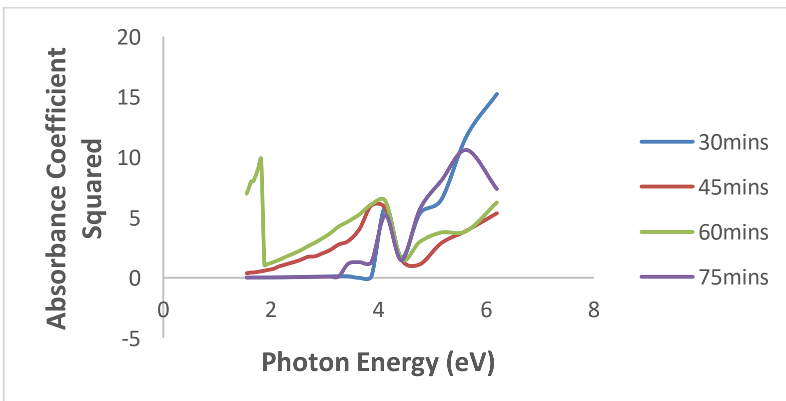

Fig. 4. Plot of Absorption coefficient Squared against Photon Energy at different time intervals.

Optical Extinction Coefficient Spectra

Figure 5 depicts the extinction coefficient Spectra of the as-deposited ZnO/CuO film. The extinction coefficient plotted against the wavelength for all the deposited films showed that the extinction coefficient reached its peak in the ultraviolet region at 6%, with a gradual and consistent decrease observed for the films grown at 45 minutes and 60 minutes in the visible and near-infrared regions, while those of the films grown at 30 minutes and 75 minutes experienced a significant decrease and maintained this decrease throughout the visible and near-infrared regions. Overall, the material demonstrated enhanced optical transparency, facilitating the light transmission with minimal absorption and scattering. This characteristic is valuable in applications such as optical windows, lenses, and display technologies, where transparency is crucial for optimal performance. The tables 1 to 4 present a summary of the optical characteristics of the films. Hussain et al. (2014) established that post-growth annealing enhances the crystalline quality and influences the electrical properties. Arafat et al. (2022) facilitated the growth of nanowires through thermally oxidized (Cu-37.2 wt% Zn) and Cu (99.9 wt%) brass wires at room temperature. The grown films revealed the formation of ZnO and CuO nanowires on brass and Cu wires, respectively.

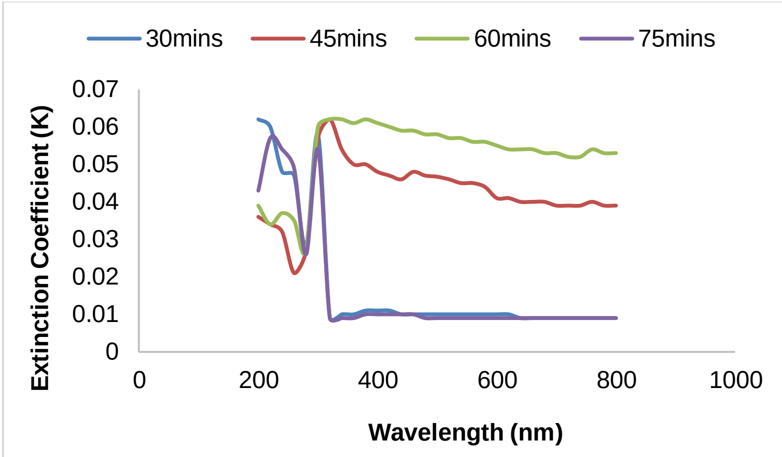

Fig. 5. Plot of Extinction Coefficient against wavelength at different time intervals.

Table 1. Optical characteristics of the ZnO/CuO blend film grown at 30 minutes.

λ(nm)	A	T	R	α x (10^6)m^{-1}	$α^2$ x (10^{12})m^{-2}	E(eV)
200	0.818	0.152	0.029	4.09	16.728	6.20
300	0.912	0.122	-0.034	3.04	9.241	4.13
400	1.411	0.039	-0.449	3.52	12.443	3.10
500	1.335	0.046	-0.381	2.67	7.128	2.48
600	1.281	0.052	-0.333	2.13	4.558	2.06
700	1.226	0.059	-0.285	1.75	3.067	1.77
800	1.204	0.062	-0.266	1.50	2.265	1.55

Where A is the absorbance, T is the transmittance, R is the reflectance, α is the absorption coefficient, E is the bandgap energy.

Table 2. Optical characteristics of the ZnO/CuO blend film grown at 45 minutes.

λ(nm)	A	T	R	α x (10^6)m^{-1}	$α^2$ x (10^{12})m^{-2}	E(eV)
200	0.463	0.344	0.192	2.31	5.359	6.20
300	0.990	0.102	-0.092	3.30	10.890	4.13
400	0.609	0.246	0.144	1.52	2.318	3.10
500	0.588	0.258	0.153	1.17	1.382	2.48
600	0.526	0.297	0.176	0.87	0.768	2.06
700	0.500	0.316	0.183	0.71	0.510	1.77
800	0.497	0.318	0.184	0.62	0.385	1.55

Table 3. Optical characteristics of the ZnO/CuO blend film grown at 60 minutes.

λ(nm)	A	T	R	α x (10^6)m^{-1}	$α^2$ x (10^{12})m^{-2}	E(eV)
200	0.500	0.316	0.183	2.50	6.250	6.20
300	0.757	0.174	0.068	2.52	6.367	4.13
400	0.768	0.170	0.061	1.92	3.686	3.10
500	0.731	0.185	0.083	1.46	2.137	2.48
600	0.692	0.203	0.104	1.15	1.330	2.06
700	0.670	0.213	0.116	0.95	0.916	1.77
800	0.669	0.214	0.116	0.83	0.699	1.55

Table 4. Optical characteristics of the ZnO/CuO blend film grown at 75 minutes.

λ(nm)	A	T	R	α x (10^6)m^{-1}	$α^2$ x (10^{12})m^{-2}	E(eV)
200	0.543	0.286	0.170	2.71	7.371	6.20
300	0.884	0.130	-0.014	2.94	8.682	4.13
400	1.301	0.050	-0.351	3.25	10.578	3.10
500	1.238	0.057	-0.295	2.47	6.130	2.48
600	1.211	0.061	-0.272	2.01	4.073	2.06
700	1.179	0.066	-0.245	1.68	2.836	1.77
800	1.164	0.068	-0.232	1.45	2.117	1.55

CONCLUSION

ZnO-CuO blend thin films deposited using the chemical bath technique employed 0.2M Copper chloride and Zinc acetate dehydrate. The deposition commenced at a constant temperature of 90ºC, and the process was conducted at a different reaction time of 30 minutes, 45 minutes, 60 minutes and 75 minutes, respectively. The films characterized for their optical properties using a UV-visible spectrophotometer displayed low reflectance. Again, the film deposited at 45 minutes and 60 minutes exhibited high absorbance with low transmittance, while the film deposited at 30 minutes and 75 minutes showed low absorbance with high transmittance. The band gap energies showed to be 3.87eV, 3.36eV, 2.14eV, and 3.65eV, respectively, with the film deposited at 45minutes as the bulk band gap of ZnO, suggesting optimal functionality of the material at this specific time interval. The unique features of these nanocomposites hold significance for practical applications like optoelectronics and sensing technologies, emphasizing the importance of controlling their surface properties, shapes and sizes in nanocomposites synthesis for improved practical use. Moreover, this necessitates an in-depth understanding of ZnO/CuO blend synthesis and its environmental implications, particularly in the context of gas sensing and photoreaction, representing promising areas for future research. Furthermore, future research is essential to comprehend the interaction between two metal oxides for applications in optoelectronics and optimize the ZnO/CuO blend for enhanced light harvesting functionality.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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