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# Optical Characterization of Cu-Doped Zno Nano Thin Films Prepared by Successive Ionic Layer Adsorption and Reaction (SILAR) Using EDTA As Complexing Agent

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***Abstract- ZnO:Cu thin films were successfully deposited on glass substrates by Successive Ionic layer adsorption Reaction method. The chemical compositions and thickness were obtained by Rutherford backscattering spectrometer. Samples B1 and B2 have elemental compositions of Cu:6.68%, O:23.72%, Zn:13.60% and Cu:5.14%, O:25.45%, Zn:13.42% respectively. The films optical properties were characterized using UV double beam spectrophotometer series 1800, for transmittance measurements and other optical properties such as Absorbance, reflectance, absorption coefficient, refractive index, were determined using appropriate equations. The Transmittance increases with increasing wavelength (42%-61%) for B1 and B2(49%-63) at the UV regions of electromagnetic spectrum for the two samples. The SILAR process allowed for the controlled incorporation of Cu ions into the ZnO lattice, resulting in a tunable band gap and enhanced optical properties. The doping concentration was systematically varied to optimize the performance of the ZnO:Cu thin films for optoelectronic applications, such as UV-sensitive photodetectors and light-emitting diodes (LEDs). B1 and B2 have high optical energy band gaps of 3.40eV and 3.15eV with average of 3.30eV which make them suitable material for optoelectronic applications and transparent electrodes.***

***Keywords: Transmittance, Band Gap, Spectrophotometer, Absorbance, Reflectance***

## I. INTRODUCTION

Nano materials play a vital role in this modern age of science and technology. Various kinds of materials are used in warfare, industry, housing, agriculture, transportation, etc., to meet individual requirements. The rapid developments in the field of quantum theory of solids have opened vast opportunities for better understanding and utilization of various materials.

The spectacular success in the field of space is primarily due to the rapid advances in high-temperature and high-strength materials. In the 21st century many researchers are working on various kinds of materials for technological applications such as metal oxides, metal chalcogenides, polymers, organic dyes, etc. Transition metal chalcogenides (TMCs) semiconductor materials play an important role in the solar cell and other technological applications.

Transition metal chalcogenides are important inorganic materials with wide range of potential applications in the magnetic, electronic, catalytic and optical industry. The electrical and optical properties of these compounds can be tuned on demand by reducing or increasing the number of layers (Han et al., 2011), which makes them potential candidates for tunable nano electronics (Johari et al., 2012; Jana et al, 2011).

The production of semiconductor nano thin films, have been carried out mostly on binary compounds such as Cu2O (Onwuemeka and Nwulu, 2017), CdO (Onwuemeka and Nwulu, 2017) ZnS (Onwuemeka et al., 2013), ZnO (Onwuemeka et al., 2014) which were useful in the area of passive and active applications (Onwuemeka et al., 2017).

Also, it has also been prepared in alloyed form using dual solution synthesis (DSS): ZnSnO4 (Onwuemeka et al, 2019).

Zinc oxide (ZnO) thin films are important in optoelectronic applications due to their unique properties. ZnO has a large excitonic binding energy of 60 meV at room temperature, making it an efficient light emitter in the ultraviolet (UV) spectral region, which is favorable for optoelectronic applications. (Johnson, 2020).

ZnO thin films are also transparent and have high conductivity, making them important for applications like transparent conductors and channel materials in thin-film transistors (Johnson, 2020).

Research has been conducted on doping ZnO thin films with materials like aluminum, gallium, indium, tin, copper, and transition metals to enhance their optoelectronic properties.

(Doni and Wilson,2021; Bhubesh and Aadarsh,2022; Mohsin Khan and Ghazi, 2023).
ZnO thin films have been used in various optoelectronic devices, including light- emitting diodes, UV sensors, biosensors, and photovoltaic devices. (Johnson,2020; Bhubesh and Aadarsh, 2022).

Additionally, ZnO thin films have been used in biological applications, such as bio imaging, bio sensing, and drug delivery agents. (Mohsin Khan and Ghazi, 2023).

The Successive Ionic Layer Adsorption and Reaction (SILAR) technique is significant for depositing and characterizing thin films due to its simplicity, flexibility of substrate choice, and cost-effectiveness. SILAR allows for the deposition of stable and adherent films on large areas, making it suitable for various applications.

It also enables the control of film thickness and is compatible with low processing temperatures, which is advantageous for energy efficiency. Additionally, SILAR has been used for the deposition of a variety of materials, such as metals, oxides, and sulfides, making it a versatile technique for optoelectronic applications. Despite some limitations, such as the potential for contamination due to organic additives, the benefits of SILAR outweigh these drawbacks, making it a significant technique for depositing and characterizing thin films in optoelectronic applications. (Abdul, 2022).

ZnO:Cu thin films have potential applications in various optoelectronic devices due to their unique properties, such as low electrical resistivity, p-type conductivity, and high transmittance (Bhubesh and Aadarsh,2022).

Some potential applications of ZnO:Cu thin films in optoelectronic devices include:
Light-emitting diodes (LEDs): ZnO:Cu thin films can be used as active layers in LEDs, providing efficient light emission in the ultraviolet (UV) spectral region and UV sensors, which can detect and respond to UV radiation and biosensors: ZnO:Cu thin films can be doped with biocompatible materials, such as Au or Ag, to create biosensors for various biological applications (Johnson,2020).

(Johnson, 2020).
Photodetectors: ZnO:Cu thin films can be used to create photodetectors, which can detect and respond to light radiation (Mohsin et al,2023).

The performance of these optoelectronic devices depends on the quality of the ZnO:Cu thin films, which can be influenced by the deposition methods, doping techniques, and characterization tools. By optimizing these methods, it is possible to develop high-performance optoelectronic devices based on ZnO:Cu thin films. (Bhubesh and Aadarsh,2022).

### Pre-Deposition Processes

To deposit ZnO:Cu, 0.5M of $ZnCl_2$ was made to react with EDTA forming complex Zn-ion as given in Eqn. (2.1). In order to remove the unabsorbed ions on the substrates, the glass substrates were carefully cleaned and inserted into the solution in beaker (a) containing Zn complex it is the ion as given in Eqn (2.2) removed and rinsed in deionized $H_2O$ in beaker (b) and it is then immersed in deionized $H_2O$ and subsequently immersed in the third beaker (c) containing hydrogen peroxide ($H_2O_2$) as given in Eqn (2.3) and then immersed into the fourth beaker labeled beaker (d) containing deionized $H_2O$ as given in Figure 2.1. The substrates were dipped into complex copper ion as given in Eqn (2.4) and pulled out after five seconds and were allowed to dry in air.

### The reaction mechanism

$$Zn(NO_3)_2 + \text{EDTA} \rightarrow [Zn(\text{EDTA})_4]^{2+}$$
(2.1)

$$[Zn(\text{EDTA})_4]^{2+} H_2O_2 \rightarrow ZnO + H_2O + \text{EDTA}$$
(2.2)

$$CuSO_4 + NH_3 \rightarrow [Cu(EDTA)]^{2+}$$
(2.3)

$$ZnO + [Cu(EDTA)]^{2+} \rightarrow ZnCuO + \text{EDTA}$$
(2.4)

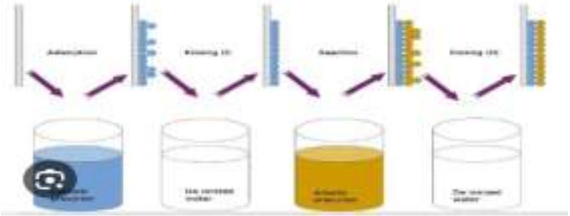

Figure 2.1 Experimental setup of successive Ionic layer adsorption and reaction (SILAR) (Jose, 2016).

The deposited samples were annealed using an electric oven of temperature range of 1000C-25000C. The suitable pH value for this work is 11 for ZnO:Cu as detected by the pH meter.

## II. CHAPTER FOUR

### RESULTS AND DISCUSSION

### Composition and Thickness Characterizations

It is often necessary to determine the elements and the thicknesses of the thin film samples. In this work, elemental compositions and the thicknesses of the samples were determined using Rutherford Back Scattering equipment: 2.2MeV alpha beam, obtained from CERD Ion Beam Analysis (IBA) Facility with Model: NEC 5SDH 1.7 MV Pelletron Tandem Accelerator equipped with a Radio Frequency Charge Exchange Ion Source Alphatron.

As depicts in Table 2.1, sample B1 shows that 6.68% of Cu, 23.72% of O and 13.60% of Zn combined to form a new compound alloyed thin films of ZnO:Cu.

Table 2.1 The elements in sample B1 of ZnO:Cu

| Elements | Layer (1) %Comp. | Layer (2) %Comp. |
|---|---|---|
| O | 79.72 | 56.00 |
| Ca | - | 1.83 |
| Fe | - | 0.52 |
| Na | | 12.60 |
| Al | - | 0.53 |
| Si | - | 28.00 |
| Cu | 6.68 | - |
| Zn | 13.60 | |

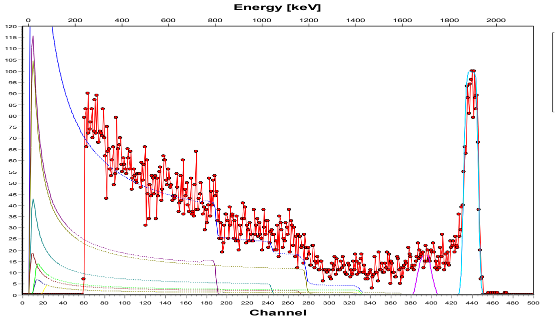

Figure 2.2 The composition of sample B1 of ZnO doped with copper and its thickness, 191.0nm as measured by Rutherford backscattering spectroscopy

As depicts in Table 2.2, sample B2 shows that 5.14% of Cu, 25.45% of O and 13.42% of Zn combined to form a new compound alloyed thin films of ZnO:Cu.

Table 2.2 The elements in sample B2 of ZnO:Cu

| Element | Layer (1) %Comp. | Layer (2) %Comp. |
|---|---|---|
| O | 81.45 | 56.00 |
| Ca | - | 1.83 |
| Fe | - | 0.52 |
| Na | | 12.60 |
| Al | - | 0.53 |
| Si | - | 28.00 |
| Cu | 5.14 | - |
| Zn | 13.42 | |

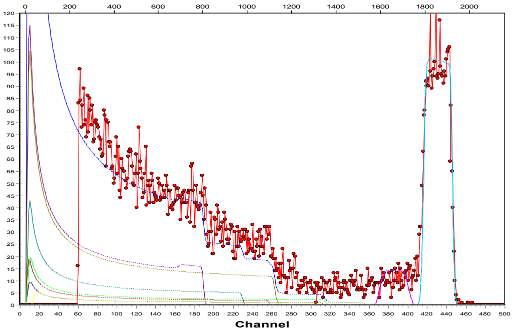

Figure 2.3 the composition of sample B2 of ZnO doped with copper with thickness, 388.52nm as measured by Rutherford backscattering spectroscopy.

## III. OPTICAL PROPERTIES

The transmittance spectrum shows that the films of samples B1 and B2 have good transparency in the UV, visible and near infrared regions of electromagnetic spectrum. Sample B1 has transmittance range 42%-60% at the wavelength between 321nm-361nm in the UV region. Sample B2 has transmittance range 49%-63% at the wavelength between 321nm-400nm in the UV region.

The transmittance of sample B1 increases to its maximum value of 60% at wavelength, λ=451nm in the visible region. The transmittance of sample B2 increases as wavelength increases up to a certain value 62% at wavelength λ=480nm after which it falls and rises up to maximum value of 68% at wavelength, λ=1081nm in the near infrared region of electromagnetic spectrum.

The transmittance of B1 falls as wavelength, increases within the visible and has almost linear characteristics in the near infrared region of electromagnetic spectrum as shown in Figure 2.4.

This makes the film a good material for UV filter, good material for solar cell applications and a good material for transparent electrode for optoelectronic applications (Onwuemeka et al., 2014).

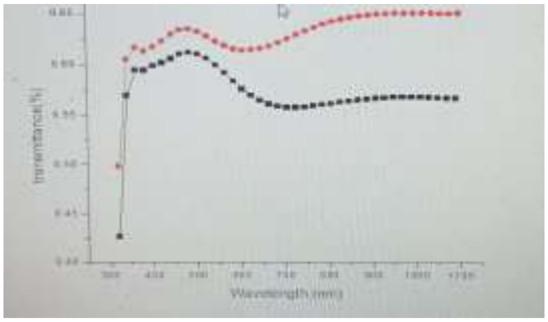

Figure 2.5 Graph of transmittance against wavelength for ZnO doped with copper

The optical energy band gap is obtained in k space. The energy band gaps of samples B1 and B2 are evaluated by extrapolating the linear portion of the plot (αh□)2 against photon energy h□at (αh□)2 = 0 where α is the absorption coefficient as shown in Figure 2.6

The direct band gap values of 3.40eV and 3.15eV are obtained for samples B1 and B2 respectively. The average band gap value 3.30eV.

The wide band gap obtained in this work makes the alloy of ZnO:Cu a good material for the production of laser diodes and light emitting diodes (LEDs) used to produce field effect transistors where P-n junction may not be required if produced for solar applications (Onwuemeka et al., 2017; Look, 2001).

It can also be used to produce field effect transistors where P-n junction may not be required if produced for solar applications (Onwuemeka et al., 2017).

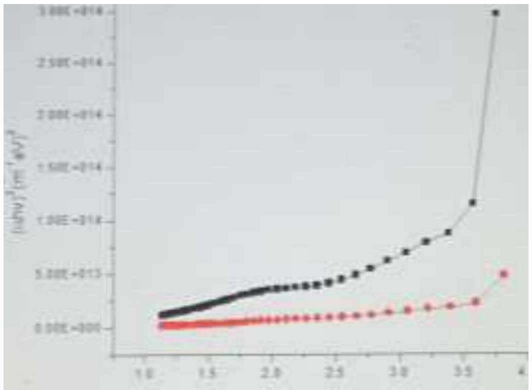

Figure 2.6 The Graph of (αh□) 2 against photon energy h□ for ZnO doped with copper

## IV. CONCLUSION

The ZnO:Cu thin films have successfully been deposited on glass substrates. This was achieved using successive ionic layer adsorption and reaction (SILAR). It is cheap, effective, accurate and easy to execute.

The substrates were prepared in aqua regia before being used for the deposition. The complexing agent used is (EDTA) ethane diamine tetra acetic acid. The precursor materials used as the sources of cations are solutions of hydrated $CuSO_4$, $ZnCl_2$ and $H_2O_2$ as the source of anions.

The deposition of ZnO:Cu was carried out at room temperature of 20°C. The samples were annealed at 1000C, 1500C, 2000C and 2500C for 1hour. The compositions and thickness measurements were determined using Rutherford Backscatering Spectroscopy (RBS).

The graphs of the optical characterization were plotted against wavelength for the samples produced. The energy band gaps of the samples were determined from the graph of $(\alpha h\upsilon)$ 2 against $h\upsilon$ by extrapolation of straight portion of the curves to $h\upsilon$ axis where $(\alpha h\upsilon) = 0$. The average band gap of the four samples is 3.30eV.

As a material with wide energy band gap, it can be found useful as photovoltaic and photoconductive thin films for optoelectronic applications, solar cell production, sensor devices, chemical detectors in oil and gas productions and as material for solar control coatings and good material for flat panel displays because its wide band gap.

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