CHAPTER 4

Al Doping Influence on Structural, Morphological and Optical Properties of CuO Films

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1. Introduction

Copper oxide nanostructured materials is very interesting semiconductor material. Characteristically, copper oxide can be originated different forms as cuprous oxide (Cu_2O) and copper monoxide (CuO), and it shows crystal form of Cu_4O_3 (Suda et al., 1992). These crystal properties are encouraging materials owing to their excellent optical and electrical properties, environmentally friendly, richness in environment, low-cost, strong absorption coefficient in the region of UV-Vis, etc (Sultana et al., 2017).

While copper oxide compound is a characteristic *n*-type conductivity, cuprous oxide is a monoclinic *p*-type conductivity. Copper oxide nanostructured materials are generally used in application of microelectronics (Zhen et al., 2018), field-emission instruments (Chen et al., 2005)

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biotechnology (Hassan et al., 2019), catalysts (Prasad and Rattan, 2010), photovoltaic application (Wang et al., 2011), super-capacitors application (Nandhini et al., 2019), *p-n* junctions (Zhao et al., 2021), lithium ion battery anodes (Ko et al., 2012), high-temperature superconductors sensors (Cava et al., 1987) because of the fact that it have important structural, electrical, magnetic and optical properties related to those of conventional bulk materials. In general, CuO has monoclinic *p*-type electrical conductivity for fabricating variety of procedures owing to the holes which is seen in the valence band of the nanostructured material. Additionally, the material of nanostructured has an indirect optical energy band value which allows it to fold extra energy (Masudy-Panah et al., 2016). The informed optical energy band value for CuO material changes between 1.2 and 2.1 eV (Venkateswari et al., 2017; Zheng and Liu, 2007). In the Cu_2O nanostructured materials, the direct energy band value changes between 2.1 and 2.6 eV and the crystal configuration of this nanostructured material was given as cubic; it is similarly given as cuprite in the works (Dolai et al., 2017). Similarly, the Cu_2O nanostructured material has indicated a *p*-type conductivity due to negative vacancies and strong electronegativity value of the copper element.

Shape controlled topologies have an important role in the properties of the transition metal oxides films in the nanoscale region. Also, a number of metals can be used as doping elements to improve quality of crystalline properties of thin films with excellent physical and chemical properties of CuO thin films. Ramyaet et al. (2016) have synthesized Ni:CuO nanostructured materials using precipitation technique and reported that metal doping has tailored the structure of energy band gap and luminescence properties which in turn improved the antibacterial activity of CuO materials. Shaikh et al. (2011) demonstrated that Ru doped CuO film has an important role in improving green chemistry approach for more efficient supercapacitors. Huang et al. (2012) reported that Ag particle loaded on the CuO nanosheet arrays affected the electrical conductivity of the electrode and increased the electrical interaction among the used substrate using a template-free fabrication technique and silver mirror reactions.

The effects of various parameters such as annealing methods, storage temperature, film thickness, distance from solution spray head, solvent property and storage time were investigated so far. These parameters have changed the physical properties including crystal parameters, absorbance and transmittance value of the thin films, and this has led the researchers to improve the both chemical and physical properties of the CuO samples to be obtained by using different metals. While the physical and chemical properties of nanostructured CuO thin films have been examined by groups (Bae and

Choi, 1999; Chaudhary et al., 2004; Mageshwari and Sathyamoorthy, 2013; Morales et al., 2005; Tamaki et al., 1998), Al:CuO thin films fabricated by using spin-coating method have not comprehensively been studied to date.

Metal doping has a great influence on the crystal parameters and optical properties of the CuO nanostructured film. However, there are few experimental studies on Al contribution. Therefore, further experimental studies are needed to better understand the effect of Al doping on the physical properties of the pure CuO. There is limited information about the effects on the crystal parameters, absorbance and transmittance value of Al:CuO samples prepared by method of spin coating, and Al:CuO films obtained by this technique have not been extensively investigated until now. In this study, Al:CuO thin films of were obtained by using the spin coating technique, which is an efficient, cost-effective and simple preparation method, and the crystal and optical properties of these thin films were investigated. The effect of the variation of the Al doping on the crystal structure and structural properties on thin film was evaluated using XRD. The transmittance, absorption properties the films in the visible region were analyzed using the UV-Vis device.

2. Experimental details

In the present study, Al doped CuO samples with three unlike weight ratios (0, 2 and 4 at wt% of Al) were fabricated on SLG substrate by employing a solution comprising 0.1 M copper(II) acetate ($Cu(CH_3COO)_2{\cdot}H_2O$) and 0.01 Al deposited under optimized condition. 0.1 M copper(II) acetate was stirred in 100 ml of absolute ethanol for 18 h at temperature of 300 K. 0.01 M Al was stirred in 20 ml of ethanol for the same condition. After this, a certain amount of Al was slowly embedded into the solution of copper(II) acetate to give dissimilar doping and finally, the gained Al:CuO solutions were stirrer on magnetic stirring at room temperature for around 8 h until a homogenous solution was gained. Before the deposition procedure, the all SLG substrates were cleaned by boiling in enough quantities of a mixture of H_2O, NH_3, and H_2O_2 at 120 °C and then in sufficient quantities of a mixture of H_2O, H_2O_2, and HCl at 120 °C to eliminate any remaining waste. Then, the substrates were stirrer in deionized water for 5 min on magnetic stirring and later dried under N_2 atmosphere. After gaining the final Al:CuO solutions and washing the SLG substrates, the samples were grown via spin coated at 1800 rpm for 60 s in air conditions. The obtained solutions were grown onto the substrate of SLG sheet by sheet, and all sheets were heated to around 220 °C for 8 min. After this process, obtained samples were annealed at around 500 °C for 1h in air. The influence of different Al doping on the CuO's structural and optical properties are studied in this work.

The crystal parameters of obtained Al:CuO thin films were determined with the help of Rigaku Smart Lab X-ray diffractometer (XRD: Cu Kα radiation, λ=1.540056 Å). Surface topology of Al doped CuO samples were investigated using Park System XE 100 Atomic Force Microscope (AFM) at room temperature. A Shimadzu UV-3600 system was used to record the energy gap, absorbance and transmittance value of the samples.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis

Fig. 1. demonstrations the typical XRD patterns for Al: CuO films grown onto SLG annealed at 500 °C in furnace. As seen as this figure, the strong peaks at 35.5° and 39.0° were appeared for all films in XRD patterns and correspond to (-111) and (200), respectively and there are phases of oxide associated to the phase of impurity due to the compound formation containing Al and Cu_2O. The XRD patterns show that Al:CuO samples are a single-phase monoclinic crystal structure. Peak positions (*hkl*), values of crystallite size (D) in nanometers, full width at half maximum (FWHM) value which is known as β, and inter planar spacing (d) are given in table 1. Furthermore, there are differences in the peak positions while the intensity of the (-111) and (200) orientations peaks changed which correspond to a preferred orientation of obtained polycrystalline structure. Al addition changed the crystal structure of the films, which may be attributed to the significant difference ionic radii of the Al^{+3} ion (0.5 Å) and Cu^{+2} ion (0.73 Å), thus, Cu and Al can be changed the crystal structure of CuO. These results (the intensity of peaks, peak broadening and shift in the peak position) indicate that Al^{3+} ions were effectively inserted into the CuO lattice.

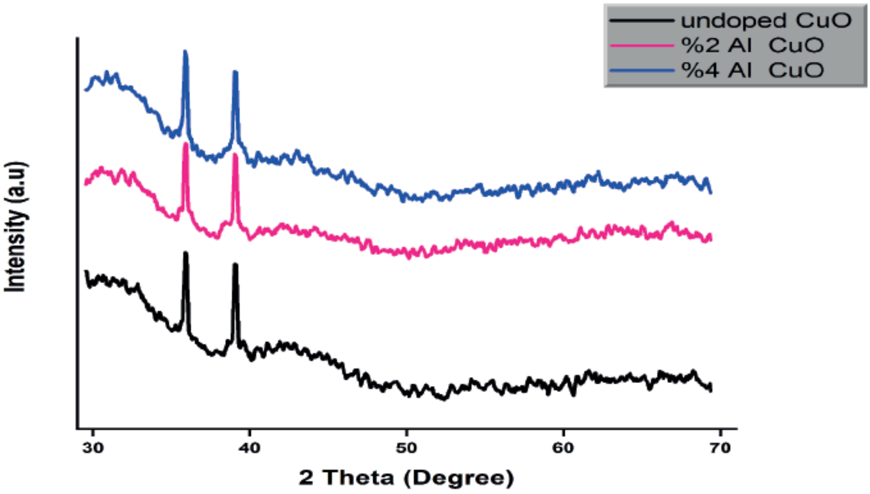

Fig. 1. XRD patterns of Al doped CuO thin film

We used Scherer's equation to calculate D value of Al doped CuO samples from data of XRD. Scherer's equation is as follows;

$$D = \frac{k}{\beta \cos\theta} \tag{1}$$

where $\lambda = 1.540056$ Å is the wavelength of Cu Kα, θ is Bragg's diffraction angle. Calculated crystallite size for (111) peak decrease from 52 to 14 nm by increasing Al doping ratio. Devi et al. (Devi et al., 2018) point out that the crystallinity of the La:CuO film increases as increasing the temperature value. La doping in CuO solution decreases the crystallinity because of the difference of ionic radii and also mains to peak shift. This is owing to strong ionic mobility and minor radius of Al ions in CuO solution. d values of the Al:CuO samples is theoretically calculated using the Bragg's equation (Cullity, 1978):

$$2d sin\theta = n\lambda \tag{2}$$

where is the order of diffraction. d values of the sample of (-111) and (200) peaks are found to be around 2.50 and 2.30 Å.

Table I. Crystallite parameters of the Al:CuO films obtained by XRD data

Sample	2 Theta Peak (Degree)	Grain Size (nm)	d-spacing (Å) (calculated)	d-spacing (Å) (standart)	Orientation	Dislocation Density ($x10^{15}m^{-2}$)	Strain ($x10^{-4}$)
Undoped	35.96	51.87	2.538	2.493	(-111)	0.37	0.23
	39.87	10.93	2.261	2.305	(200)	8.37	0.97
2 % Al:CuO	35.53	13.09	2.527	2.525	(-111)	5.83	0.91
	38.19	14.06	2.356	2.355	(200)	5.06	0.79
4 % Al:CuO	35.82	16.13	2.507	2.501	(-111)	3.84	0.73
	39.10	13.90	2.304	2.323	(200)	5.18	0.78

The dislocation density value (δ), which indicates the amount of defects in films, is calculated using the following equation [26]:

$$\delta = \frac{1}{D^2} \tag{3}$$

The change in the strain value of the samples is found by following formula:

$$\varepsilon = \frac{\beta}{4tan\theta} \tag{4}$$

The dislocation density value of (-111) plane is changed between 3.7 x 10^{14} and 5.83 x 10^{14} m^{-2} and 83.7 x 10^{14} and 50.6 x 10^{14} m^{-2} for (200) owing to the expansion of structural parameters with Al dopant content in solution. The strain value of (-111) and (200) planes is radically changed related to increase Al dopant content. Thus, it was seen that the main effect of change in crystallite size is related to difference in strain and dislocation value. Mageshwari and Sathyamoorthy (2013) demonstrated that value of the film decreases with the increase in fabrication cycles.

3.2. Morphological Properties

The surface morphologies of the deposited Al doped CuO films are very important to analyze the surface properties of the obtained samples. Al affects the surface morphology of CuO films for different doping concentrations: Fig. 2 indicates the 3-D images of AFM of Al doped CuO thin films grown by the spin-coating method at different scales. The figures indicate that the thin films with rod-like particles and a grain structure. The obtained results revealed that samples are comparatively smooth in the valley area while many crystals-like structures are seen in the hill area which indicates definite orientations. It could be seen in the figure that the thin film surface is not uniform. It can be seen that the all thin films are comparatively smooth and well adhered to the SLG substrate. The coverage rate of the nanoparticles on surface changed as Al doping ratio rise, which change the mobility and resistivity value of CuO thin film. Abed et al. (2021) showed the same morphological properties and they analyzed the surface properties of thin films of carbon doped CuO:NiO to modify the physical properties of carbon.

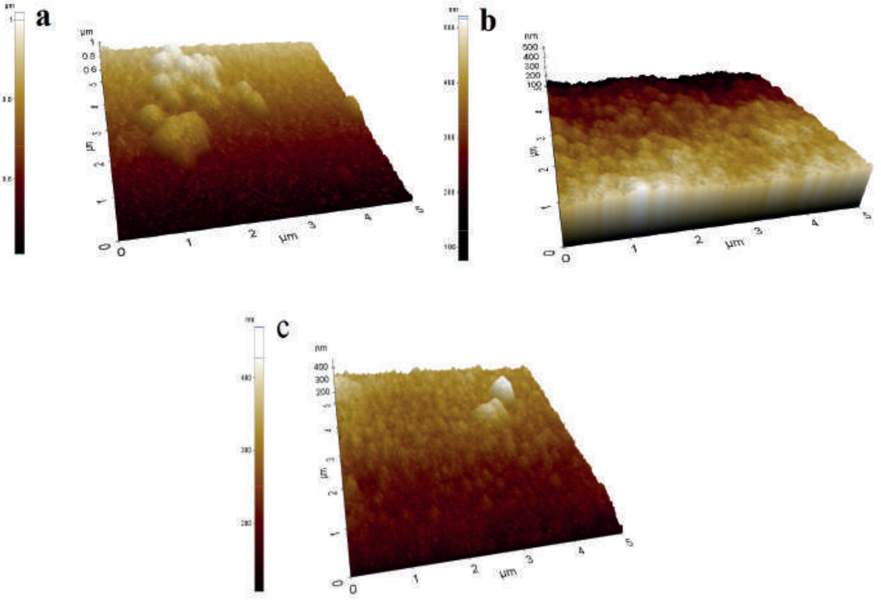

Fig. 2. 3-D AFM images of Al: CuO thin film

3.3. Optical Properties

The absorbance and transmittance of used nanostructured materials effect with many variables like the deposition technique, surface topology, and some deposition conditions (temperature, film thickness, annealed time), related to their interaction with the ambient. To investigate the effect of different metal doping concentrations on the absorbance and transmittance value of each film were carried out in 300-1100 nm spectrum range. The analysis of the value of absorption coefficient for any nanostructured gives extra knowledge concerning the levels of electrons in the high-energy range of the spectral absorption spectra, while the low-energy range of the spectral absorption spectrum related to the atoms' vibration (El-Hagary et al., 2012; Urbach, 1953). Dissimilar applications are dependent on the spectral absorption spectrum of the Al:CuO film, and the coefficient of absorption can be calculated from the measurement of absorbance data with the wavelength in nm and calculated from the Beer–Lambert law (Abdul Nabi et al., 2014).

$$lnI / I_0 = e^{-\alpha t}, \alpha = 2.303^{*} A / t \tag{5}$$

where α is a constant which shows the value of absorbance coefficient, A is the value of absorbance, and t is the value of film thickness.

α value of the Al doped CuO thin film is dependent on the wavelength value in UV-Vis region, as shown in Fig 3. The obtained consequences in this Figure indicates that the optical absorption coefficient upsurge with the change in wavelength for Al:CuO samples until a certain wavelength.

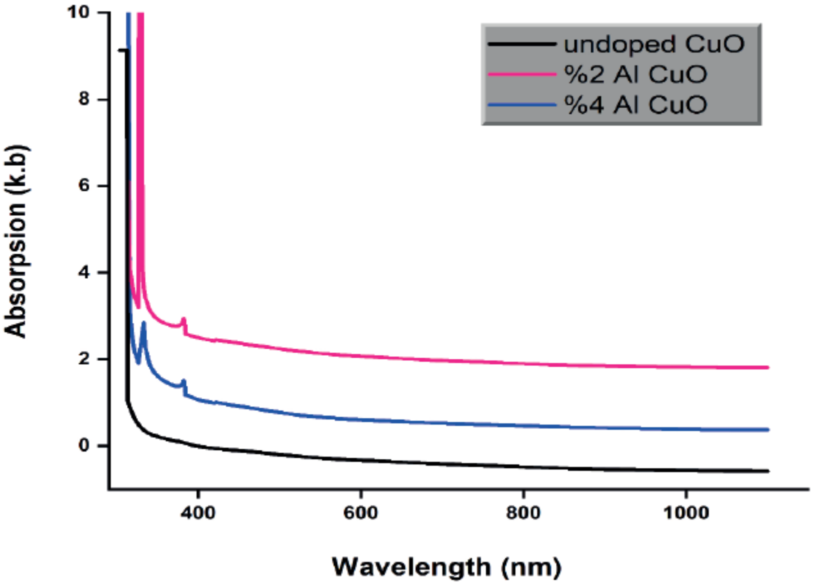

Fig. 3. Absorbance of Al: CuO thin film

The obtained samples have high absorption in the region of UV-Vis and have a high affinity for UV light. It can be said that the change in the absorption value is a result of the different crystal nature of the films and the Moss-Burstein effect (Manjunatha et al., 2018). The obtained results show that the optical properties of the samples change depending on Al doping. The change in the absorption value of the films shows that the obtained films can be applied in various optical applications.

Transmittance changes of Al:CuO samples annealed at 500 ˚C are indicated in Fig. 4. While pure sample indicated an average transparency value of ~42 % in the visible range of UV-Vis region, together with the Al doping average transmittance value decreased to ~30% for 4% Al doped sample.

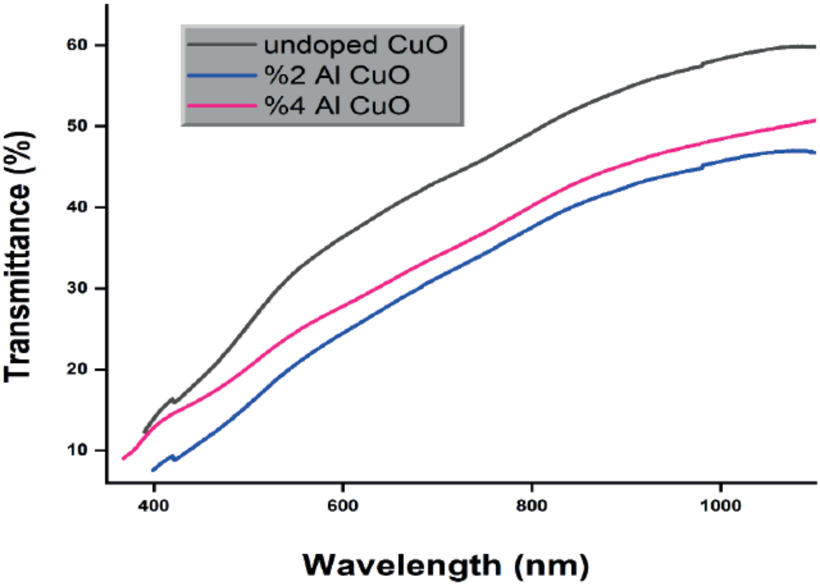

Fig. 4. Transmittance of Al doped CuO thin film

Optical properties of nanostructured CuO samples can be improved by Al doping in the UV-Vis spectra. The change in the optical transmittance value suggests that Al:CuO samples may be used as some applications like optical windows (Muiva et al., 2011).

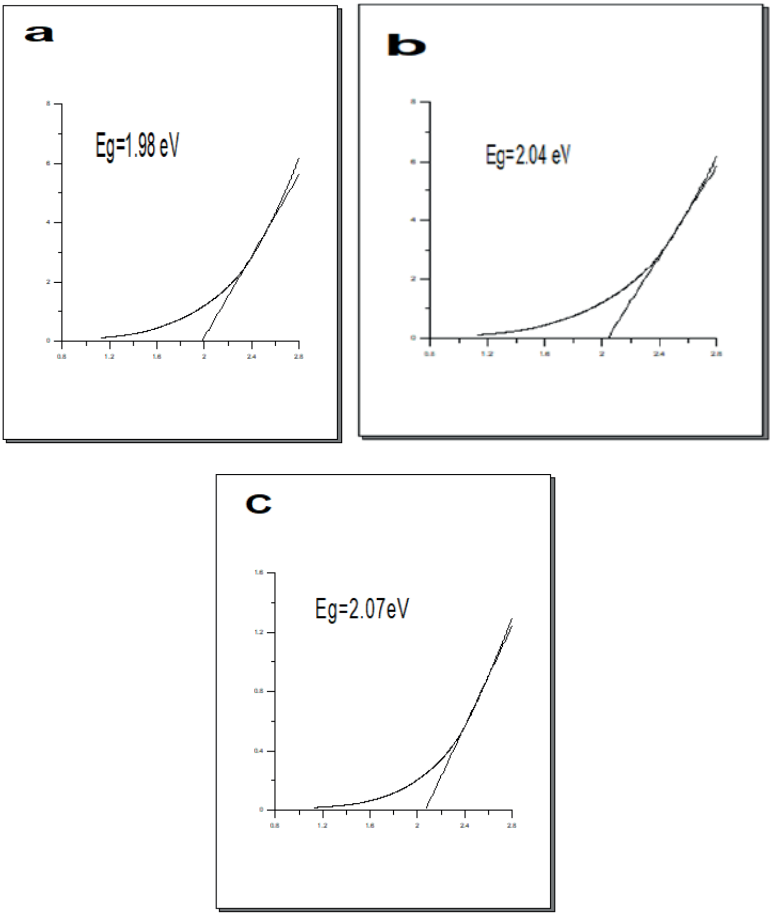

Fig. 5. Energy band gap of a) 0% Al:CuO, b) 2% Al:CuO , c) 4% Al:CuO thin film

The optical band gap energies are determined using the following equation

$$(\alpha h\nu)^2 = \beta\left(h\nu - E_g\right) \tag{6}$$

where β is an energy-independent constant, $h\nu$ is incident photon energy. The band gap energy values for all the films increased from 1.98 (no doping) to 2.04, 2.07 eV (2%, 4%, respectively) because of the basis of Moss-Burstein- (M-B) shift (Zhao et al., 2002). Jan et al. (2019) indicated that the presence of Al ions in CuO lattice has been seen to significantly affect the optical properties including transmittance and energy band gap because of difference in electro negativities, which may be associated with particle size and oxygen vacancies and formation of defects of used ions. They are also said that the optical energy band gap of CuO has been increased with the metal doping ratio which may be attribute to oxygen vacancies and particle size.

4. Conclusions

p-type nanostructured Al: CuO samples were grown onto glass substrate using spin coating method and the crystal and optical properties of all films were studied related to Al doping ratio. The XRD spectra shown that all the Al:CuO samples had polycrystalline nature with preferential (-111), (200) orientations. The grain sizes of all the films for different concentrations at 500 ^{0}C determined from the value of FWHM by Scherer 's equation. Calculated crystallite size for (111) peak decrease from 52 to 14 nm by increasing Al doping ratio. *d* values of the sample of (-111) and (200) peaks are found to be around 2.50 and 2.30 Å. AFM images indicate that the thin films with rod-like particles and a grain structure. The spectral absorption coefficient for Al:CuO film increase with the increase in wavelength for Al:CuO thin film until a certain wavelength (about ~ 1100 nm). While pure sample indicated an optical transparency of ~42 % in the visible range, together with optical transmittance value decreased to ~30% for 4% Al doped sample. The band gap energy values for all the films changed from 1.98 (no doping) to 2.04, 2.07 eV (2%, 4%, respectively).

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