Electrical and Structural Properties of Copper Oxide Thin Films Deposited on Plastic Substrate by Spray Pyrolysis Technique

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Abstract— **In this paper, copper oxide (CuO) thin films were deposited on polyimide plastic substrates by spray pyrolysis technique at different temperatures from 250 to 300°C. All the deposited films were characterized by X-ray diffraction (XRD) technique, ultraviolet (UV)-visible spectrophotometer, and hall effect measurements for the investigation of structural, optical, and electrical properties. The effects of substrate temperature on the structural, optical, and electrical properties of the films were studied. The XRD results revealed that all the CuO films have a face-centered cubic structure. The crystallite grain size was calculated using Scherrer formula and it was found that at the substrate temperature of 300°C, the CuO film presented maximum crystallite grain size of about 81.2 nm. The root mean square (RMS) roughness of the films was measured by scanning tunneling microscopy. RMS was increased with the rise of temperature. The optical transmission measurements by UV-visible spectrophotometer were used to determine the energy gap of the CuO films. Results showed that the optical energy gap has decreased with increasing the substrate temperature. Hall effect measurements showed that all the films are of p-type conductivity. Depending on the substrate temperature, hall measurement showed that the electrical resistivity and carrier concentration are varied from 77.4 Ω cm to 52.7 Ω cm and from 6.3×10^{15} cm^{-3} to 10.1×10^{15} cm^{-3}, respectively.**

Index Terms — **Copper oxide, Chemical spray pyrolysis, Thin film, Polyimide.**

I. Introduction

Copper oxide (CuO) is an important semiconductor material due to their important applications in many technological fields such as gas sensors (Mariammal, et al., 2013; Hubner, et al., 2011) and solar cells (Chandrasekaran, 2013; Amri, et al., 2013). This is due, first, to the low cost, the non-toxicity, and the availability of copper in nature, second to the simplicity of the deposition process of its components. CuO is a p-type semiconductor.

Regarding the preparation of CuO thin films, different physical and chemical deposition techniques are adopted, such as magnetron sputtering, spin coating, thermal evaporation, and shower pyrolysis (Dolai, et al., 2017; Nalbant, et al., 2013; Akkari, et al., 2007; Morales and Sanchez, 2005). Among the previously mentioned systems, splash pyrolysis is a promising technique because of its minimal effort nature and appropriateness for saving expansive zone thin-films (Faraj and Taboada, 2017).

Research on CuO testimony on adaptable polymeric substrates, for example, polyimide (PI) is gaining immense interests because of their adaptability, light-weight, minimal effort, high temperature opposition (regularly up to 400°C handling temperature), low coefficient of warm development coefficient of thermal expansion, low dampness take-up, and high dampness discharge qualities, its amazing electrical properties and furthermore expanded voltage perseverance (Faraj and Taboada, 2017; Faraj, et al., 2017). Because of its predominant properties, PI has discovered applications as substrates in adaptable thin-film sun oriented cells, adaptable printed circuits, and high thickness interconnects (Faraj and Pakhuruddin, 2015; Faraj, et al., 2017; Faraj and Omar, 2014).

A study has been reported on the characterization of CuO thin film on glass substrates with a spray pyrolysis technique (Chaudhary, et al., 2004). The novelty of the current work is to prepare and characterize thin film of CuO fabricated on PI plastic substrates.

In this paper, CuO thin films are prepared through chemical spray pyrolysis technique on PI plastic substrates at different substrate temperatures (250, 275, and 300°C). The influence of the substrate temperature on the structural, optical, and electrical properties of the CuO films is then studied.

II. Experimental Details

In this work, PI plastic substrates from DuPont corporation were used. Substrates were first cleaned using alcohol for 10 min to get rid of contamination, rinsed with deionized water, and dried with nitrogen gas. CuO thin films have been prepared on PI plastic substrates by chemical spray

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pyrolysis. The precursor solution was prepared by dissolving 0.1 M copper chloride ($CuCl_2.2H_2O$) in distilled water. To prepare 40 ml of the precursor solution the required quantity of salt is dissolved in double-distilled water. The substrate temperature was kept at different (250, 275, and 300°C) and the deposition time was fixed for 20 min.

The thickness of the film was optimized to be 500 nm. The film thickness was measured by the weighting method through a digital balance type (Meter AE-160) with sensitivity of 10^{-4} g, and the thickness was calculated according to the following equation (Ismail and Faraj, 2009).

$$t = \frac{\Delta m}{\rho . A} \quad (1)$$

Where, t is the thickness of the film, Δm is the mass of the film, ρ is the total density of the film, and A is the area of the film. The crystallographic structure of the prepared CuO thin films was determined using a high-resolution X-ray diffractometer (XRD) system (model: Panalytical empyrean) with CuKα radiation (λ) of 0.154 nm. The surface morphology of the CuO films was studied by scanning tunneling microscopy (STM) (model: NT-MDT Solver Nano). The optical properties of the films were characterized by a ultraviolet (UV)-visible spectrophotometer (model: UV-1240, Shimadzu). The hall measurement was implemented with HL5500PC system.

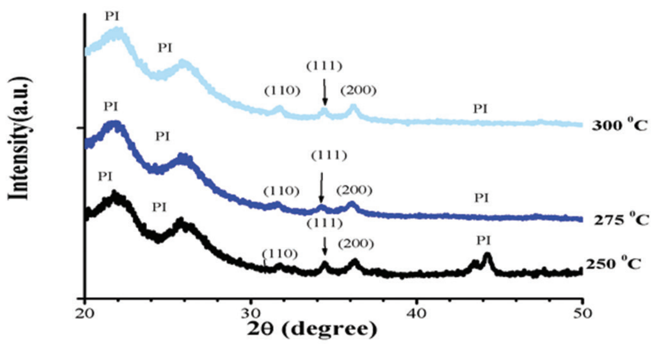

Fig. 1. X-ray diffraction patterns of copper oxide films on polyimide plastic at substrate temperatures of 250, 275, and 300°C.

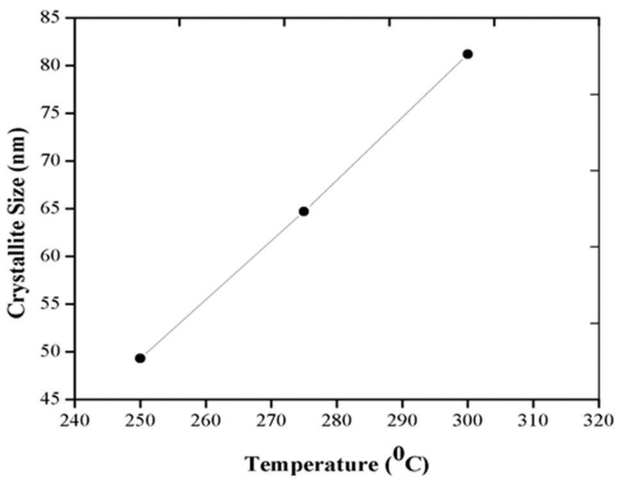

Fig. 2. Crystalline grain sizes as a function of substrate temperatures.

III. Results and Discussion

A. Structural Properties

Fig. 1 displays the patterns of XRD for the CuO thin films deposited on PI plastic for three different substrate temperatures. All CuO films have face-centered cubic structure (JCPDS card No.03-1005). The three pinnacles which have a place with the PI polymer are situated at 22.1°, 26.0°, and 44.6°, as shown in Fig. 1. This outcome concurs

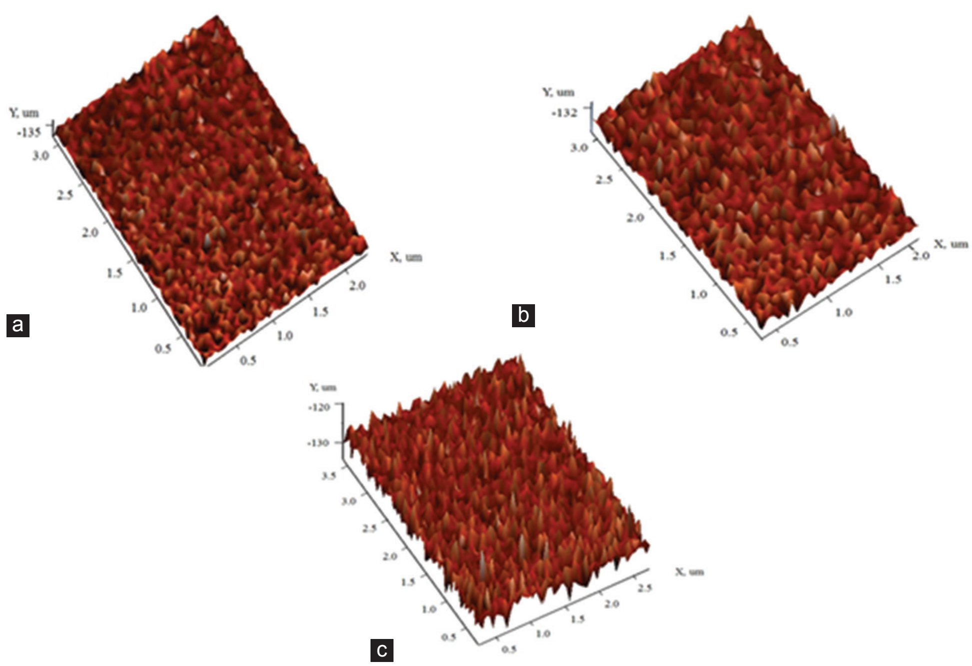

Fig. 3. Scanning tunneling microscopy images of copper oxide films deposited on polyimide substrate with different substrate temperatures (a) 250°C, (b) 275°C, and (c) 300°C.

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with recently revealed information (Faraj, et al., 2014). XRD patterns of all the CuO thin films showed (110), (111), and (200) peaks planes corresponding to the face-centered cubic structure of CuO thin films. These XRD results confirm the proper phase formation of the CuO films.

The crystalline grain size (D) of the CuO films was determined with the Scherrer formula (Birks, 1946).

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (2)$$

Where β is the full width at half maximum (FWHM) of the peak, λ is the wavelength of the X-ray of 1.5406 Å, and θ is their peak position. Based on the line width of the (111) diffraction peak, the crystalline grain size for the CuO films with different substrate temperatures is shown in Fig. 2, where the grain size is increased with the increasing of substrate temperature, especially at 300°C. It was observed that the increase of the substrate temperature acts on increasing the diffraction peak intensity of (111) plane which resulted in an increase in crystallite size of the films. This behavior is a consequence of the decrease in density of nucleation centers as the substrate temperature increases. Under this condition, smaller numbers of nucleation centers start to grow, resulting in larger grains in agreement with previous reports using other deposition techniques (Abbas, et al., 2013).

STM images of CuO thin films deposited on PI plastic substrate are shown in Fig. 3. The root mean square (RMS) surface roughness of the films was 5.69, 8.28, and 10.78 for films at temperature in the range of 250–300°C at 25°C steps. It should be noted that the RMS surface roughness slightly increases with increasing substrate temperature (Haug, et al., 2001).

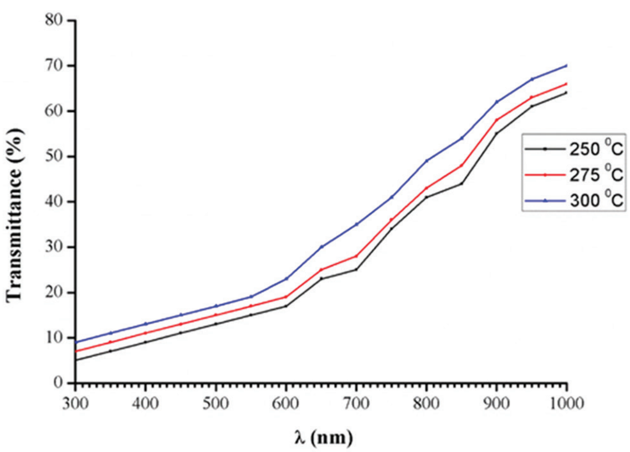

Fig. 4. Optical transmission spectra of copper oxide films deposited on polyimide substrate at different substrate temperatures.

B. Optical Properties

Fig. 4 shows the variation of the optical transmission as a function of wavelength from 300 mm to 1000 nm for the films deposited at different substrate temperatures. The transmission in the visible region is found to increase with increasing substrate temperature. An increase in substrate temperature improved the transmission of the CuO films. This improvement can be attributed to either the decrease in thickness or the improvement in perfection and stoichiometry of the films. Similar transmission profiles of CuO films have been previously reported (Hussein, et al., 2015).

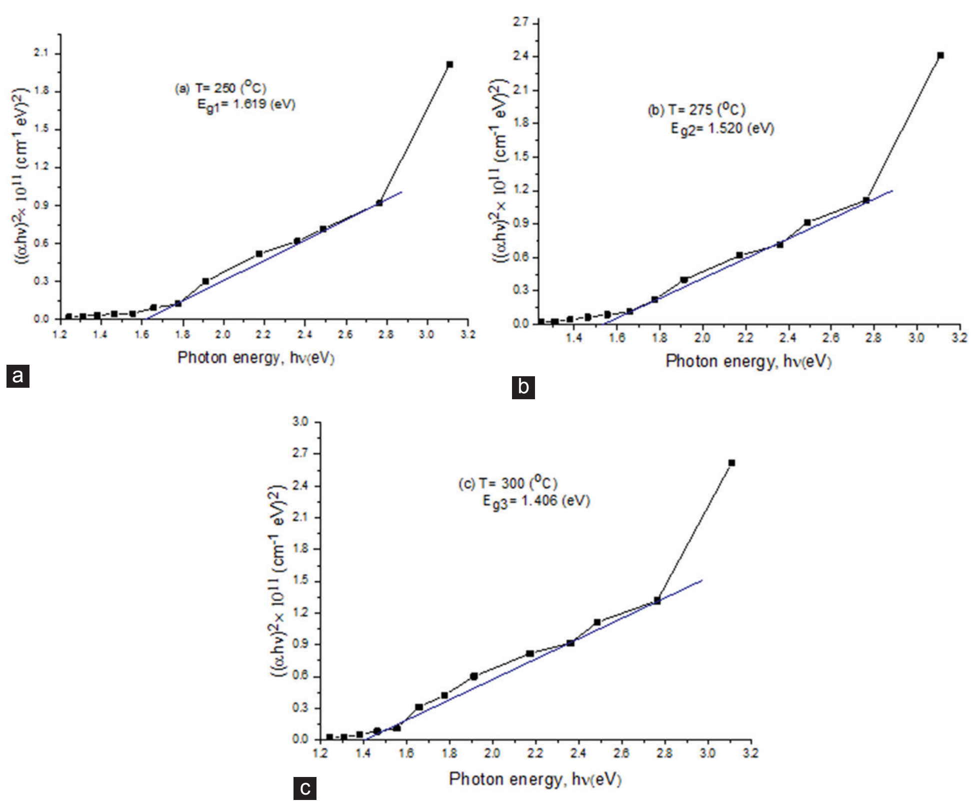

Fig. 5. (a-c) Plot of $(\alpha h\nu)^2$ against photon energy for copper oxide thin films deposited on polyimide substrate at different substrate temperatures.

TABLE I
Dependence of Electrical Resistivity and Carrier on the Temperature Substrates

T(°C)	Resistivity (Ω m)	Carrier concentration (cm^3)
250	77.4	6.3×10^{15}
275	63.5	8.5×10^{15}
300	52.7	10.1×10^{15}

The optical band gap (E_g) was determined by analyzing the optical data with the expression for the optical absorbance (α) and the photon energy ($h\nu$) using Tauc's equation (Tauc, 1974).

$$(\alpha h\nu) = k(h\nu - E_g)^n \tag{3}$$

Where n = ½ for allowed direct transition (for a direct band gap semiconductor), and k is a constant. The energy band gap was then estimated from the straight line of the plot $(\alpha h\nu)^2$ versus photon energy for CuO thin films, as shown in Fig. 5. Extrapolation of the linear portion of the graph to the energy axis at α = 0 gives the band gap energy (E_g) (Muhammad, et al., 2017; Muhammad and Sulaiman, 2011). The results of E_g for the CuO films were estimated to be in the range from 1.619 to 1.406 eV with respect to various substrate temperatures (250, 275, and 300°C), respectively. These values were found to be close to the value of energy gap for bulk CuO (1.5 eV) (Valladares, et al., 2012).

C. Electrical Properties

Hall effect measurements showed that all the films are of p-type conductivity. The dependence of the electrical resistivity and the carrier concentration on the temperature substrates is shown in Table I. It is seen that the electrical resistivity of the films decreases with the substrate temperature and the carrier concentration increases from 6.3 × 1015 cm−3 to 10.1 × 1015 cm−3 with increasing temperatures. The increased bulk carrier concentration caused by increasing the substrate temperature reduced the grain boundary potential barrier. The decrease in resistivity can be ascribed to the increase in carrier concentration. This outcome concurs with recently revealed information (Mohamed, et al., 2016). The increase in the carrier concentration causes shrinkage in the gap and also due to the decrease in resistivity. This signifies that density of dislocation and density of grain boundaries decrease. Therefore, it could be related to an improvement of the crystallinity leading to a decrease of donor sites trapped at dislocations and grain boundaries (Lee and Park, 2004; Oztas, et al., 2006).

IV. Conclusion

CuO thin films were deposited on PI plastic substrates with chemical spray pyrolysis. The effects of substrate temperature (250, 275, and 300°C) on the structural, optical, and electrical properties of the films deposited were studied. XRD patterns confirm the proper phase formation of the CuO. The crystallite grain sizes for as-deposited CuO films were 49.3–81.2 nm at different temperatures ranging from 250 to 300°C in 25°C steps. It was observed that crystallite grain size increased with increasing film temperature. The RMS roughness of the films increased as the film temperatures increased. The transmittance increases with increasing of substrate temperature. The optical band gap was also found to vary from 1.619 to 1.406 eV. Depending on the substrate temperature, hall measurement showed that the electrical resistivity and the carrier concentration varied from 77.4 Ω cm to 52.7 Ω cm and 6.3×10^{15} cm^{-3} to 10.1×10^{15} cm^{-3}.

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