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Correlation between molar concentration and properties of sprayed copper oxide thin films

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ABSTRACT

Copper oxide precursor solutions containing 0.10 M, 0.15 M, 0.20 M and 0.25 M concentration of copper were deposited on a glass substrate using the spray pyrolysis method. The structural, optical and surface properties of the resulting copper oxide thin films were studied using x-ray diffraction, UV–visible spectroscopy and scanning electron microscopy. Structural studies indicate the absence of secondary phases of copper oxide in the spray-deposited copper oxide thin film with 0.10 M concentration. Optical characterization reveals highest absorbance and lowest transmittance at 0.10 M concentration with an estimated optical bandgap of 1.2 eV. The SEM micrographs reveals a non-porous and comparatively more homogenous surface at 0.10 M concentration. The results show that molar concentration of copper plays a vital role in the development of copper oxide (CuO) thin film for solar cell application. The results have further validated the theoretical predictions of the GW approximations on phases of copper oxide thin films.

1. Introduction

Copper oxide (CuO)is a novel chemical compound that is non-toxic, and its nanostructured form can find applications in biomedical engineering as antimicrobial agent (Verma & Kumar, 2019). Composite propellants as combustion catalyst is also an application of copper oxide (Yadav et al., 2021). A very common application of nanostructured CuO can be found in thin film solar cells where it can be utilized as an absorber layer. Burning of fossil fuels for production of electricity has impacted negatively on the environment, therefore, opting for renewable source of energy as an alternative to fossil fuels has become highly necessary. Solar energy is prominent among the several renewable sources of energy due to abundance of the sun and can be directly converted to electricity by a solar cell. CuO absorber-based thin film solar cell can serve as an alternative to popular silicon solar cells that is in use today. The reason is: copper oxide absorber-based solar cell will be affordable due to its direct bandgap, high absorption coefficient (Ozga et al., 2020) and abundance of copper in the earth crust. CuO thin film layers can be easily synthesized using wet chemical methods. Recent works on chemical synthesis of CuO can be found in refs. (Kurniawan et al., 2021; Daoudi et al., 2020; Toupin et al., 2019; Aroussi et al., 2022). Almost all the chemical methods of deposition can be easily developed or assembled from cheap materials, but spray pyrolysis is superior to others in wide area deposition ensuring its industrial scalability (Ajayi et al., 2021). Deposition parameters can also be easily optimized for an optimum thin film deposition process. Optimization of these parameters and their influence on properties of CuO thin films have been investigated in recent works (Prabu et al., 2017; Asl & Rozatti, 2018; Ozga et al., 2020). The influence of concentration on properties of copper oxide thin films prepared by spray pyrolysis have been rarely studied at concentrations higher than 0.10 M especially when using copper acetate as precursor. This may have been due to precipitation in the solution which will impede the deposition process. It should also be noted that very few works have been done on experimental verification of the electronic structure of oxide phases of copper oxide (Zheng et al., 2018). In this work, copper oxide thin films have been synthesized using spray pyrolysis method, its structural and optical properties have been studied in correlation to concentration of copper in precursor solution and the results compared with theoretical predictions.

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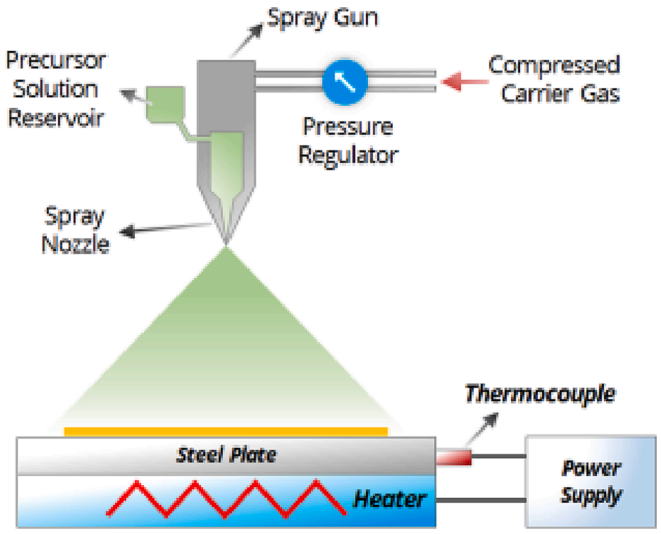

Fig. 2.1. Schematics of spray pyrolysis assembly (Park et al., 2016).

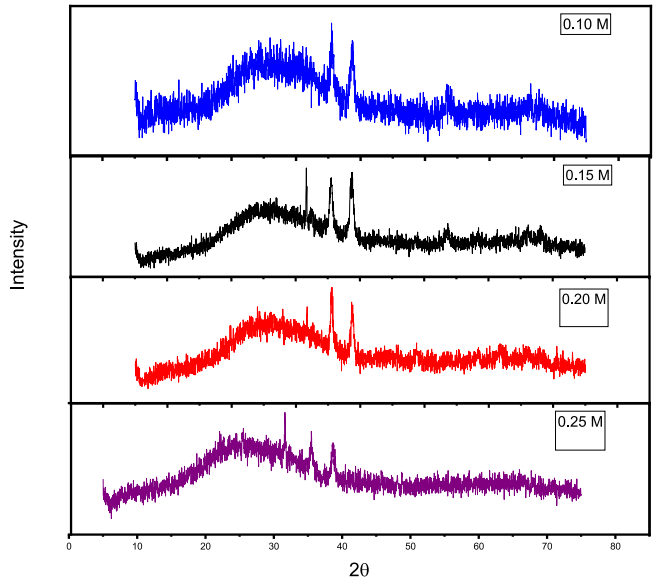

Fig. 3.1. X-ray diffractograms of concentration-varied copper oxide thin films.

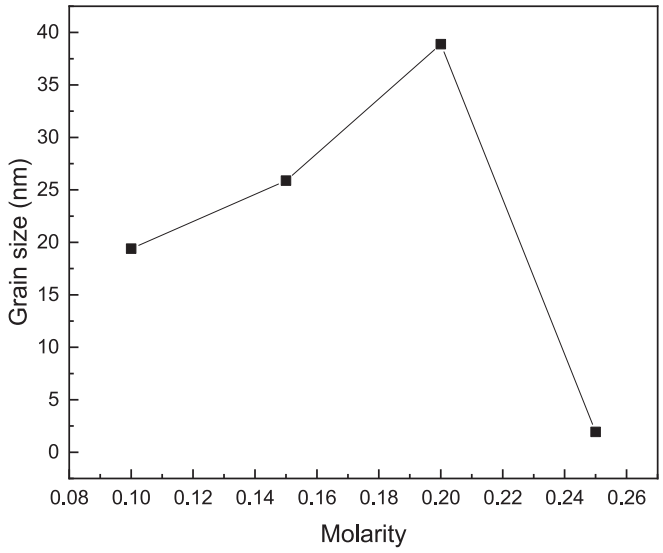

Fig. 3.2. Plot of grain size versus molarity.

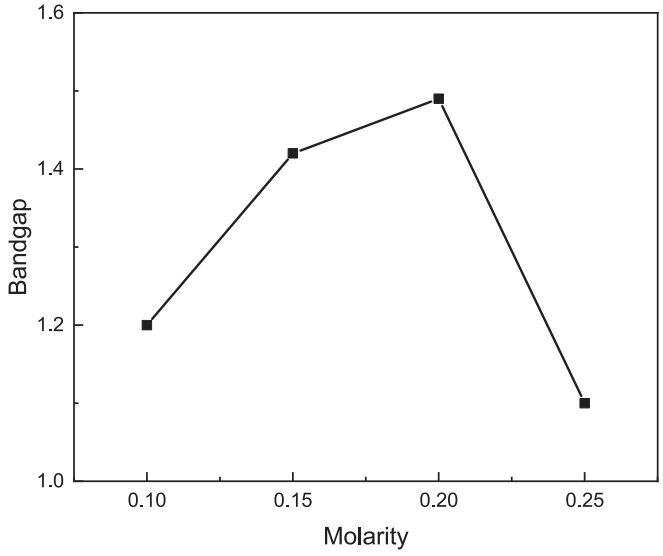

Fig. 3.3. Plot of bandgap versus molarity.

Table 1
Summary of X-ray diffraction patterns.

Sample	CuO					Cu_4O_3/CuO				
	2θ (deg.)	**(*hkl*)**	**D (nm)**	**ε (x10^{-3})**	**δ (x10^{14}) (lines/m^2)**	**2θ (deg.)**	**(*hkl*)**	**D (nm)**	**ε (x10^{-3})**	**δ (x10^{14}) (lines/m^2)**
0.10 M	35.60	002								
	38.70	111	19.40	1.79	26.57					
0.15 M						31.63	103			
						35.54	002	25.88	1.34	14.90
						38.79	111			
						53.50	020			
0.20 M						31.63	103			
						35.50	002	38.80	0.89	6.64
						38.70	111			
						48.66	$20\bar{2}$			
0.25 M						31.66	103	19.41	1.79	26.54
						35.48	002			
						38.64	111			

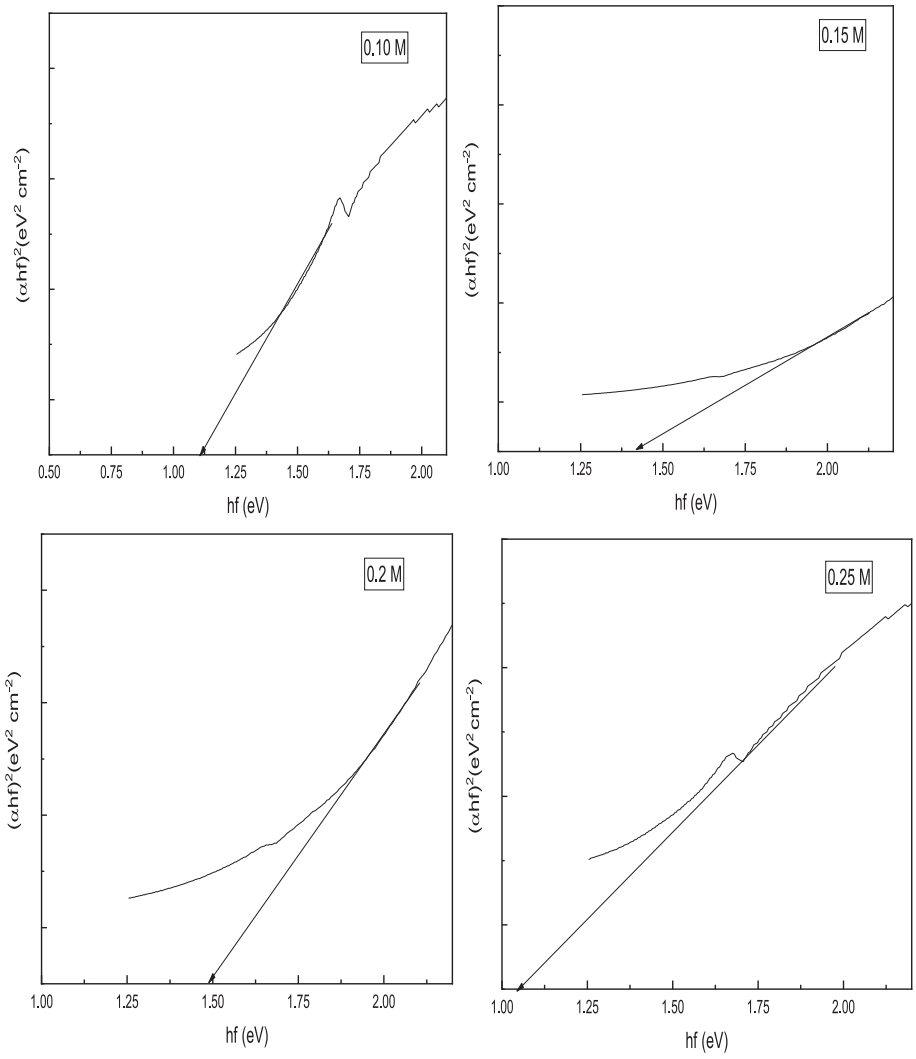

Fig. 3.4. The plot of $(\alpha hf)^2$ versus hf of copper concentration varied copper oxide thin films.

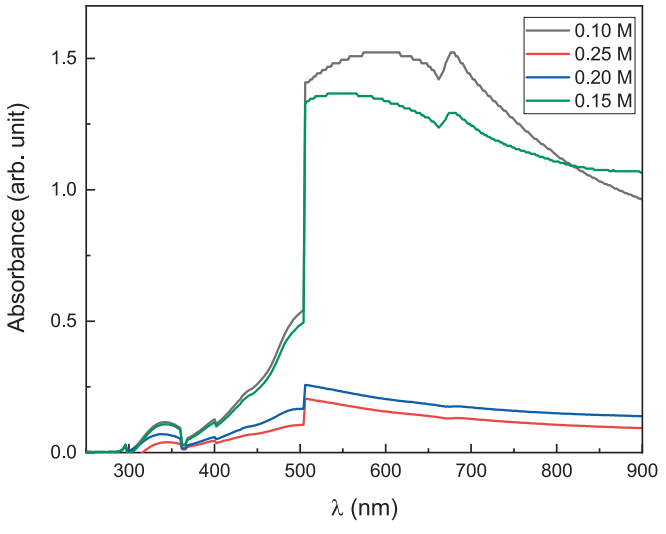

Fig. 3.5. Absorbance spectra of copper concentration-varied copper oxide thin films.

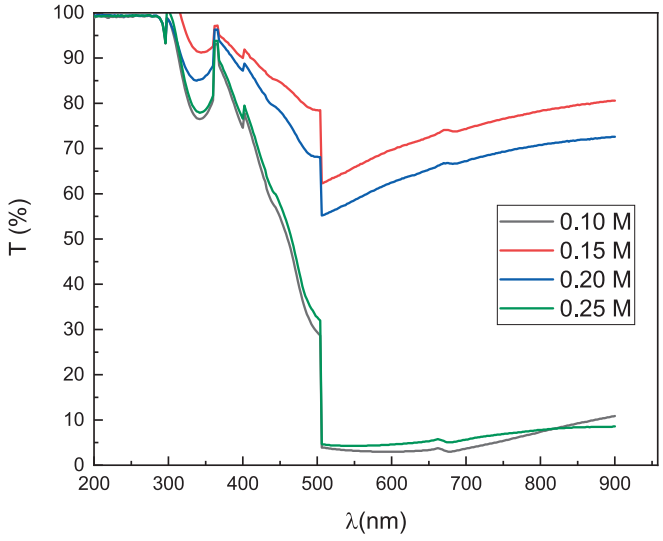

Fig. 3.6. Transmission spectra of copper concentration-varied copper oxide thin films.

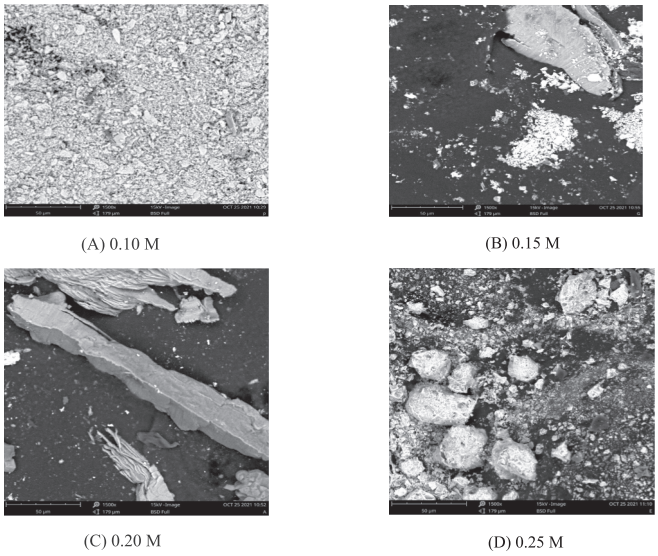

Fig. 3.7. Scanning electron micrographs (SEM) of concentration-varied CuO thin films.

2. Experimental detail

2.1. Synthesis of CuO thin films

0.10 M, 0.15 M, 0.20 M and 0.25 M precursor solutions were prepared by dissolving copper (II) acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$) in a solvent containing 70% deionized water and 30% alcohol. A pipette drop (0.05 ml) of HCl was added to prevent precipitation in the solution. The solution was later stirred without heating using a magnetic stirrer for 60 min. CuO thin films were obtained by spraying the solutions on thoroughly cleaned glasses heated up to 350 ± 10 °C. Schematic diagram of a spray pyrolysis assembly is shown in Fig 2.1. The details of a spray technique can be obtained from the ref. (Ajayi, et al. Influence of solvents on properties of ZnS thin films synthesized by chemical spray pyrolysis technique, 2021). Air was used as carrier gas and spraying was done at 40 psi with nozzle to target distance maintained at 28 cm. The nozzle diameter was 0.25 mm. The resulting copper oxide thin films were later annealed in a muffled furnace at 350 °C for one hour.

2.2. Characterization

The structural properties of the synthesized CuO thin films were characterized using X-ray diffractometer (EMPYREAN). The diffractometer was operated at current and voltage of 40 mA and 45 kV respectively for the specimens. Surface morphology studies of the sample was carried out using a Phenom ProX desktop scanning electron microscope (model number: 800–07334). Optical characterization was done using ultraviolet–visible fiber optics spectrophotometer.

3. Results and discussion

3.1. Structural characterization

X-ray diffraction patterns of concentration-varied sprayed CuO thin films are shown in Fig. 3.1 and it can be observed that structural properties of the spray-synthesized copper oxide thin films have been widely influenced by molar concentration. 0.10 M specimen exhibited diffraction peaks identical to tenorite phase (CuO) of copper oxide (JCPDS card no: 65–2309). No other phases of copper oxide were detected. Specimens 0.15 M, 0.20 M and 0.25 M show diffraction peaks identical to paramelaconite (Cu_4O_3) phase (JCPDS card no: 49–1830). Crystallite sizes of the copper oxide thin films were calculated using the Debye-Scherrer equation (Hajizadeh et al., 2022). A crystallite size of 19.40 nm was calculated for 0.10 M specimen. Higher grain sizes of 25.88 nm and 38.80 nm were calculated for specimens 0.15 M and 0.20 M respectively. Copper oxide thin film synthesized at 0.2 M concentration of copper exhibited a crystallite size of 19.41 nm. Table 1 shows the summary of x-ray diffraction data of observed copper oxide phases. The grain sizes have been calculated from the (1 1 1) preferential reflection plane. The dependence of grain size on molarity is shown in Fig. 3.2. Microstrain and dislocation densities of the films were calculated from expressions obtained from refs. (Almazan et al., 2021) (Klug & Alexander, 1974). A decrease in microstrain and decrease in dislocation densities of the films with increasing molar concentration can be observed until the concentration became 0.25 M. The increase in the microstrain and dislocation densities at 0.25 M is an indication of low levels of crystallinity in the film. Molar concentration may have played an important role in the phase transition of copper oxide. Cu^{2+} atoms occupying oxygen vacancies may have been responsible for the presence of paramelaconite phase in the copper oxide thin films.

3.2. Optical characterization

Fig. 3.4 shows the Tauc's plot for the solvent varied copper oxide thin films. Bandgaps (Eg) of the concentration varied copper oxide thin films have been obtained using the Tauc's relation (Zheng et al., 2018). It can be observed from the plot that 0.10 M specimen has a bandgap of 1.2 eV which is in agreement with a previous work on the tenorite phase of copper oxide (Wang et al., 2016). Bandgap calculated for 0.15 M and 0.20 M specimens are 1.42 eV and 1.49 eV and this can be confirmed from recent works (Dolai et al., 2017; Alajlani et al., 2017). Generally, an increase in bandgap was observed until the concentration became 0.25 M with a corresponding decreased bandgap of 1.1 eV. The dependence of bandgap of the spray-synthesized films on concentration is shown in Fig. 3.3. Concentration may have played an important role in the tuning the bandgap. In this work, the bandgap of CuO thin film synthesized at molar concentration of 0.10 M is closer to that predicted by the GW approximation which has been reported to give the correct description between the oxide phases of copper oxide (Wang et al., 2016). While bandgap is expected to decrease with increase in grain size, high porosity of 0.15 M and 0.20 M may have been responsible for the increase in bandgap (Sheng & Ee, 2018). Figs. 3.5 and 3.6 shows the transmission and absorption spectra of the copper oxide thin films revealing highest absorbance and lowest transmittance in 0.10 M. It can also be observed from the absorption spectra that absorbance increases with increase in wavelength which may have been due to quantum size effect (Takada et al., 2019). Rapid increase in absorbance and a redshift can be observed in the absorbance and transmittance of all sprayed copper oxide films at 500 nm wavelength. This can be attributed to the surface roughness of the CuO thin films. Increase in surface roughness will increase the amount of absorbed light. An increase in copper concentration will lead to more electrons in the conduction band and reduction in the density of the localized states in the conduction band, which will consequently raise the bandgap.

3.3. Surface studies

The SEM images of surface of copper concentration-varied thin films are shown in Fig. 3.7. SEM images indicates the surface of sprayed CuO thin films is widely influenced by concentration of copper in the precursor solution. Specimen 0.10 M and 0.25 M exhibit dense morphology in comparison with 0.15 M and 0.20 M, both of which exhibit high porosity with irregularly shaped and non-homogenous grains. 0.20 M shows less homogenous distribution of grains and greater porosity in comparison with 0.10 M, though, the surface morphology is spherical.

4. Conclusion

This study concluded that, molar concentration of copper plays a vital role in the synthesis of CuO thin films. The results have further validated the theoretical predictions of the GW approximations on phases of copper oxide thin films.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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