

Sol-Gel Fabricated CuO Thin Film: Characterization for Device Application

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(Received 06 November 2020; revised manuscript received 20 October 2021; published online 25 October 2021)

In this paper, a wide band gap semiconductor CuO has appeared as a promising material suitable for high-temperature, high-frequency, and high-power operations in electronics as well as optoelectronic devices because of its exceptional characteristics. In particular, CuO films have an outstanding ability to materialize short-wavelength light-emitting devices due to the large band gap energy. CuO films are widely used for optoelectronic applications in the short wavelength visible light region especially for laser diodes (LDs) and light-emitting diodes (LEDs). Here, we report the properties of a copper oxide thin film prepared by the sol-gel technique, which is very economical and involves a sophisticated method. The prepared film is characterized by X-ray diffraction (XRD) for structural analysis. The scanning electron microscope identifies porous morphology, and the elemental composition of CuO is confirmed by EDS. The appearance of strong and weak Raman peaks at $300\text{-}350\text{ cm}^{-1}$ is observed. The optical study is carried out by UV-visible absorbance from the direct band gap calculated for the prepared film, that is 2.43 eV. The I - V measurements are performed using a two-probe technique, and the CuO film shows semiconductor behavior with an activation energy of 0.21 eV. Thus, the obtained results indicate the prepared sample for electronic devices and various other optical applications.

Keywords: CuO, Sol-gel, Optical band gap, Nanoparticles, DC conductivity, Optoelectronic.

DOI: [10.21272/jnep.13\(5\).05018](https://doi.org/10.21272/jnep.13(5).05018)

PACS numbers: 81.20.ka, 81.70.Pg, 61.72.Uj

1. INTRODUCTION

Transition metal oxides (TMOs) have become an essential part of modern technologies that demand both electrical and optical transparency in the visible domain of the electromagnetic spectrum [1]. The thin film based copper oxide (CuO) has been used in many electronic and optoelectronic devices such as thin-film transistors, cross-point memories, gas sensors, and lithium-ion batteries [2] over recent decades. The main advantages of this oxide include low production cost, thermal stability, nontoxicity, and relatively high optical absorption [3]. CuO is a degenerate p -type II-VI semiconductor possessing special features such as high electrical conductivity (even without doping), high optical transmittance, exceptional luminescence characteristics, and an optical energy band gap of 2.13 eV [4]. Nowadays, studies of copper oxide (CuO) nanoparticles continue due to their p -type semi-conducting properties with a narrow band gap, monoclinic structure, and giant magnetic field resistance [5].

Various deposition techniques have been deployed for the preparation of CuO thin films, such as chemical vapor deposition [6], magnetron sputtering [7], thermal oxidation [8], electrodeposition [9], sol-gel [10], and spray pyrolysis [11]. In this paper, we report the synthesis and characterization of CuO thin films by a simple sol-gel dip-coating technique. In contrast to other methods, the sol-gel dip-coating technique has distinct advantages such as simplicity, cost-effectiveness, eco-friendliness and high porosity over a large area. To our best knowledge, the sol-gel dip-coating has not been implemented for any TMO film preparation. We have

investigated the XRD, optical and electrical properties of CuO thin films prepared by this simple technique for optoelectronic applications.

2. EXPERIMENTAL

Initially, a gel solution made of copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$) and citric acid ($\text{C}_6\text{H}_8\text{O}_6$) with a molar ratio of 1:3.6 was prepared. Next, the as-prepared solution was continuously stirred at a temperature of $70\text{ }^\circ\text{C}$ for half an hour. Then, the solution was heated at a temperature of $100\text{ }^\circ\text{C}$ until it is converted into a dry powder. Further, the sample was annealed at a temperature of $200\text{ }^\circ\text{C}$ for 1 h to reduce grain boundaries. Finally, the obtained powder was calcined at a temperature of $500\text{ }^\circ\text{C}$ for 5 h to remove impurities. The obtained calcined powder was found to be a good crystalline CuO phase. The process is shown in Fig. 1a. Prior to sol-gel dip-coating, glass substrates were cleaned with a mild soap solution and thoroughly rinsed with distilled water followed by boiled water. Finally, the glass substrates were immersed into the solution as shown in Fig. 1b. The films thus prepared were inserted into a muffle furnace and kept at $300\text{ }^\circ\text{C}$ for 10 min in order to evaporate the organic material. Fig. 1c depicts the required stable film.

All the characteristic measurements were carried out at room temperature in air. The characterization techniques such as X-ray diffraction (XRD), Raman spectroscopy, UV-Vis spectroscopy, and Scanning Electron Microscope (SEM) were used to confirm the formation of CuO and effect of doping on its structural and morphological features.

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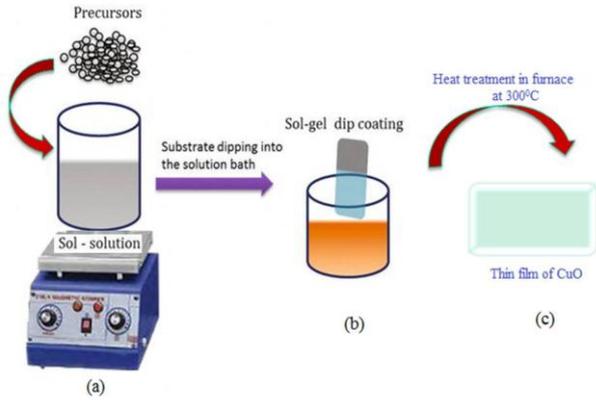


Fig. 1 – Schematic diagram for the preparation of a thin film of CuO by the sol-gel technique

3. RESULTS AND DISCUSSION

3.1 XRD Pattern

XRD pattern is the most suitable technique to identify the crystalline nature of the prepared samples. The XRD pattern of the thin film is shown in Fig. 2. All the peaks could be clearly indexed to the monoclinic phase with lattice constants $a = 0.4675$, $b = 0.3418$, $c = 0.5095$, which agrees well with the literature. In addition, the XRD pattern shows that the copper oxide is crystalline in nature and the diffraction peaks match very well with the pdf file (JCPDS-05-0661). The peaks at $2\theta = 32.51^\circ, 35.33^\circ, 38.01^\circ, 49^\circ, 53.88^\circ, 58.93^\circ, 62.11^\circ, 66.51^\circ, 68.78^\circ, 72.68^\circ, 75.53^\circ$ are assigned to the (110), (-111), (111), (-202), (020), (202), (-113), (022), (220), (321), and (203) reflection lines of monoclinic CuO particles, respectively. No characteristic peaks of any impurities are detected except for a few traces of copper. The crystallite size is calculated from the Debye-Scherrer formula:

$$D = (K\lambda / \beta \cos\theta), \tag{1}$$

where K is the shape factor equal to 0.94, λ is the CuK α radiation wavelength (1.5406 Å), β refers to the full width half maximum (FWHM) in radians, and θ is the angle of incident radiation, which is 34.96 nm.

To get more crystal quality information, dislocation density (δ) must be determined according to the relation (2) and is about $8.18 \cdot 10^{18}$ lines/m² [12]:

$$\Delta = (1/D^2). \tag{2}$$

In thin films, strain originates mainly from the mismatch between a polycrystalline film and an amorphous substrate or from the difference in the thermal expansion coefficients of the film and the substrate. Microstrain can be calculated by the following formula and is found to be equal $1.037 \cdot 10^3$ lines⁻²/m⁴ [13]:

$$\varepsilon = \beta \cos\theta/4. \tag{3}$$

The above structural parameters are in good agreement with reported values of Basith et al. [14].

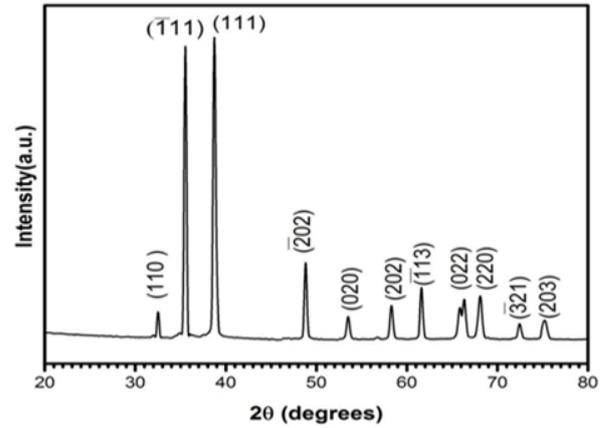


Fig. 2 – XRD pattern of CuO thin film

3.2 Morphology and Elemental Examination

The as-synthesized samples were directly transferred to the FESEM chamber without disturbing the original nature of the products. Fig. 3 shows the morphology of nanoclusters obtained after the reaction of copper with water at 120 °C for 18 h. The nanoclusters constituting of nanocrystals are almost spherical in shape and have diameters varying between 15 to 25 nm, with an average diameter of 15 nm. In some regions, we notice that large nanoparticles (with an average diameter of 40 nm) are surrounded by smaller nanoparticles. In addition, the EDS spectrum revealed only the elements Cu and O, and the atomic ratio of Cu to O was 1:1, which was consistent with stoichiometric CuO. This EDS spectrum is shown in Fig. 4.

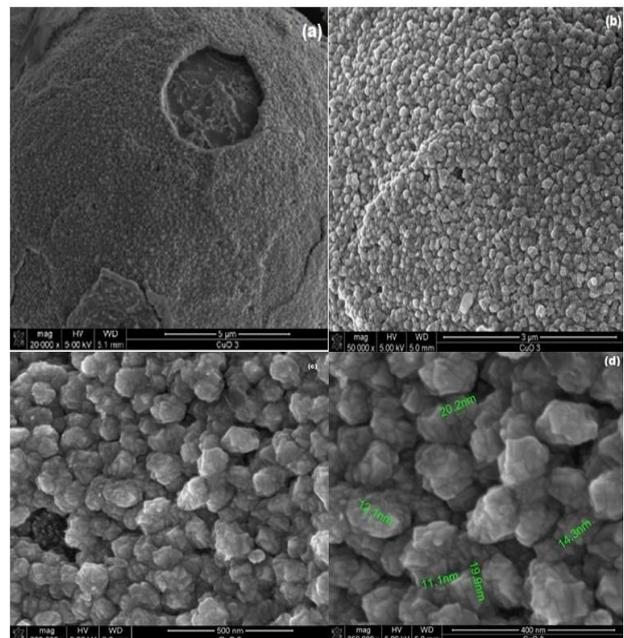


Fig. 3 – FESEM images of CuO thin film prepared at 300 °C with different magnifications

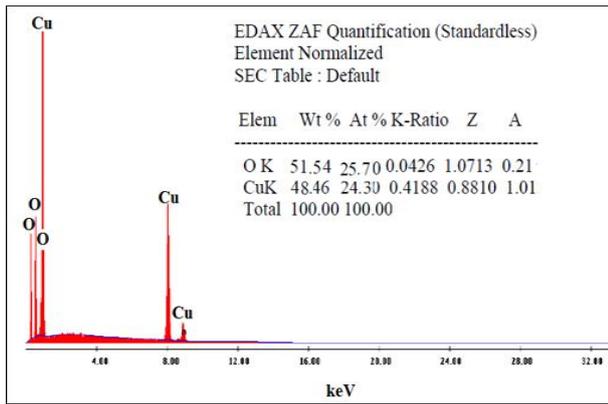


Fig. 4 – EDS pattern of CuO thin film

3.3 Raman Spectroscopy

Raman spectroscopy is a good complementary method to determine the film phase structure in the surface vicinity. Here, Raman analysis of CuO thin film at room temperature (300 °C) was carried out. CuO has a monoclinic structure with space group symmetry of C_{2h}^6 . It has 12 phonon branches: four atoms in the primitive cell (four Cu–O molecules per unit cell and two CuO units in the primitive cell). A factor-group analysis gives the following zone-center modes [15]:

$$\Gamma_{vib} = A_g + 2B_g + 4A_u + 5B_u. \quad (4)$$

Fig. 5 revealed three Raman active modes at 283, 330 and 616 cm^{-1} . The peak at 283 cm^{-1} corresponds to the A_g mode, and the other two peaks at 330 and 616 cm^{-1} correspond to two B_g modes, which are the basic band of CuO [16]. In both XRD and Raman, the CuO peaks were identified.

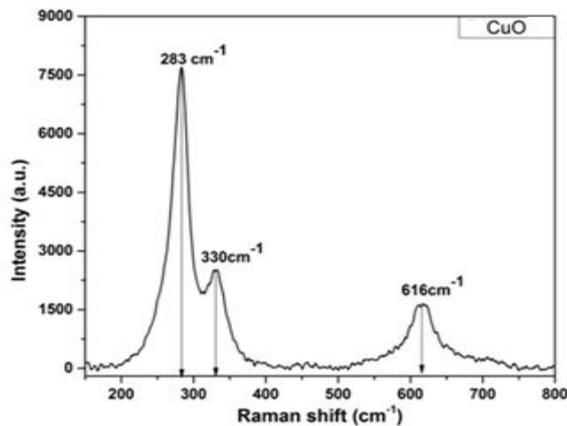


Fig. 5 – Raman spectra of CuO thin film

3.4 FTIR Analysis of CuO Thin Film

FTIR spectroscopy, a phenotypic technique, identifies chemical bonds in a molecule by producing an infrared absorption spectrum. It is an effective analytical instrument for detecting functional groups, intra/inter molecular interactions via hydrogen bonding and molecular geometry [17]. The infrared spectrum of CuO film is shown in Fig. 6. This spectrum of CuO sample is presented in three regions. In the first region, the

peaks observed at 523 and 856 cm^{-1} represent a strong absorption band. In this band, the stretching of Cu–O is along the (-202) direction because CuO is monoclinic in phase [18]. In the second region (1435-1636 cm^{-1}), the peaks can be attributed to the presence of CO_2 in air. The third region starts from 2948 to 3513 cm^{-1} , and moistening in air and hydrated CuO material are responsible for the creation of peaks. Therefore, the results of the FTIR spectrum confirm that synthesized CuO thin film dipped into the solution is a pure and monolithic phase.

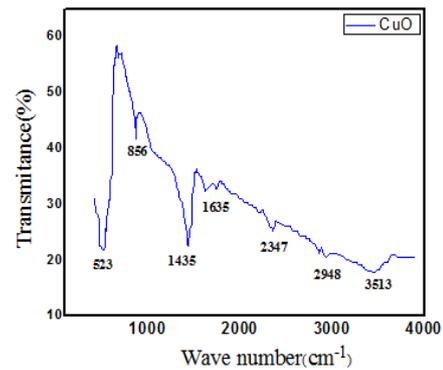


Fig. 6 – FTIR spectrum of CuO thin film

3.5 UV-Visible

The optical properties and the energy band gap of CuO thin film were studied by UV-visible absorbance spectroscopy in the wavelength range 250-1100 nm, as shown in Fig. 7. This spectrum shows the excitonic absorption edge at 553 nm for the film as prepared. The corresponding band gap energy (E_g) for the given film is determined using the Einstein's equation (5) [19]:

$$E_g = \frac{hc}{\lambda_s}, \quad (5)$$

$$E_g = \frac{1240}{\lambda_s} eV, \quad (6)$$

where h is the Planck's constant, c is the velocity of light, and λ_s is the excitonic absorption edge. The energy band gap is calculated to be ~ 2.25 eV. This value is suitable for optoelectronics devices like LEDs, solar cells, sensors etc.

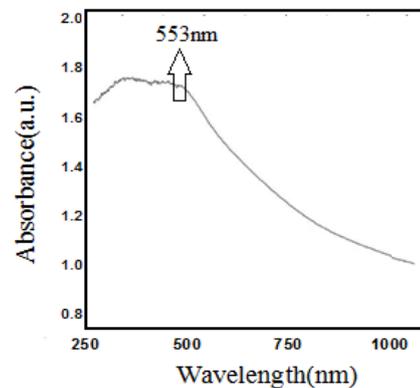


Fig. 7 – Absorbance spectrum of CuO thin film

3.6 Electrical Conduction

Electrical characterization plays the main role in the identification of photovoltaic materials, and in this report, the DC resistivity measurement of the fabricated CuO film was carried out using a Keithley 4200 semiconductor characterization system. It was observed that the CuO film has a high resistivity due to grain boundary effects and a larger band gap of CuO, which will create a potential barrier that causes a reduction in conductivity [20]. The temperature dependence of dark electrical resistivity (DC) can be depicted using the popular Arrhenius relation given by:

$$\rho = \rho_0 \cdot \exp\left(\frac{E_a}{kT}\right), \quad (5)$$

where ρ_0 , E_a , k and T are the pre-exponential factor, activation energy, Boltzmann constant, and temperature in Kelvin, respectively. The activation energy for CuO fabricated film was calculated from the slope of the graph shown in Fig. 8. The activation energy was found to be 0.21 eV, which is a suitable value for optoelectronic applications.

4. CONCLUSIONS

A thin film of CuO on a glass substrate was prepared on a home-made sol-gel syringe pyrolysis unit. XRD showed that the film has a monoclinic crystal structure with the lattice parameters $a = 0.4675 \text{ \AA}$, $b = 0.3418 \text{ \AA}$, and $c = 0.5095 \text{ \AA}$. According to the XRD pattern, the material thus prepared is in single CuO phase with preferential orientation along the (111) plane. The Raman spectra are in good agreement with the XRD. The average grain size was found to be about

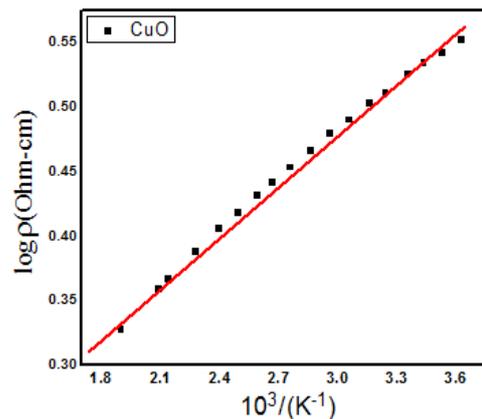


Fig. 8 – Linear fit of temperature-dependent resistivity of CuO thin film

34.96 nm. The optical band gap of the material was found to be 2.25 eV. The FTIR spectrum confirmed the Cu–O stretching modes without any trace of impurities. The DC conductivity measurement revealed the semi-conducting behavior of the film with an activation energy of 0.21 eV. This showed that the charge conduction process is thermally activated. The present study applied the quality of CuO thin films prepared by this technique to be used in optoelectronic devices.

ACKNOWLEDGEMENTS

The authors are thankful to BGSB University for the support and encouragement, as well as to Dr. A.H. Sofi from the Department of Physics at Central University of Kashmir for helpful suggestions.

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**Тонка плівка CuO, виготовлена методом золь-гелю:
характеристики для застосування в пристроях**

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Широкозонний напівпровідник CuO є перспективним матеріалом, придатним для високо-температурних, високочастотних та високопотужних застосувань в електроніці і оптоелектронних пристроях через свої виняткові характеристики. Зокрема, на основі плівки CuO реалізуються короткохвильові світловипромінювальні пристрої завдяки великій ширині забороненої зони. Плівки CuO широко використовуються для оптоелектронних застосувань у короткохвильовій частині видимого світла, особливо для лазерних діодів та світлодіодів. У роботі ми повідомляємо про властивості тонкої плівки з оксиду міді CuO, виготовленої дуже економічною технікою золь-гелю. Підготовлена плівка характеризується рентгенівською дифракцією (XRD) для структурного аналізу. Скануючий електронний мікроскоп визначає пористу морфологію, а елементний склад CuO підтверджується EDS. Спостерігається поява сильних і слабких раманівських піків у діапазоні 300-350 cm^{-1} . Оптичне дослідження проводиться за допомогою поглинання в УФ та видимій областях з прямої забороненої зони, розрахованої для підготовленої плівки, яка становить 2,43 еВ. Вимірювання характеристик *I-V* виконуються за двозондовою технікою, а плівка CuO демонструє напівпровідникову поведінку з енергією активації 0,21 еВ. Таким чином, отримані результати вказують на можливість використання CuO в електронних пристроях та різних інших оптичних застосуваннях.

Ключові слова: CuO, Золь-гель, Оптична ширина забороненої зони, Наночастинки, Провідність за постійним струмом, Оптоелектронний.