

# Influence of doping concentration on the properties of Ga doped CuO thin films by the spray pyrolysis technique

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Transparent thin films of pure and Ga doped CuO thin films were deposited on the glass plates at 450°C by spray pyrolysis technique. The various volumes of Ga precursor solution from 0.5, 1.0, 1.5 and 2.0 ml were mixed with CuO precursor solution. The deposited films were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and optical studies. X-ray diffraction patterns of pure and Ga doped CuO thin films reveal the polycrystalline nature and cubic structure. The surface morphology of the film is found to be influenced with the Ga doping. Optical transmittance and absorption studies were also recorded in the wavelength range 300 nm to 1100 nm. The band gap of the film is found to be decrease from 2.79eV to 2.24eV.

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## 1. Introduction

Transparent conductive oxide (TCO) thin films have been widely applied as a transparent electrode in various devices such as organic solar cells (OSCs) and organic light-emitting diodes (OLEDs). Alongwith this, wide and direct band gap semiconductor materials areof much interest for blue and ultraviolet (UV) optical devices, such as light-emitting diodes and laser diodes[1]. In particular, copper oxide thin films have manyadvantages for catalysts and solar energy conversion applications because they have a high activity and selectivity in oxidation and reduction reactions [2]. The growth of high-quality p-type CuO thin films is essential for fabricating p-n junction-based oxide devices, such assolar cells, light-emitting diodes and transistors.Theopticaltransmittance and electrical resistivity of the thin films aretwo critical parameters in evaluating the performance of photovoltaic cells and electro-chromic devices. The parameters have been reported to depend on the growth conditions, such as the method of fabrication, the oxygen partial pressure, and the growth and annealing temperatures [3,4]. Ray prepared copper oxide films using a methanol solution of cupric chloride by the sol-gel like dip technique at different bathing temperatures [5]. Hani Khallaf et al studied the effect of Ga-doped CdS thin films, with different Ga and Cd concentrations using chemical bath deposition [6]. Keun Jung et al investigated the electrical and optical properties of Ga-doped Zinc oxide thin films deposited at different substrate temperatures [7].Recently the present authors reported the Ga doped SnO<sub>2</sub> thin films by the spray pyrolysis technique [8].

Based on these details in this paper, we report on the effects of gallium on the properties of CuO thin films

grown on glass substrates. This study may provide a means of developing high-quality CuO films and devices, and for controlling the optical transmittance and the electrical resistivity of the films. Ga-doped CuO-based semiconductor thin films can be fabricated with a variety of methods, such as magnetron sputtering, pulsed laser deposition, chemical vapour deposition, thermal evaporation, the spray pyrolysis technique, and the sol–gel method. In this work, we present a simple and lowcost process to fabricate Ga-doped CuO-based transparent conductors through the spray pyrolysis technique. The variation in the optical band gap energy is observed. Furthermore, we attempt to study the morphological results to confirm the device quality nature of the Ga doped CuO films.

## 2. Experimental

The typical spray pyrolysis system was used for the thin films preparation on silica glass substrates [8]. The spray solution was prepared by mixing the appropriate volumes of Copper (II) chloride dihydrate ( $CuCl_2 \cdot 2H_2O$ ) and gallium (III) nitrate hydrate ( $Ga(NO_3)_3 \cdot H_2O$ ) dissolved in deionized water with equal molar ratio of 0.1 M. The volume composition values of mixture are listed in Table 1.The prepared mixture was stirred for 2 h at 65°C to produce a clear solution. Thesubstrate temperature was fixed at 450 °C. The temperature was controlled within 5 °C through a thermocoupleas a sensor for the temperature controller. Solutions were deposited onto glass plates using an optimized withdrawal speed of 1 ml/min to give uniform layers. The gas pressure was kept constant and 3 kg/cm<sup>3</sup>. Air was used as the carrier

gas for Ga doped CuO thin films preparations. The distance between the nozzle and the substrate was 10 cm.

Table 1 The composition values of Ga doped CuO.

Material Name	Volume (ml)
Cu	6.0
Cu + Ga	5.5 + 0.5
Cu + Ga	5.0 + 1.0
Cu + Ga	4.5 + 1.5
Cu + Ga	4.0 + 2.0

Apart from GaCuO, additional HCl, H<sub>2</sub>O and HNO<sub>3</sub> will be evaporated at 450 °C. Both X-ray diffraction and electron microscopy are found to be powerful tool and have been widely used for structural analysis of the thin films. The crystal structure and crystallinity of the copper oxide and Ga doped copper oxide thin films were determined using a Bruker X-ray diffraction diffractometer (XRD) with the grazing incidence angle of 0.8 degree. Surface morphology and surface roughness level of the films were determined using a JEOL scanning electron microscope (SEM). The transmission spectra of those thin films were recorded using a Hitachi U-2900 ultraviolet-visible (UV-Vis) spectrophotometer.

### 3. Result and discussion

#### 3.1 Structural investigations

The X-ray diffraction spectrum for pure copper oxide and Gallium doped CuO films grown with different volume compositions (0.5–2.0 ml replacement of Ga precursor solution) are shown in Fig. 1. Figure shows the well-defined peaks and it is randomly oriented. The Gallium dopant does not have significant influence on the X-ray diffraction patterns. All the films exhibit the same diffraction pattern whereas the doped one shows the variation in the intensity. The doped films give the same diffraction patterns as the undoped samples. It is observed from the figure the peak height of (111) plane is found to be higher than all other peaks in the diffractogram. The crystallite orientation can simply and intentionally be tailored by choosing an adequate solvent-chelating ligand combination. Five diffraction peaks were identified as (111), (220), (311), (222), (422) and (511) reflections of the cubic structure [9]. The crystalline nature of the film increases as the

Gallium dopant increases. This is seen from the (422) and (511) reflection peaks in the XRD spectra.

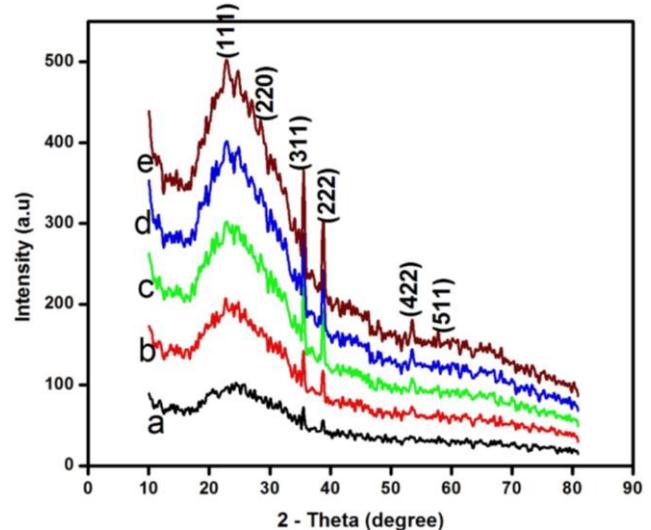
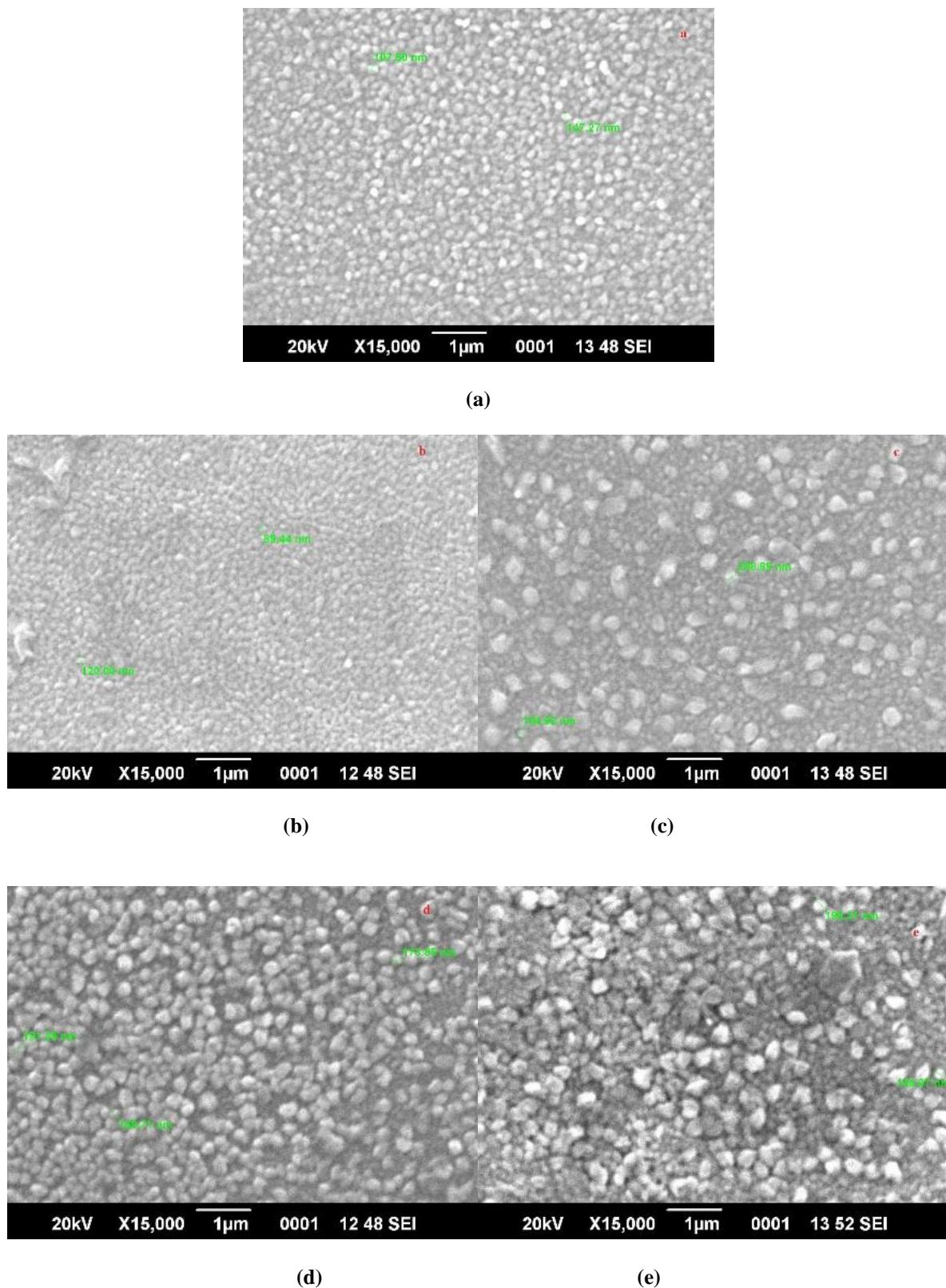


Fig. 1 XRD Patterns for (a) pure CuO and (b-e) Ga doped CuO.

#### 3.2 SEM studies

Scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces. The SEM provides the investigator with a highly magnified image of the surface of a material that is very similar to what one would expect if one could actually "see" the surface visually. The SEM uses electrons for imaging, much as a light microscope uses visible light. Generally, the surface morphology of the thin film has a great relationship with the crystal quality of the film itself. Fig. 2 shows micrographs of GaCuO films deposited at various ratios of dopant. By introducing Ga element on CuO host material, it was expected that it will be able to stimulate the transformation structure from a single crystal to polycrystal structures. With increasing volume concentration rate, different morphologies are observed. As shown in figure 2(a), the surface morphology of film is a non-compact structure, indicating the amorphous nature of the films, which is in good agreement with the above XRD analysis results. As dopant level increases, the surface morphology transforms to a compact and smooth structure. The surface is found to be compact without any undulation which is displayed in Fig. 2(e). These morphological results confirm the device quality nature of the Ga-doped CuO films prepared in the present study.



*Fig. 2 SEM images of (a) pure CuO and (b-e) Ga doped CuO.*

### 3.3 Optical studies

The UV–Visible spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves the promotion of the electron in  $\sigma$  and  $\pi$  orbitals from the ground state to higher energy states. The electronic absorption spectrum is depicted in Fig. 3. The spectrum reveals that the strong absorption band appears around 320 nm and the peak increases as the dopant level increases. The UV-Vis transmittance spectrum is presented in Fig. 4. The CuO film is highly transparent and has an average transmittance above 70% in the visible region. When the concentration of Ga increases in the starting solution, one can observe in addition to the variation of the film colour (from transparent to brown), a variation in the average transmittance, which are about 60–70 % for the Ga doped CuO films. The optical band gap ( $E_g$ ) was evaluated from the transmission spectra and the optical absorption coefficient near the absorption edge is given by [10].

$$\alpha = \frac{(h\nu - E_g)^2}{h\nu}$$

where A is a constant,  $E_g$  the optical band gap, h the Plank's constant and n the frequency of the incident photons. The band gap values were computed from the  $(\alpha h\nu)^2$  vs  $(h\nu)$  curves. The direct band gap values are 2.79, 2.67, 2.60, 2.44 and 2.24 eV for various volume compositions of CuO and Ga doped CuO films as shown in Fig. 5. The figure shows that the increment of Ga concentration reduces the band gap value. The minimum band gap of 2.24 eV is obtained for the 2 ml Ga doped CuO. The variations of band gap were dependent on the influence of free carrier electrons on the fundamental absorption edge in the near ultra-violet (UV) region.

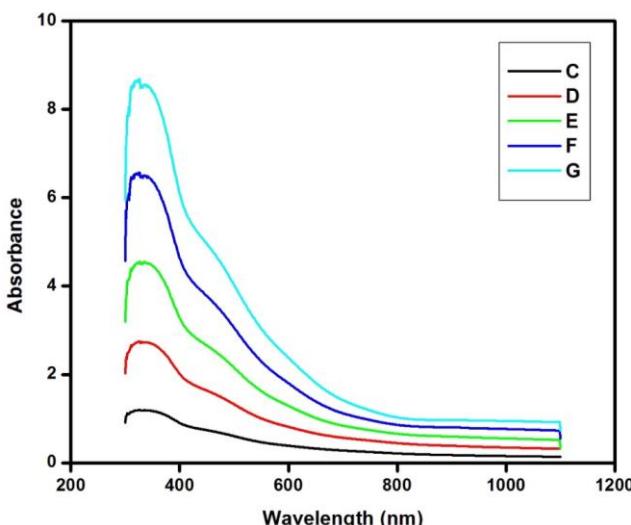


Fig. 3 Optical absorption spectrum of (c) pure CuO and (d-g) Ga doped CuO.

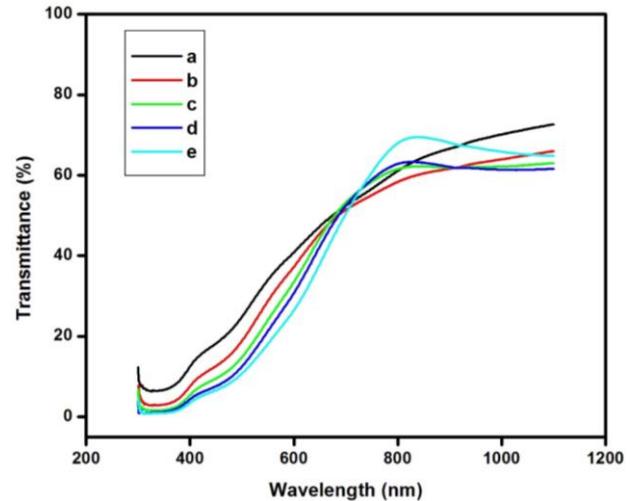


Fig. 4 Optical absorption spectrum of (a) pure CuO and (b-e) Ga doped CuO.

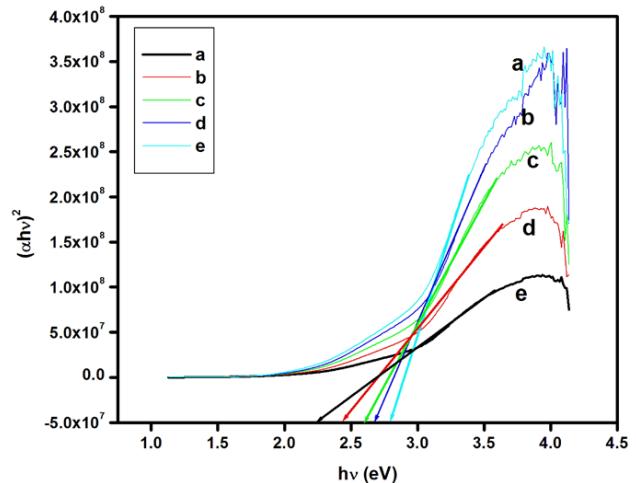


Fig. 5 Bandgap plots of (a) pure CuO and (b-e) Ga doped CuO.

### 4. Conclusion

The conductive pure and Ga doped copper oxide thin films were prepared by the spray pyrolysis technique. X-ray diffraction studies confirm that all the films are in polycrystalline nature for Ga doped CuO. SEM study exposed very good surface morphology for pure and Ga doped films. The grains are uniformly distributed over the entire scanned surface without any patches for concentrated 2 ml Ga doping. The surface is found to be smooth without any undulation. A variation in the average transmittance, which is about 60–70% for the Ga doped CuO films and the maximum band gap value of 2.24 eV is obtained for the 2 ml Ga doped CuO. In overall Ga doped CuO thin films show improved morphological and optical properties and it confirms the suitability of these films for photocatalytic and opto-electronic applications.

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