

# Influence of substrate temperature on crystalline copper aluminium oxide thin films synthesized through chemical spray pyrolysis (CSP) technique

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**Abstract** Copper aluminium oxide ( $\text{CuAlO}_2$ ) of well ordered crystalline films were deposited on to glass substrates with Cu/Al ratio  $r = 0.8$  at the substrate temperatures of 250, 300, 350, 400 and 450 °C. Films which were characterized had a thickness of the order of few micrometers. Films deposited at the optimized deposition temperature (450 °C) revealed well-crystalline  $\text{CuAlO}_2$  phase with XRD peak at  $2\theta = 31.7^\circ$  corresponds to (006) reflection. The peak positions of the core level XPS spectra, confirm the presence of delafossite  $\text{CuAlO}_2$  phase. The optical transmission of 80 % has been observed in the visible spectrum. The obtained band gap energy is 4.1 eV. From the observed results it was evidenced that the substrate temperature has strong influence on the structural and optical properties of the spray pyrolysed copper aluminium oxide films.

## 1 Introduction

Delafossite oxides of semiconducting nature have recently attracted the researchers in the field of Transparent Conducting Oxides (TCOs) after the reported p-type conductivity in a highly transparent thin film of Copper aluminum Oxide ( $\text{CuAlO}_{2+x}$ ) [1]. Then extensive works have been

done in the field of TCO to prepare new types of TCOs with wide ranging applications [2–4]. Delafossite type oxides ( $\text{ABO}_2$ ) have been extensively studied due to their promising applications in catalytic [5, 6] and luminescence properties [7, 8]. The present study focuses mainly the  $\text{CuAlO}_2$ , as it exhibits p-type conductivity and has wide range of applications. Different approaches have been developed to prepare such nanostructures that yield diverse structural, optical and electrical properties. In this work,  $\text{CuAlO}_2$  films were synthesized by spray pyrolysis technique on glass substrates for the first time. Comparing with other deposition techniques, the film production cost is very low, large area coating is possible and the coated films are compact and uniform. Thus, in this work, we report a reliable approach to grow highly crystallized rhombohedral  $\text{CuAlO}_2$  (R-3m) films and in particular the influence of substrate temperature on the crystallization behaviour of  $\text{CuAlO}_2$  thin films have been demonstrated.

## 2 Experimental details

For preparing copper aluminium oxide thin films, 0.085 g of  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$  and 0.0833 g of  $\text{AlCl}_3$  were dissolved in 18 ml methanol and 32 ml deionised water so as to obtain a solution of  $\text{pH} = 2$ . Since the molar ratio (A/B) play a crucial role in forming the delafossite-type  $\text{ABO}_2$  system in spray pyrolysis deposition technique, the copper and aluminium bearing precursors were prepared for the molar concentrations of 0.01 and 0.0125 M respectively. Prepared solution for the molar ratio  $r = 0.8$  was then sprayed onto the preheated glass substrates maintained at different temperatures 250, 300, 350, 400 and 450 °C.

During deposition, the solution flow rate was maintained at 0.5 ml/s and was monitored using a simple solution flow

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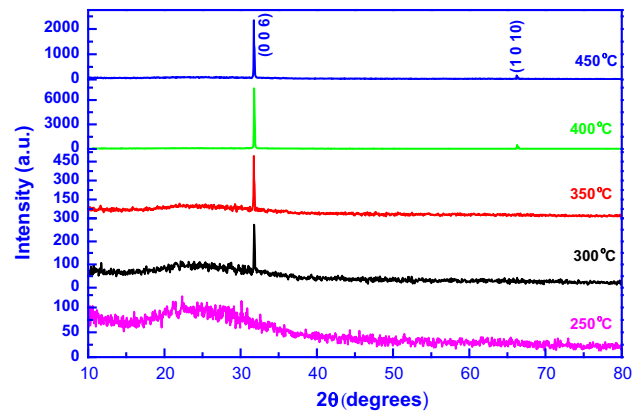
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meter (SKC make) capable of measuring to a precision of 0.05 ml/s. Compressed air was used to form and guide the droplets to the substrate surface that undergoes pyrolytic (endothermic) decomposition and forms a single crystalline or cluster of crystallites as a product. The other volatile by-products and solvents escape in the vapour phase. The compressed air flow was kept constant that turn out a pressure of 0.3 kg/cm<sup>2</sup>, recorded using a mass gas flow meter (Omega make). In each deposition, the nozzle to substrate distance was held to a constant value of 30 cm. Droplets were sprayed continuously for a total duration of 100 s without any intermittent spray in between. The thickness of the films was measured using Stylus profiler (Mitutoya SurfTest SJ-301). The X-ray diffraction patterns of CuAlO<sub>2</sub> films were obtained with an X-ray diffractometer (XPRT-PRO) using CuK $\alpha$  (30 mA, 40 kV,  $\lambda = 1.5406 \text{ \AA}$ ) at a continuous scan type with step size of 0.0330 ( $^{\circ}$ 2 $\theta$ ). The surface properties of all films were investigated using JEOL Model JSM-6390LV Scanning electron microscope. The chemical environment of the CuAlO<sub>2</sub> films was investigated using VG Microtech Multilab ESCA 3000 spectrometer with a non-monochromatized Mg K $\alpha$  X-ray source at the vacuum level of 10<sup>-10</sup> Torr. The optical properties were measured with UV-Vis-NIR Spectrometer (Varian-Cary: 5000) in the wavelength range 250–1050 nm. The two probe technique was used for measuring electrical resistivity of CuAlO<sub>2</sub> films of size 2.5  $\times$  1 cm<sup>2</sup>. Prior to measurement, electrical contacts were made by applying aluminium paste and then the measurements were carried out by noting the current for a known potential difference that was sent through the film and a sensitive electrometer (Keithley 2400) placed in series for measurements. The p-type electrical conduction was confirmed through the hot probe technique by testing the thermally excited majority free charge carriers.

### 3 Results and discussion

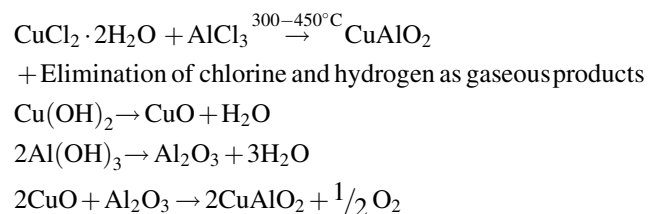
XRD analysis (Fig. 1) shows that the substrate temperature plays a significant role in the structural properties of the CuAlO<sub>2</sub> films. The thin films were identified as delafossite structured with the R-3m space group. The diffraction peak located at  $2\theta = 31.7^{\circ}$  corresponds to (006) reflection of CuAlO<sub>2</sub> phase. The peak positions were matched with the standard rhombohedral phase which was similar to those reported by Saha et al. [9]. Calculated lattice parameters ( $a = 2.837 \text{ \AA}$  and  $c = 16.909 \text{ \AA}$ ), unit cell volume (120.35  $\text{\AA}^3$ ) and density 5.06 g/cm<sup>3</sup> are in good agreement with the JCPDS No: 35-1401 values ( $a = 2.856 \text{ \AA}$ ,  $c = 16.943 \text{ \AA}$ ,  $V = 119.74 \text{ \AA}^3$  and  $\rho = 5.097 \text{ g/cc}$ ). As substrate temperature increases, the crystallite size increases which in turn reduces the grain boundary region.



**Fig. 1** X-ray diffraction of CuAlO<sub>2</sub> films deposited at different substrate temperatures

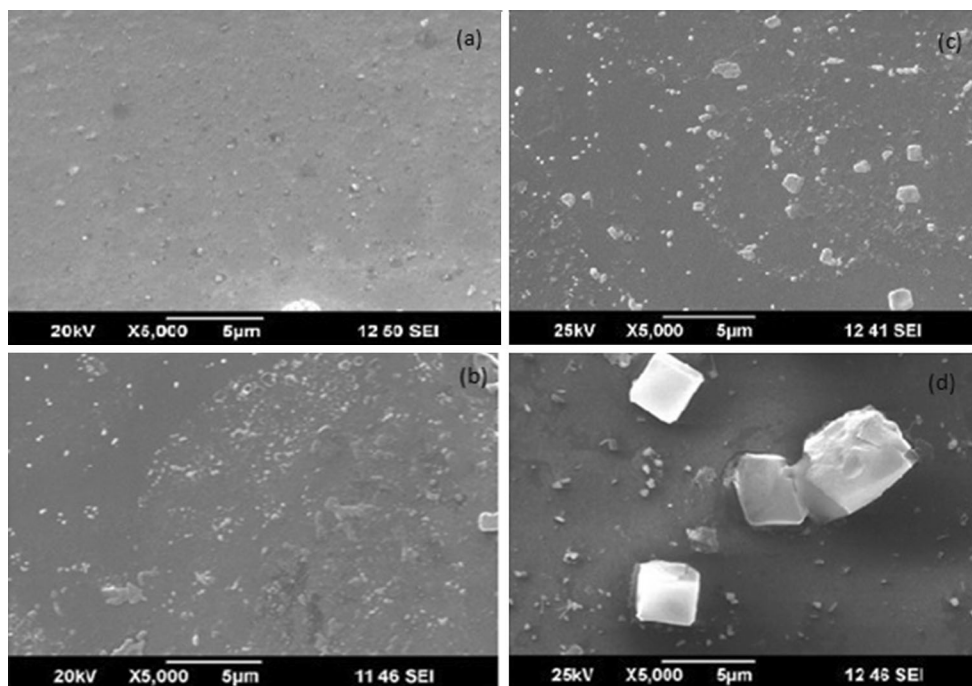
Improved crystallinity is expected to yield larger domains and fewer grain boundaries in the films, both of which lead to an increase in electron mobility with processing temperature. Therefore the microstrain and dislocation density decrease conversely with temperature. Prepared films at 450  $^{\circ}$ C have less value of microstrain and dislocation density.

According to the previous report of Bouzidi et al. [10], spray deposited p-CuAlO<sub>2</sub> films at high substrate temperatures (450–525  $^{\circ}$ C) were amorphous and post-deposition annealing was done to transform it to crystalline character. However in the present case, relatively a low temperature deposition even at 300  $^{\circ}$ C is sufficiently enough for preparing CuAlO<sub>2</sub> films without any additional thermal treatments. Within the deposition temperature range, available thermal energy initiated the following reaction mechanism for the formation of crystalline CuAlO<sub>2</sub> [11].



Based on the above reaction, during the flight of droplets to the substrate surface; initially the respective hydroxides are formed and then release of water converts the hydroxide into respective oxides. On reaching the substrate surface, the solid state reaction between these two products results the required CuAlO<sub>2</sub> compound.

Figure 2 clearly shows the increase of grain size with the substrate temperature. The thickness of the films were 0.86, 1.02, 1.17, 1.21  $\mu\text{m}$  deposited at 300, 350, 400, 450  $^{\circ}$ C respectively. In view of the fact that the grain size is limited in thinner films, the surface of the films deposited at lower substrate temperatures shows small nano-sized



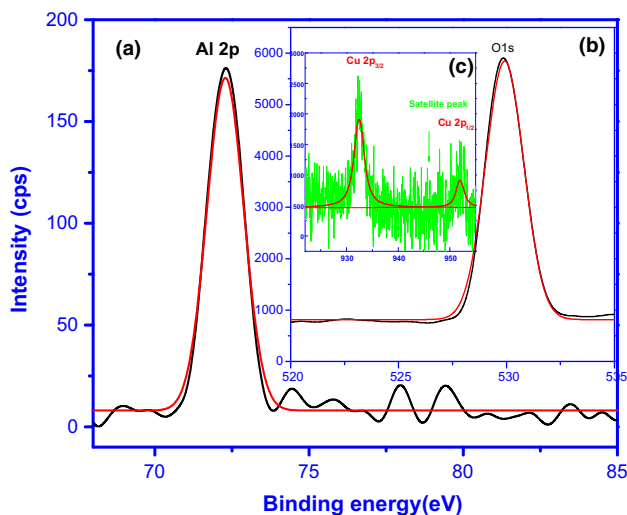
**Fig. 2** SEM micrographs of CuAlO<sub>2</sub> films deposited at different substrate temperatures **a** 300 °C, **b** 350 °C, **c** 400 °C, **d** 450 °C

grains. The large grains with faceted shape were randomly grown between small nano-sized grains for the film deposited at 450 °C.

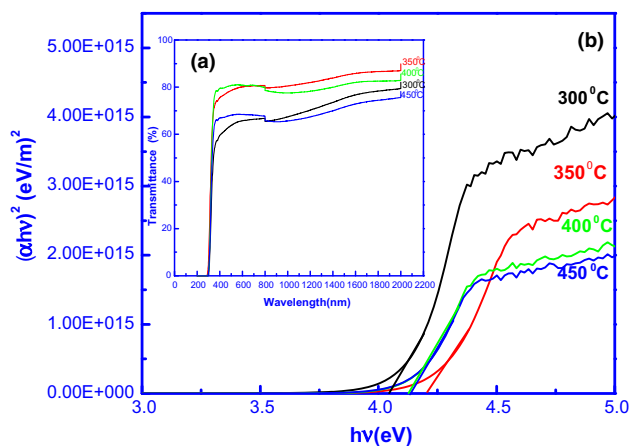
The high resolution spectrum of Cu 2p displayed in Fig. 3c shows the main peak of Cu 2p<sub>3/2</sub> at 932.5 eV. This main peak can be assigned to Cu<sup>2+</sup> ions, suggesting Cu<sup>2+</sup> mainly exists in CuAlO<sub>2</sub> phase. Moreover, the main peaks of Cu 2p<sub>1/2</sub> are located at the higher binding energy side, which is 19.38 eV higher than that of their

Cu 2p<sub>3/2</sub> main peak. The Al 2p peak at 72.5 eV (Fig. 3a) is ascribed to the Al–Al chemical state of the CuAlO<sub>2</sub> phase. The dominant peak at 530.5 eV in the O 1s spectra shown in Fig. 3b can be assigned to the lattice oxygen, interacting with the copper atoms to form the CuAlO<sub>2</sub> phase.

From the optical Transmittance (T) spectra shown in Fig. 4a, it is observed that all films have a sharp fall at the band edge, which is an indication of the good crystalline nature of the deposited films [10]. Prepared films at 450 °C have low transmittance value compared with other films due to its high thickness values around 1 μm and its



**Fig. 3** *a* High resolution Al 2p *b* O 1s *c* Cu 2p core level XPS spectra of CuAlO<sub>2</sub> thin films



**Fig. 4** *a* Transmittance spectra *b* Tauc plot of CuAlO<sub>2</sub> films prepared at different substrate temperatures

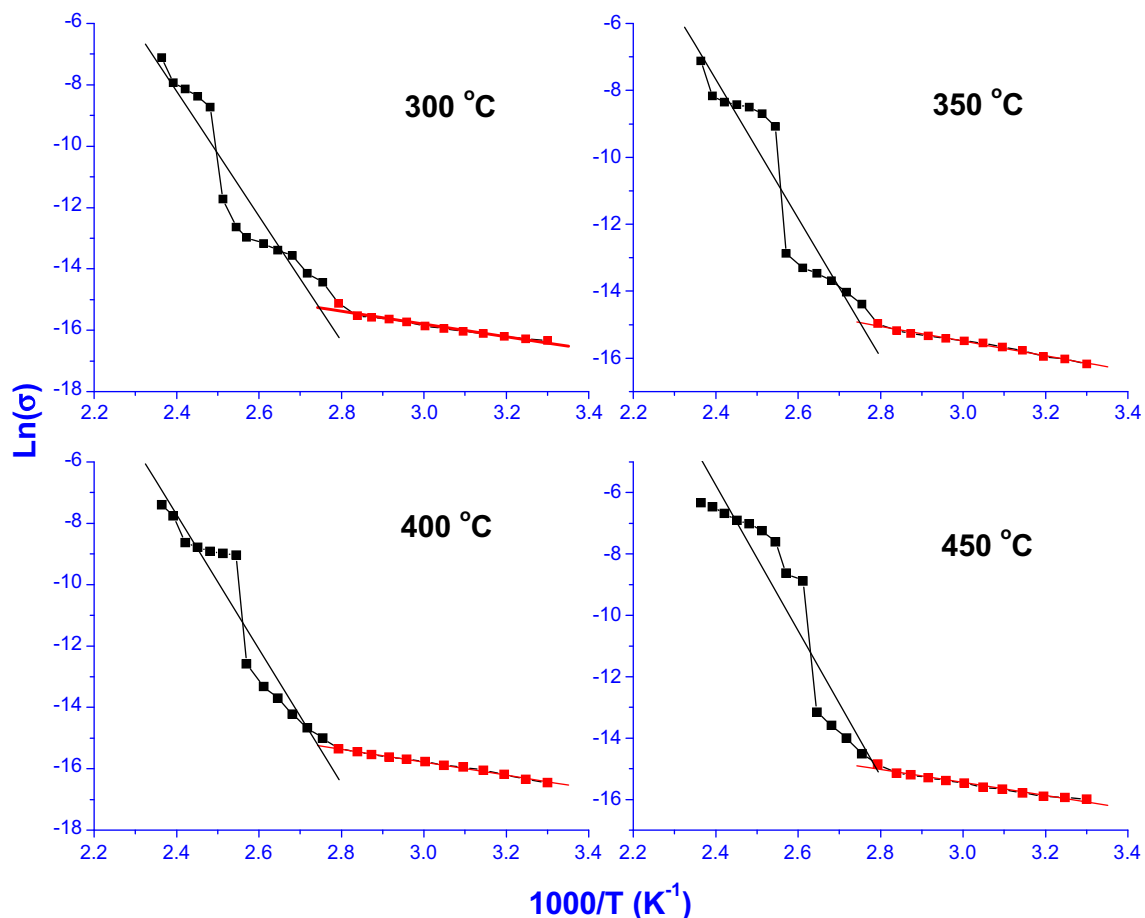
transparency is comparable with other published reports [12, 13]. Figure 4b shows the Taue plot, from which the direct band gap energy can be estimated. The values of  $E_g$  were found to be 4.05, 4.2, 4.14 and 4.13 eV for the films deposited at substrate temperatures 300, 350, 400 and 450 °C respectively, using the linear extrapolation method. The direct band gap of  $\text{CuAlO}_2$  was already reported as 3.95 eV [9]. This widened band gap in  $\text{CuAlO}_2$  thin films confirms the transparent conducting nature of the prepared films.

The variation of conductivity with temperature is shown in Fig. 5. The cause of p-type conductivity shown by the films is due to metal scarcity or surplus oxygen within the crystallite sites of the material [9]. In the prepared samples at lower temperatures the oxygen molecules on the film surface encumber the electrical transport and acts as potential barrier. On heating, oxygen molecules escape from the film surface and the conductivity increases with temperature. At higher temperatures (above 420 K), conductivity increases and attains maximum values. The activation energies extracted from the slope of the  $\text{Ln}(\sigma)$  versus  $1000/T$  showed a tenfold increase i.e., 0.4154–4.0509 eV as the temperature increases from low

(303–358 K) to high (363–423 K) range. The activation energy values show the presence of two different conducting mechanisms in the measured temperature range.

#### 4 Conclusion

Copper Aluminium oxide thin films have been prepared using the chemical spray pyrolysis technique for the first time on glass substrates. The structural and optical properties of  $\text{CuAlO}_2$  films deposited with Cu/Al ratio 0.8 and its variation with substrate temperature were analyzed. Films deposited at the optimized deposition temperature (450 °C) revealed well crystalline and the peak was indexed for the rhombohedral phase. The peak positions of the core level spectra, along with XRD results, confirm the presence of delafossite  $\text{CuAlO}_2$  phase. The optical studies confirmed the good transmission of the films and the variation of band gap energy with deposition parameters was determined. The electrical studies showed two different activation energies and the conductivity was high above 420 K.



**Fig. 5** Arrhenius plot of  $\text{CuAlO}_2$  films deposited at various substrate temperatures

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