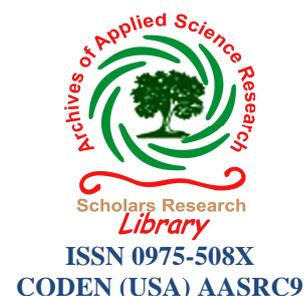




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Investigation on the variation of conductivity and photoconductivity of CuO thin films as a function of layers of coating

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ABSTRACT

CuO is a promising candidate for application as material for solar cell fabrication owing to its excellent optical properties with selective solar absorbency and low thermal emittance. In the present work, CuO thin films have been successfully coated by spin coating technique using copper acetate as precursor. The precursor was prepared by sol gel method. Single layered, three layered and five layered CuO thin films were spin coated at 2500 rpm for 10 sec and annealed at 550°C. The as-synthesized CuO thin films were subjected to FTIR, UV-Vis, field dependent and temperature dependent conductivity and SEM studies. The FTIR confirmed the presence of Cu-O stretching vibrations in all the three as-synthesized samples. The UV-Vis spectra of all the three samples were similar while exhibiting a slight increase in intensity upon increase in number of coating layers. The temperature dependent conductivity study confirmed the semiconducting nature of the films in all cases and the five layered films recorded the least activation energy. The three layer coated CuO thin films showed a significance rise in photocurrent over dark current. The three layered CuO thin films exhibited highly uniform homogenous layers of reduced particle size and improved texture. Thus three layered CuO thin films could be considered as good candidates for harvest of solar energy for solar cell applications.

Keywords: sol-gel, conductivity, thin films, Copper oxide

INTRODUCTION

Cupric oxide (CuO) is one of the most important I-IV compound semiconductors with many applications such as diodes [1], cathodes in lithium batteries [2], catalysis [3], lithium-copper oxide electrochemical cells [4], field emission device [5], gas sensor [6] and so on. It is also a promising semiconductor for solar cell fabrication due to its suitable optical properties [7]. Furthermore, it is attractive as a selective solar absorber since it has a high solar absorbency and a low thermal emittance [8]. It also possesses unusual antiferromagnetic properties. Recently, it has been discovered that CuO also shows high-temperature superconductivity [9]. CuO has a monoclinic structure with the lattice parameters $a = 4.684\text{\AA}$, $b = 3.425\text{\AA}$, $c = 5.129\text{\AA}$, and $\beta = 99.28^\circ$ [10]. CuO is a p-type semiconductor which has a band gap reported between 1.2 and 1.9eV with a black color and partial transparency in the visible range. An important advantage of using CuO in device applications is that it is non-toxic and its constituents are available in abundance. Various synthesis methods such as sputtering, thermal oxidation, vacuum evaporation, electrospun [11] and sol-gel [12] have been reported in literature. However, the sol-gel method is the most preferred technique due to the simple equipment involved and low costs compared to other techniques. Although the sol-gel method is considered as a suitable method to synthesize ultra-fine particles, this method needs a large quantity of solution, longer processing time and heat treatment for crystallization [12, 13]. Photoconductivity is a useful tool to study the properties of semiconductors. It is also considered to be an important tool for providing information about the nature of the photo-excitations. Since last decade the photoconductive properties of the inorganic nanoparticles have been subjected to intensive study [14]. Not only because of fundamental interest on electronic excitation but also due to their application in wide range of optical and electronic devices. A good photoconductive device requires efficient charge separation and efficient transport of charge carriers to electrode [15, 16]. The conductivity of the

material depends upon the carrier density and complex process of carrier generation, trapping and recombination. It is also a function of temperature, applied field, intensity of light and energy of radiation [17].

In the present work, we report the fabrication of single layered, three layered and five layered CuO thin films synthesized by sol-gel technique which is a soft bottom-up approach to achieve a good control over film composition and microstructure. The as-synthesized CuO thin films were characterized using Fourier Transform Infrared Spectrophotometer (FTIR), UV-Vis Spectrophotometer (UV-Vis), and Scanning Electron Microscope (SEM). Also the variation in field dependent dark and photoconductivity of CuO thin films and temperature dependent conductivity were studied as a function of the number of layers coated.

MATERIALS AND METHODS

Copper Oxide (CuO) thin films were synthesized by sol-gel method. All the reagents and solvents were of analytical grade and were used without any further purification. 0.25 molar concentration of precursor solution was formed by dissolving copper acetate in iso propyl alcohol and diethanol amine in suitable proportions. The final solution, with concentration of 0.25 M, was clear and dark blue without any suspension of particles. The solution thus obtained was spin coated with a spinning speed of 1500rpm for 30 sec. Immediately after coating, the film was dried on a hot plate at 250°C for 5 min and subsequent deposition of further layers [18] was done. Five layers of CuO thin films were coated one over the above. After the coating of the last layer, the thin films were placed into the furnace at 250°C. The furnace temperature was raised to 550°C and held at that temperature for 30 min.

3. Characterization

The Fourier transform infrared spectra of the samples were studied using Perkin – Elmer infrared spectrophotometer. The spectrum is recorded in the range of wavenumber 500 – 1000 cm^{-1} . The UV-Vis spectra were obtained using UV-Vis-NIR spectrophotometer. The spectra were recorded at room temperature in the range 200-1000 nm. The field dependent dark and photoconductivity studies were carried out using Keithley picoammeter. The experimental setup for the measurement of field dependent dark and photoconductivity is as used by D. Ponniah and F. Xavier [19]. Temperature dependent conductivity studies were performed using Keithley Picoammeter to find the activation energy of the as-synthesized samples [19]. The activation energies of the as-synthesized samples were calculated using the relation

$$I = I_0 \exp (-E_a/kT) + C$$

where I is the resultant current, I_0 the current at initial thermal equilibrium, k the Boltzmann constant, E_a the activation Energy and C the constant due to leakage current [20]. By solving the above equation the activation energy could be obtained from the slope of the graph. The microstructures of the as-synthesized samples were analyzed by JEOL JSM 6360 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Fourier Transform Infrared (FTIR) spectrum of as-synthesized single layered, three layered and five layered CuO thin films are shown in Fig. 2. All the three spectra exhibit similar peak patterns and are in good agreement with standard FTIR spectrum of CuO thin films reported in literature [21]. In the case of single, three and five layered CuO films, the absorption band at 532 cm^{-1} is attributed to Cu-O stretching [21]. This confirms the presence of Cu-O bonding in the as-synthesized CuO thin films. It could also be observed that the single and five layer coated CuO thin film peaks are little broader, whereas the three layered CuO thin film exhibited a sharper and more intense peak around 650 cm^{-1} attributed to the Cu-O stretching vibrations [22].

The UV-Vis spectrum of as-synthesized single layered, three layered and five layered CuO thin films are shown in Fig. 3. All the three exhibit similar absorption patterns whereas, the three layered and five layered coated CuO thin films show more intense absorption peaks than the single layered one. The absence of any absorption peak in the visible region of as-synthesized CuO thin films spectrum is in good agreement with the wide band gap nature of the material and its inability to absorb in the visible range. However, with increase in the number of layers, it is observed that the pattern indicates a slight rise in the intensity of absorption. This could be attributed to the increase in the exposed surface area with increase in number of layers and consequently the film thickness.

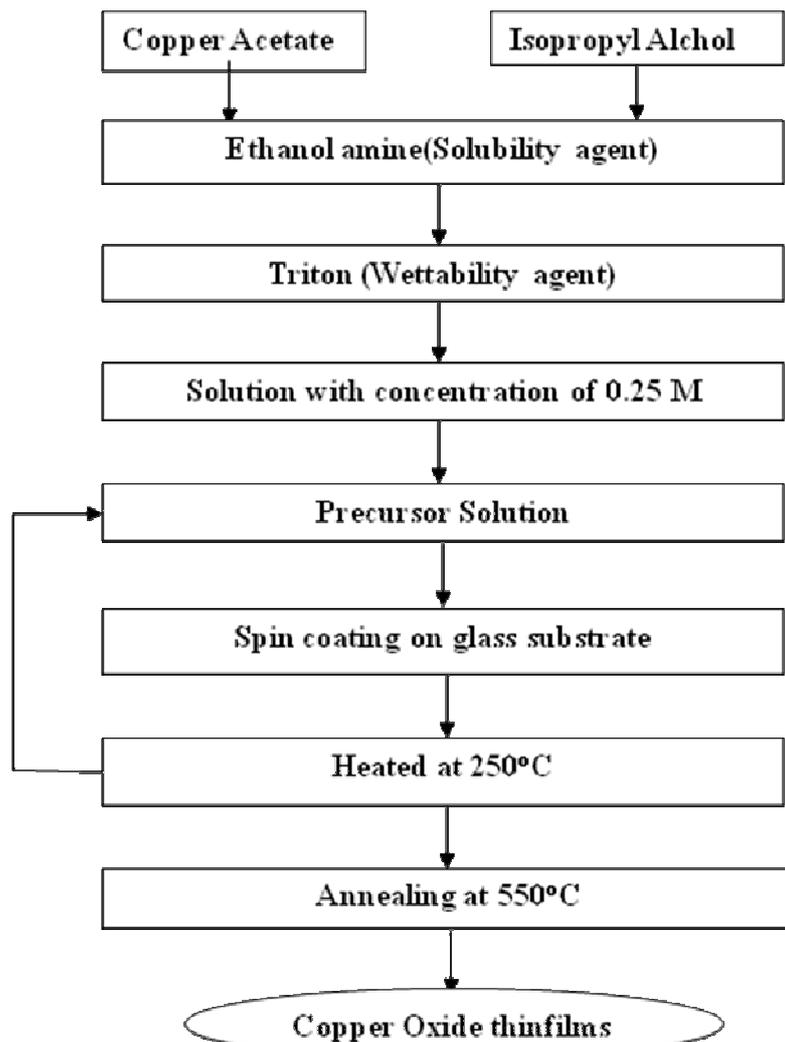


Fig. 1: Experimental flow chart for the synthesis of CuO thin films

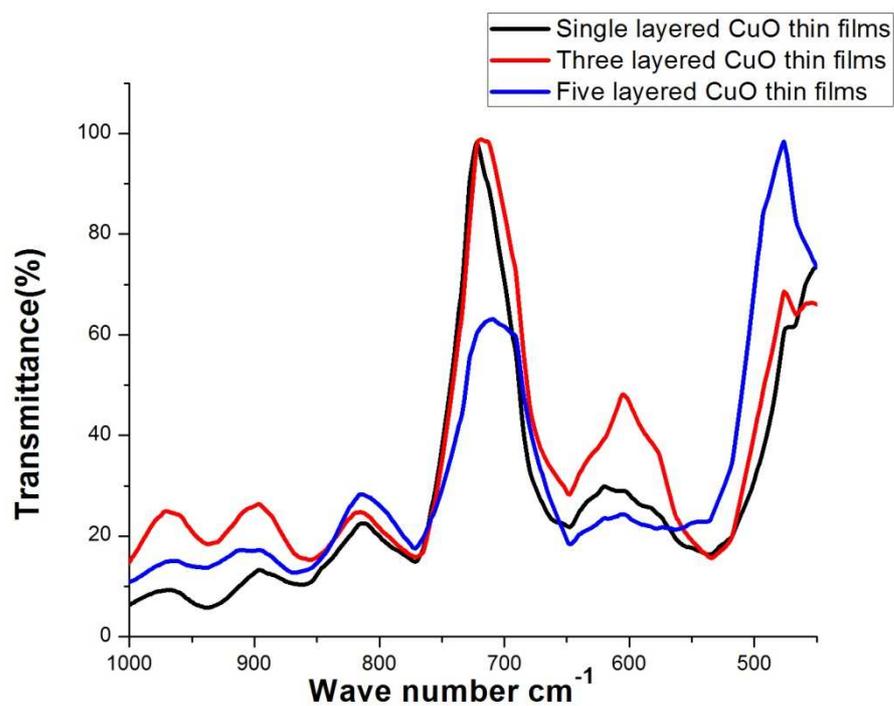


Fig. 2: FTIR spectrum of as-synthesized CuO thin films

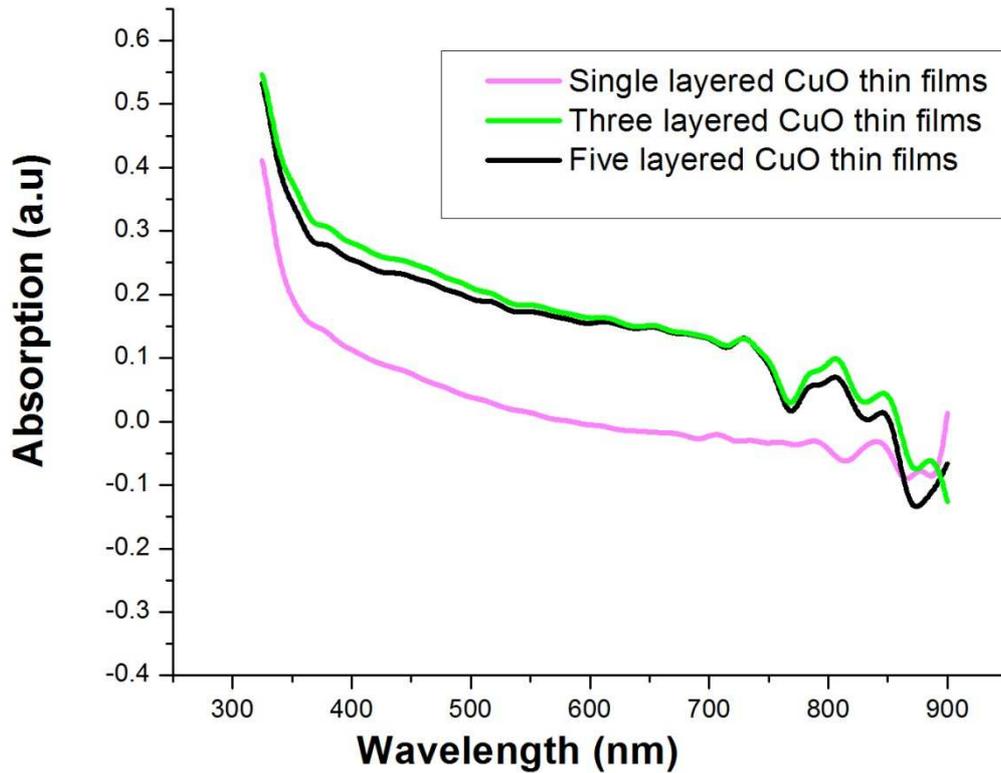


Fig. 3: UV-Vis spectrum of as-synthesized CuO thin films

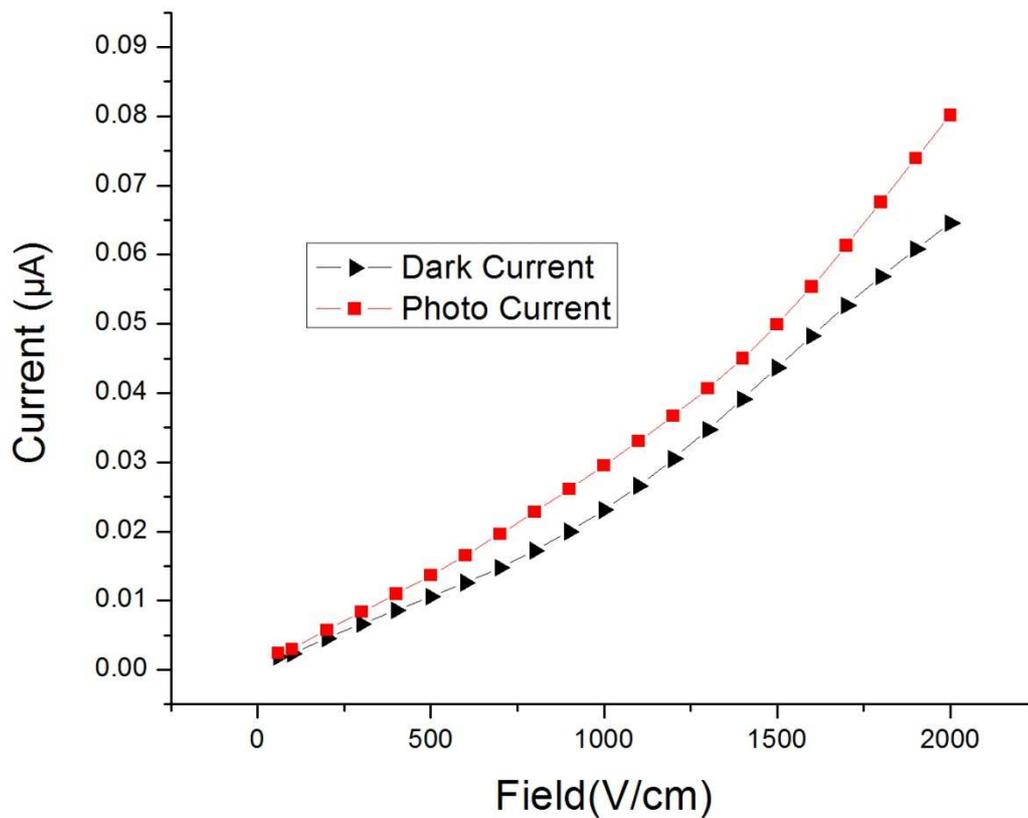


Fig. 4: Field dependent dark and photoconductivity of single layered as-synthesized CuO thin films

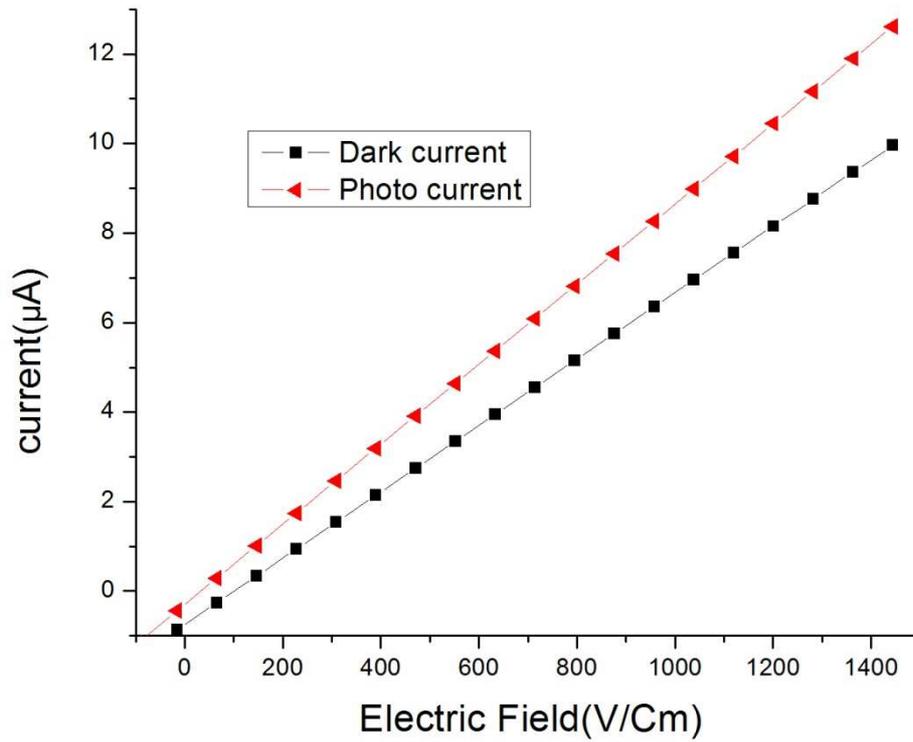


Fig. 5: Field dependent dark and photoconductivity of three layered as-synthesized CuO thin films

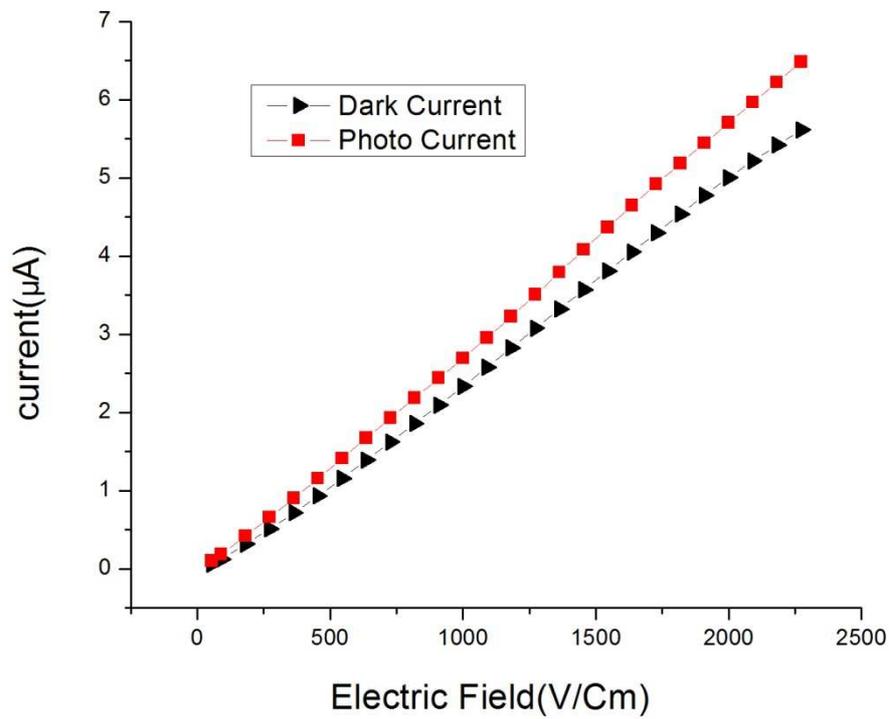


Fig. 6: Field dependent dark and photoconductivity of five layered as-synthesized CuO thin films

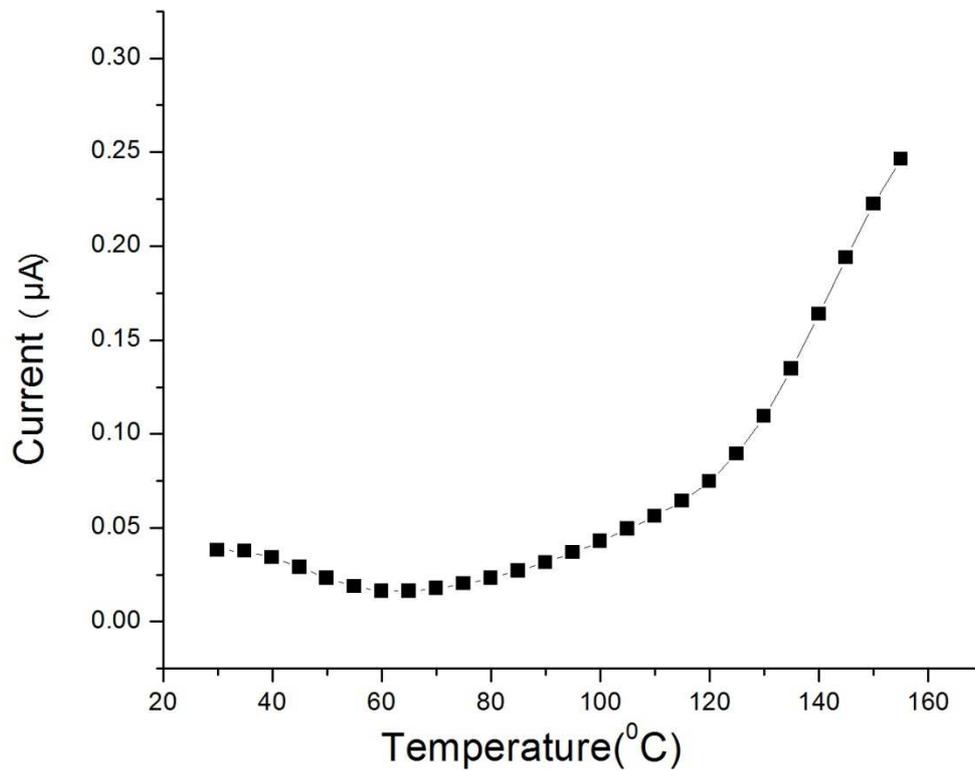


Fig. 7: Temperature dependent conductivity of single layered as-synthesized CuO thin films

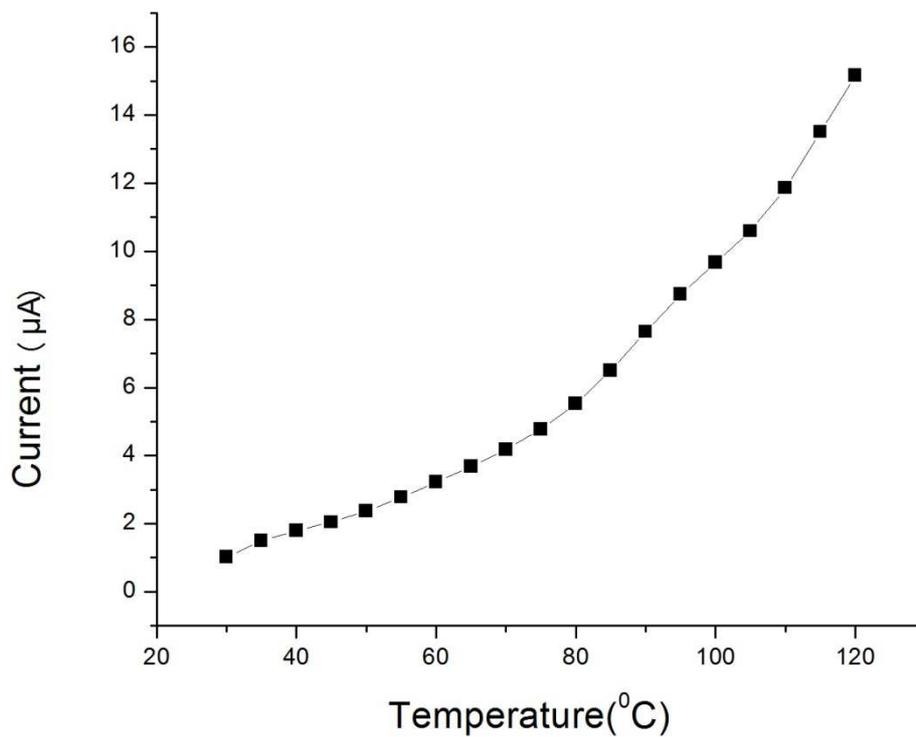


Fig. 8 : Temperature dependent conductivity of three layered as-synthesized CuO thin films

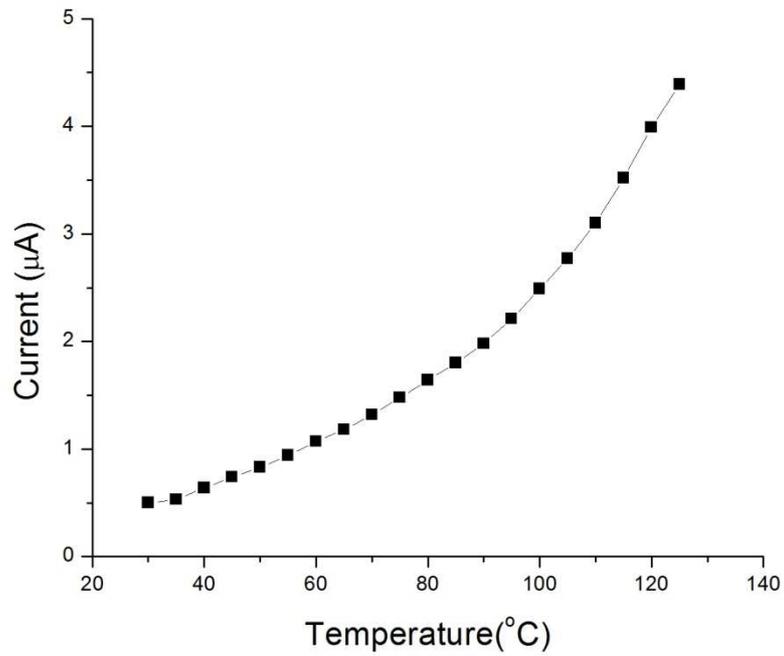


Fig. 9: Temperature dependent conductivity of five layered as-synthesized CuO thin films

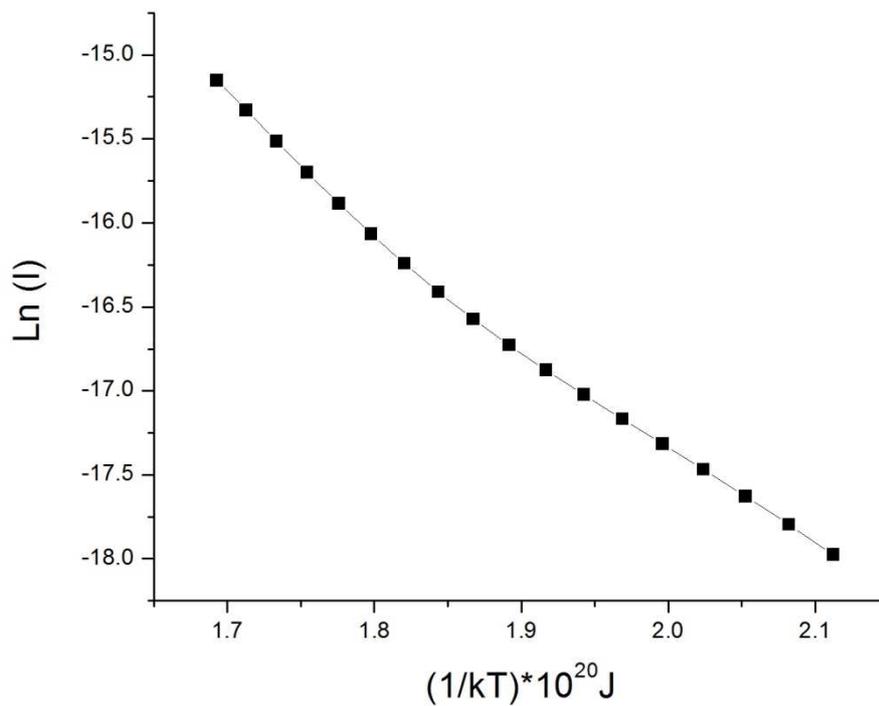


Fig. 10: ln I (vs) 1/kT graph of single layered as-synthesized CuO thin films

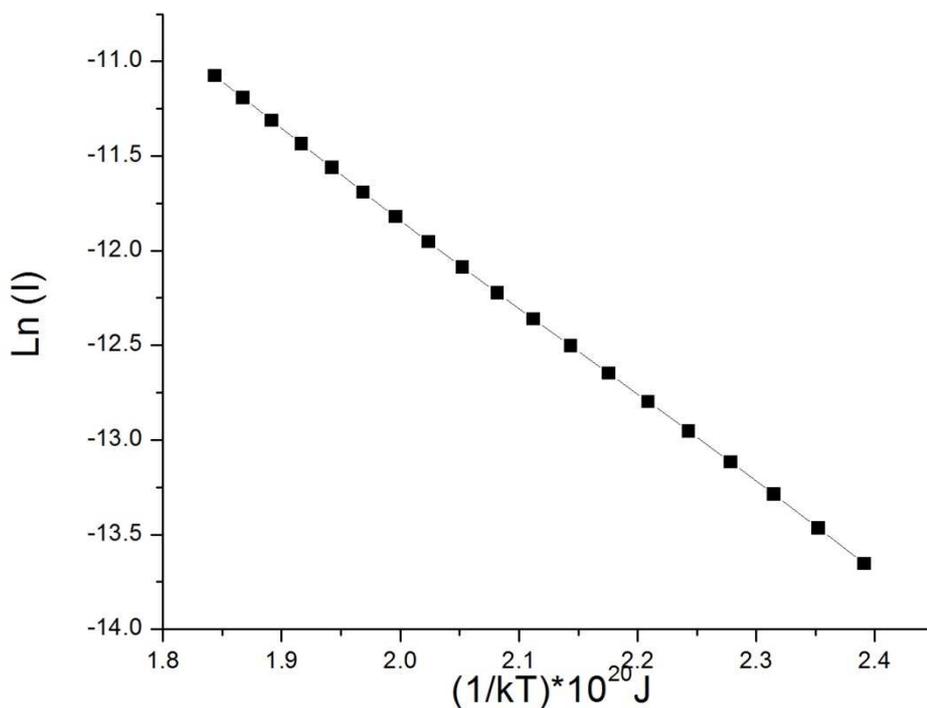


Fig. 11: $\ln I$ (vs) $1/kT$ graph of three layered as-synthesized CuO thin films

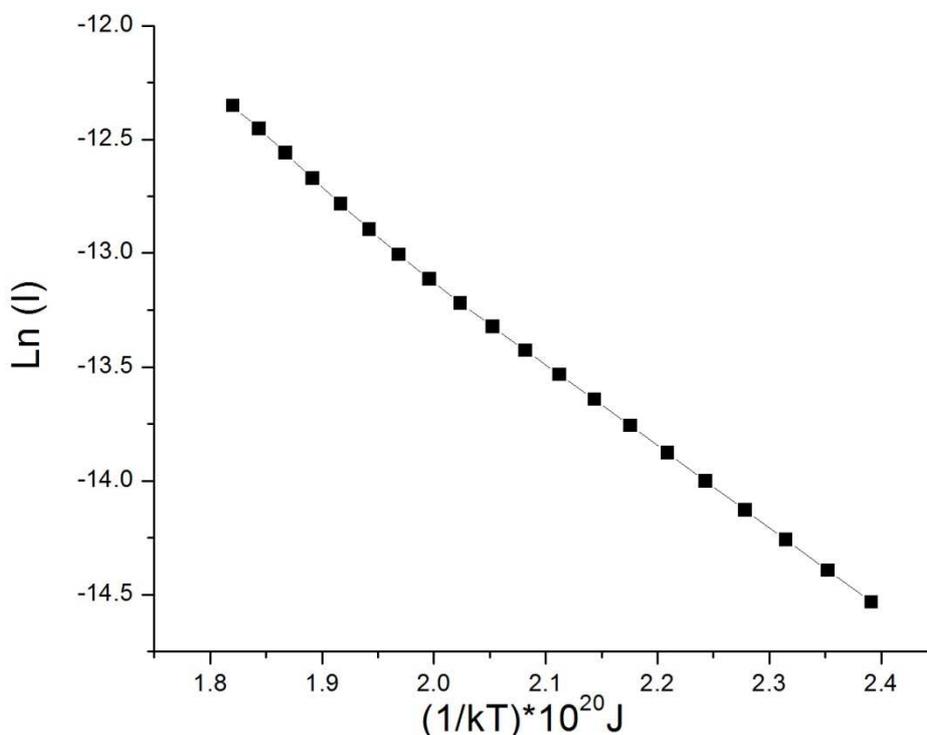


Fig. 12: $\ln I$ (vs) $1/kT$ graph of five layered as-synthesized CuO thin films

Field dependent dark and photoconductivity plots of as-synthesized single, three and five layered CuO thin films are shown in Figs. 4, 5 and 6 respectively. The plots indicate a linear increase of current in the dark and visible light illuminated samples in all the three cases with an increase in applied field depicting the ohmic nature of the contacts [12, 19]. The low values of dark current and insignificant rise in photocurrent upon the visible light illumination are

as expected. This is due to the wide band gap of CuO which has a capability of absorbing light only below wavelengths of 400 nm. Out of the varied layers of CuO coatings, the three layered showed better photocurrent. For example, for an applied field of 1000 V/cm, the single layered CuO showed photocurrent $\sim 0.025 \mu\text{A}$, the five layered CuO thin films showed $\sim 2.5 \mu\text{A}$ whereas the three layered CuO thin films recorded $\sim 7 \mu\text{A}$. This could be due to the enhanced surfaced area available for conduction and better quality of the three layered thin film coatings.

Fig 8, 9 and 10 shows the temperature dependent conductivity of as-synthesized single layered, three layered and five layered CuO thin films respectively. All the plots indicate the exponential behavior of temperature dependent current confirming the semiconducting nature of the material [23]. Also it is found that the temperature dependent current increases with increase in the number of layers and consequentially the film thickness. The $\ln I$ (vs) $1/kT$ for as-synthesized single layered, three layered and five layered CuO thin films shown in Fig 10, 11 and 12 respectively. The activation energy was calculated for as-synthesized single, three and five layered CuO thin films and the results are tabulated in table I. On analysis the activation energy decreases with increase in the number of coated layers. This could be attributed to the increased density of shallow traps with increase in porosity and the large surface area as a result of enhanced film thickness. These traps with short residence times may be filled with excitons at low temperature and could be later excited by raising the temperature upon thermal activation [24]. The charge carriers thus excited from the traps may adopt a hopping mechanism to cross the potential barrier and hence produce enhanced current [19, 25].

Table 1: Activation energy of as-synthesized samples

Sample	Activation Energy in eV
Single layer coated CuO thin films	0.397
Three layer coated CuO thin films	0.288
Five layer coated CuO thin films	0.272

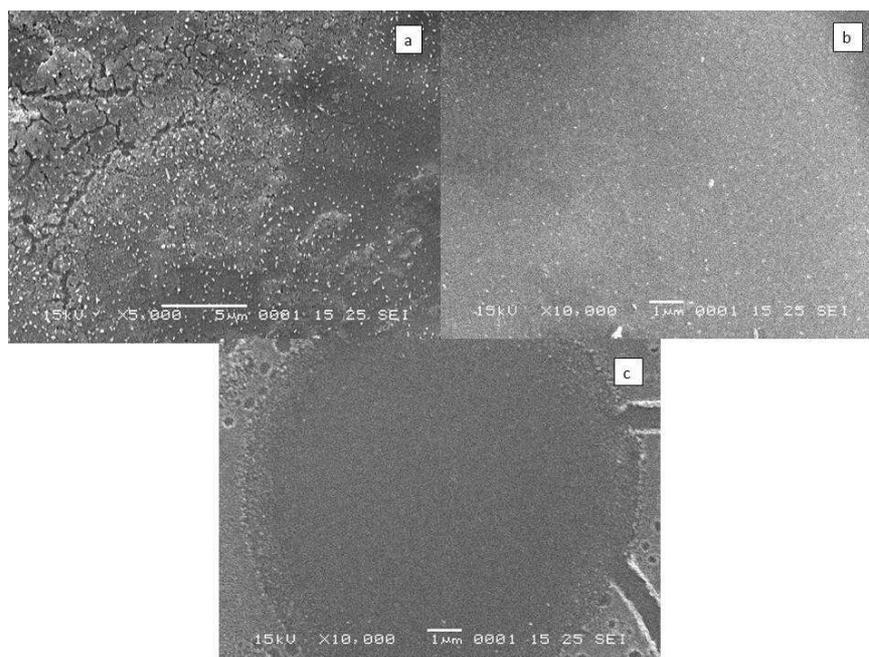


Fig. 13: SEM images of (a) single layered (b) three layered (c) five layered CuO thin films

The surface morphology of as-synthesized CuO thin films was investigated using Scanning Electron Microscope (SEM). The SEM photographs of single layered, three layered and five layered CuO thin films are shown in Fig. 13. On comparison of the three photographs it could be observed that the single layer coating though exhibit uniform coating also reveals micro cracks and discontinuities on the surface of the film. The three layered coating show high uniform homogenous layer of reduced particle size and improved texture of CuO thin films. On the other hand five layered CuO coated thin films show lack in uniformity and good quality. Thus it could be concluded that three layer coated CuO thin films are of high quality and would be more suitable for photovoltaic applications.

CONCLUSION

The CuO thin films were successfully coated onto glass substrate by spin coating using copper acetate as precursor. Single layered, three layered and five layered CuO films were synthesized and subjected to FTIR, UV-VIS, field

dependent dark and photoconductivity, temperature dependent conductivity and SEM studies. The presence of Cu-O stretching is confirmed in all cases using the FTIR spectra. All the three samples exhibited similar patterns of UV-VIS absorption spectrum with a slight increase in intensity upon increase in number of coating layers. The single layered and five layered CuO thin films recorded low values of dark and an insignificant rise in photocurrent upon visible light illumination whereas the three layered CuO thin films showed better photocurrent compared to the others which could be due to the better film quality which leads to enhanced surface area. Temperature dependent conductivity indicates the exponential behavior of temperature dependent current confirming the semiconducting nature of the thin films. On analysis of the activation energy, it is found that the activation energy decreases upon increasing the number of coating layers. The studies thus suggest that the three layered CuO thin films could be better photoconductors for application as potential solar energy trapping materials.

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