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Influence of Ag–Dopant on Structural Optical and Electrical Properties of Cu_(1-x)Ag_xO Thin Films Prepared By Chemical Spray Pyrolysis Technique

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ARTICLE DETAILS

Article history:

Received 13 October 2018

Accepted 27 October 2018

Available online 11 November 2018

Keywords:

Thin Film

DC Electrical Conductivity

Activation Energy

ABSTRACT

As major attention has been paid to transition metal oxide semiconductor suitable for solar cell, photo detector and gas sensor, present study embark on the structural, optical and electrical characterization of Ag doped CuO thin films prepared using chemical spray pyrolysis technique at the constant substrate temperature of 350 °C. For Ag doping, various concentrations of silver acetate (0.5–3.0 wt.%) was used in the sprayed precursor solution. Confirmed monoclinic lattice shows the tenorite phase formation of CuO in the pure and Ag doped films. The optical band gap of the films was in the range of 2.4–3.4 eV. A minimum resistivity of 0.0017 x10³ Ωcm was achieved in the 0.5 wt.% Ag doped film, and its optical band gap was 2.74 eV.

1. Introduction

Nanostructured transition metal oxide semiconductors have stimulated significant research interest in various fields including optics, optoelectronics, catalysis, biosensors and so on. These materials have unique physicochemical properties arising because of quantum size effect and high specific surface area, which are different from their bulk counterparts [1]. Among the available transition metal oxides, such as NiO, CuO, ZnO, and Fe₂O₃, synthesis of CuO is an important topic of research. Due to its interesting built-in properties, copper oxide is still the most demanded material and has been widely used for diverse applications includes semiconductors [2], gas sensors [3], battery electrodes [4], etc. CuO has a monoclinic structure in which each Cu atom has four nearest neighbors of oxygen atoms and exists at the center of oxygen rectangular, while oxygen atoms are located at the center of distorted tetrahedron of Cu [5]. It is a p-type semiconductor with a narrow band gap of about 1.2 eV [6]. To improve the performance of this oxide, doping in CuO with suitable dopants offers an effective method to adjust their properties. It is vital to satisfy the specific needs of the practical applications. In general, metal doping makes radical changes in optical, electrical, and magnetic properties of CuO by altering its electronic structure. Also, Cu has three oxidation states Cu⁺, Cu²⁺ and Cu³⁺, therefore both hole doping and electron doping mechanisms are possible [7]. Many authors have reported the changes associated when CuO is doped with transition metals, such as Mn [8], Fe [9], Ti, Cd and Zn [10]. From the literature survey, it was found that there are very few reports on Ag-doped CuO nano particles and thin film. Wang et al. [11] reported that Ag/CuO nano composite gained a stimulating attention in research because of their photocatalytic properties. Sayantan Das et al. [12] also studied the structural and optical properties of Ag-doped copper oxide thin films on polyethylene naphthalate substrate prepared by low temperature microwave annealing. But to our best knowledge, there is no report on the study of physical properties of Ag doped CuO thin film by chemical spray pyrolysis technique. Several techniques have been employed to prepare CuO thin films, such as chemical vapor deposition (CVD), thermal oxidation of copper, sol-gel dipcoating, sputtering, electrochemical deposition, pulsed laser deposition, plasma evaporation, reactive sputtering and molecular beam epitaxy etc. Among these various thin film deposition techniques, chemical

spray pyrolysis is a rather simple and inexpensive technique which enables the production of large area uniform and transparent films with good adherence and reproducibility. Further advantages of the spray pyrolysis technique include intentional doping of the films to be n-type or p-type [13]. In this present work, we investigate the influence of Ag doping on the crystalline structure and optical properties of CuO nanostructured films obtained using the Chemical Spray pyrolysis technique.

2. Experimental Methods

Pure and Ag doped CuO thin films were deposited on the glass substrates using the chemical spray pyrolysis (CSP) technique. For the preparation of CuO films, 0.2 M copper acetate monohydrate [Cu (CH₃ (COO)₂) H₂O] was used as a source material of Cu. The solution containing double distilled water and ethanol was used as the solvent. To achieve Ag doping, 0.2 M silver acetate was dissolved in required amount along with 0.2 M copper acetate. Ag was doped with CuO at different wt.% (0.5, 1, 2 and 3). The details of sample preparations are given in Table 1.

Table 1 Sample preparation details

Sample name	x	1-x	Sample code	Description
	0	1	CuO	Pure CuO thin film
Cu _(1-x) Ag _x O	0.005	0.995	Cu _{0.995} Ag _{0.005} O	0.5 wt. % Ag doped CuO thin film
	0.01	0.99	Cu _{0.99} Ag _{0.01} O	1.0 wt. % Ag doped CuO thin film
	0.02	0.98	Cu _{0.98} Ag _{0.02} O	2.0 wt. % Ag doped CuO thin film
	0.03	0.97	Cu _{0.97} Ag _{0.03} O	3.0 wt. % Ag doped CuO thin film

The resultant precursor solution was sprayed on preheated substrates at 350 °C. The substrate temperature was controlled through a thermocouple with the help of PID temperature controller. The optimized deposition parameters such as substrate-spray nozzle distance (30 cm), solution flow rate (5 mL/min), spray time (3 s), carrier gas pressure (compressed air 0.4 kg/ cm²) were kept constant. After deposition, the coated substrates were allowed to cool down to room temperature. The thickness of the prepared film was measured using Mitutoya SurfTest SJ-301 stylus type surface profiler. Microstructure and crystallinity of the films were characterized using PANalytical-3040 X'pert Pro X-ray diffractometer with copper target (λ=1.5405 Å) in θ–2θ scan mode. Continuous scanning was applied with a slow scanning speed (step size = 0.05°) and small time constant (step time = 10 s). Optical properties of the samples were investigated using a UV-Vis-NIR double beam

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spectrophotometer (Varian Carry 5000). Standard four probe technique was used for the measurement of electrical conductivity using Keithley 2400 multimeter interfaced with computer.

3. Results and Discussion

The characteristic X-ray diffraction patterns of pure and Ag-doped CuO thin films are shown in Fig. 1. All the $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$ thin samples except, Ag concentration $x = 0.03$ shows two major peaks are located at $2\theta = 35.5^\circ$ and 38.7° . This indicates the polycrystalline nature of the films. These diffraction planes are indexed as (-111) and (111) respectively by comparing the obtained inter planar spacing values (d_{hkl}) with the standard (d_{hkl}) values reported in the JCPDS of CuO (JCPDS card no= 80-1916). This confirms that the pure and Ag doped CuO thin films are crystallized in the monoclinic crystal system belongs to C2/c space group.

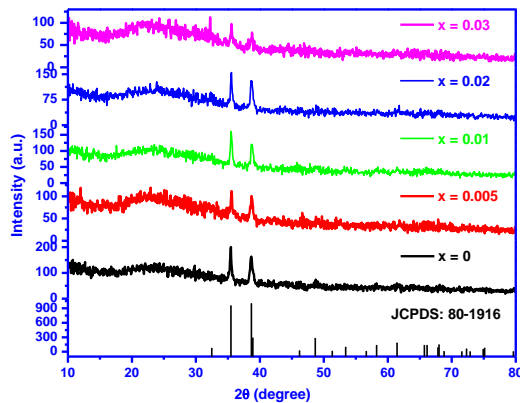


Fig. 1 X-ray diffraction patterns of $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$ thin films

Absence of peaks related to silver Ag, AgO or other Ag bearing impurities can be seen in the XRD patterns which reveal phase purity of the synthesized samples and the monoclinic structure of CuO is not distorted up to Ag doping concentration $x = 0.02$. This confirms that the Ag ions are effectively doped in the CuO lattice site.

However, the CuO film doped with Ag of doping concentration $x = 0.03$ shows the mixed phases of monoclinic CuO and AgO. This may be due to the exceeding limit of doping concentration of Ag^+ ions. In pure CuO thin film, prominent peak showed a preferential orientation along (111) direction. As the doping concentration increases to $x = 0.005, 0.01$ and 0.03 , the preferred orientation is shifted to (-111) directions. This shift in growth orientation reveals the impregnation of Ag^+ ion replacing Cu^{2+} [14]. The crystallite size was calculated by measuring the full width at the half-

maximum (FWHM) of the most intense diffraction peak using Debye-Scherrer's equation [14], $D = 0.9\lambda/\beta\cos\theta$, where D is the average crystallite size, λ is the wavelength of the incident X-ray beam (1.5406 \AA), θ is the Bragg diffraction angle and β is the peak full width at half width maximum (FWHM). The calculated crystallite size is 52 nm for pure CuO thin film and then it decreases to 44.2, 35.4, 44.3 and 25.5 nm respectively for the Ag doped films with doping concentration $x = 0.005, 0.01, 0.02$ and 0.03 . No significant variations of crystallite size are occurred in the $\text{Cu}_{1-x}\text{Ag}_x\text{O}$ thin films prepared with doping concentration ($x = 0.005, 0.02$). The smallest value of crystallite size 29.51 nm is observed for the $\text{Cu}_{1-x}\text{Ag}_x\text{O}$ thin film ($x = 0.03$). This may be due to segregation of AgO into the grain boundaries which inhibits the growth of the crystallite size in the film at the higher doping concentration [15]. The decrease of crystallite size increases the strain value. The calculated strain value of 0.695×10^{-3} for pure CuO increases to 1.02×10^{-3} and 1.22×10^{-3} when the Ag doping concentration increases to $x = 0.01$ and 0.03 respectively. The marginal increase in strain in $\text{Cu}_{1-x}\text{Ag}_x\text{O}$ ($x = 0.03, 0.005$) in comparison to pure CuO arise from the lattice expansion on substitution of Cu^{2+} with Ag^{2+} . However, addition of silver with $x = 0.03$ increases the strain value that induced the new phase AgO.

The lattice parameters ($a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$ for monoclinic structure), and the volume of the unit cell, V was calculated using the following relations,

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

$$V = abc \sin \beta$$

The origin of the strain is related to the lattice mismatch and may be calculated using the relation,

$$\varepsilon = \frac{\beta \cos \theta}{4}$$

The dislocation density ' δ ', the dislocation lines per unit area of the crystal can also be evaluated from the particle size ' D ' using the equation,

$$\delta = \frac{1}{D^2} \text{ lines / m}^2$$

Also using the particle size ' D ' and the film thickness ' t ', number of crystallites ' N ' can be estimated using the relation,

$$N = \frac{t}{D^3} / \text{unit area.}$$

Obtained lattice parameters are comparable to the reported results (JCPDS Card No.: 80-1916) and they are listed in Table 2.

Table 2 Structural parameters of the Ag doped CuO thin films

Ag doping concentration	d-spacing (2θ) $^\circ$		FWHM	Lattice constants (\AA)			Crystallite size, D (nm)	Unit cell volume, V (\AA^3)	Micro strain $\varepsilon \times 10^{-3}$	Dislocation density, $\delta \times 10^{15}$ lines/meter
	Observed	Standard		Calculated						
$x=0.00$	2.5352	2.5270	0.1673	$a=4.6857$; $b=3.4335$; $c=5.1492$	$a=4.6927$	52.0	81.66	0.695	0.369	
$x=0.005$	2.5235		0.1968	$a=4.69253$; $b=3.42204$; $c=5.13684$	$b=3.4283$	44.27	81.346	0.8176	0.510	
$x=0.01$	2.5278		0.2460	$a=4.69251$; $b=3.43340$; $c=5.13682$	$c=5.1370$	35.41	81.616	1.0222	0.797	
$x=0.02$	2.5275		0.1968	$a=4.69248$; $b=3.43364$; $c=5.13679$		44.39	81.621	0.8178	0.507	
$x=0.03$	2.5260		0.2952	$a=4.69260$; $b=3.42576$; $c=5.13691$		29.51	81.436	1.2265	1.148	

Fig. 2 showed that the typical transmittance spectra in the UV-Visible and infrared (IR) region of pure CuO and Ag doped CuO thin films.

It indicates that all the films on glass substrate are opaque for wavelengths below 300 nm. Above 300 nm all the films are transmissive and have moderate transmission less than 60%. Present study reveals that the transmittance is increased with the increase of Ag doping concentration. The average transmittance of pure CuO thin film is about 25% which is increased to 45% and 55% for the films prepared with Ag doping concentration $x = 0.005$ and 0.03 respectively. This indicates moderate transmittance in the doped samples. This increase of transmittance may be attributed to the crystalline nature of films and high transparency is associated with a good structural homogeneity and crystallinity [16]. Moreover the samples prepared with Ag doping concentration $x = 0.01$ and 0.02 shows slightly lesser transmittance. The decrease of transmittance may be due to the increased scattering of photons by crystal defects created by doping or may be the scattering of photons by the pores present in the sample [17, 18]. Li et al. have stated that films with higher transparency in the visible region can act as a transparent conducting oxide material with photovoltaic cell applications.

The higher transparency obtained for the film in the visible region shows its potential application in the photovoltaic device applications [19].

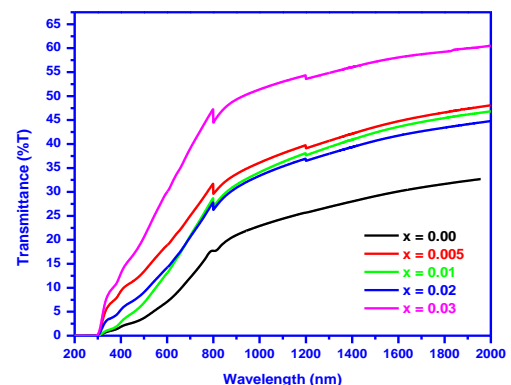


Fig. 2 UV-Vis Optical transmittance spectra of $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$ thin films

According to solid state band theory, the optical band gap (E_g) and the nature of transition in pure and Ag doped CuO thin films can be understood by constructing Tauc plot. Nature of optical transition can be identified from the relation,

$$\alpha h\nu = A(h\nu - E_g)^n,$$

where, 'A' is the band edge constant, ' α ' is the absorption coefficient, 'h' is the Planck's constant (6.626×10^{-34} J-s), ' ν ' is the frequencies of photons and the exponent 'n' depends on type of transition, 'n' may have values 1/2, 2, 3/2 and 2/3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. As CuO and Ag doped CuO have direct allowed transitions $n=1/2$ is considered. The band gap of CuO and Ag doped CuO thin films can be obtained by extrapolating the straight line portion of the $(\alpha h\nu)^2$ vs. $(h\nu)$ graph to the $(h\nu)$ axis as shown in the Fig. 3.

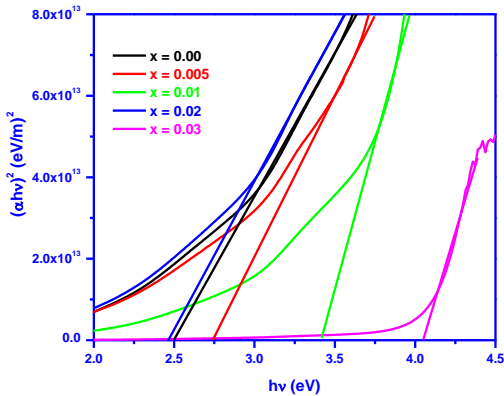


Fig. 3 Tauc's Plots of $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$ thin films prepared with different Ag concentrations

Estimated direct band gap value of pure CuO thin films is 2.5 eV, which decreases to 2.4 eV when the doping concentration $x=0.02$ and increases to 2.74 and 3.41 eV respectively on increasing the dopant concentration ($x=0.005$ and 0.01). But the optical band gap increases to 4.06 eV for the sample with $x=0.03$. This sudden increase in band gap value may be due to the presence of secondary phase AgO along with $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$. Among the prepared $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$ thin film samples, the films doped with Ag concentrations ($x=0.005$ and 0.02) are phase pure and having good transmittance and minimum optical band gap energy. On this context, these two films are the optimized samples that can be used for applications such as transparent conductive film for various optoelectronic devices and antireflection coating materials.

Fig. 4 shows the temperature dependent DC resistivity variations in $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$ thin films prepared for different Ag doping concentrations ($x=0, 0.005, 0.01, 0.02$ and 0.03).

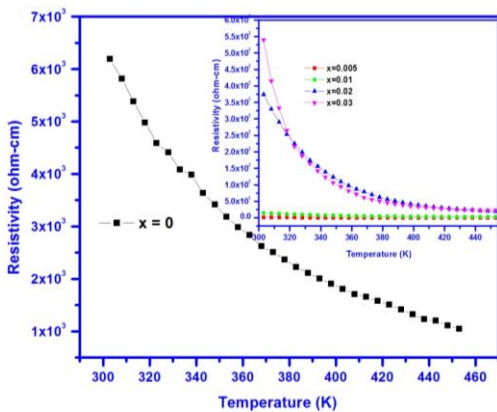


Fig. 4 Variation of resistivity with temperature in $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$ thin films

The temperature dependent resistivity of all the prepared films are measured in the temperature range 300-450 K. It is observed that Ag doped CuO thin films shows lesser resistivity than the pure CuO thin film. In the low temperature region (300-380 K), the resistivity of pure sample is found to be in the range of $(6 \times 10^3 \text{ to } 2 \times 10^3 \text{ } \Omega\text{-cm})$, while at high temperature region (380-450 K) the resistivity decreases gradually and reaches nearly a constant value of $1 \times 10^3 \text{ } \Omega\text{-cm}$. Similarly the resistivity of doped sample is found to be in the range $5.5 \times 10^2 \text{ to } 1 \times 10^2 \text{ } \Omega\text{-cm}$ in the low temperature region. While at high temperature region (380-450 K), the resistivity decreases gradually and reaches nearly a constant value of 50

<https://doi.org/10.30799/jnst.177.18040521>

$\Omega\text{-cm}$. The decrease of resistivity with temperature mainly regarded as due to the thermally activated mobility of the carriers (electrons or holes) rather than to a thermally activated generation of these carriers [20].

The electrical resistivity is also very sensitive to lattice imperfections in solids, such as vacancies and dislocations. As pointed out by Bakonyi et al. [21], besides the crystallite boundaries, the presence of a large number of other types of lattice imperfection has also been found to have an effect on the electrical resistivity in nanocrystalline materials. The change in cation distribution in nanocrystalline $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$ thin films may also contribute to the observed decrease in resistivity at high temperature.

Activation energy is the minimum amount of energy required to activate atoms or molecules to a condition in which they will undergo a reaction or transport. The activation energies are calculated from the local gradients of the $\ln(\sigma)$ versus reciprocal temperature ($1000/T$) plots, based on the following equation,

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

where, ' E_a ' is the activation energy of conduction, ' σ_0 ' is a temperature independent factor and 'k' is the Boltzmann's constant and 'T' is the absolute temperature. Fig. 5 show that the constructed Arrhenius plot of pure and Ag doped CuO thin films.

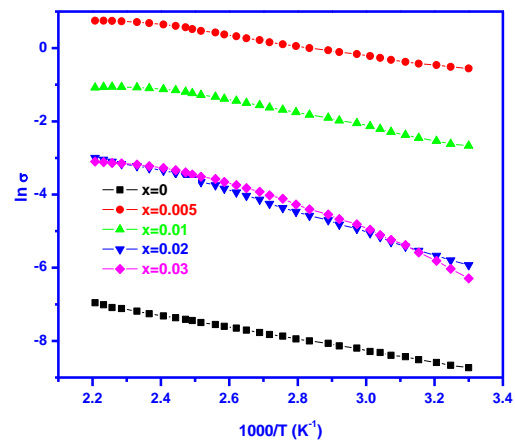


Fig. 5 Arrhenius Plot of $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$ thin films

The measured room temperature resistivity and its corresponding conductivity, calculated thermal activation energy are revealed in the Table 3.

Table 3 Electrical parameters of $\text{Cu}_{(1-x)}\text{Ag}_x\text{O}$ thin films

Dopant Concentrations	Resistivity $\times 10^3 \Omega\text{-cm}$	Conductivity $\times 10^{-3} \Omega^{-1}\text{-cm}^{-1}$	Activation energy eV
$x = 0$	6.19	0.161	0.31
$x = 0.005$	0.0017	573.9	0.26
$x = 0.01$	0.0144	69.25	0.31
$x = 0.02$	0.3742	2.672	0.55
$x = 0.03$	0.5397	1.853	0.57

In the present study, pure CuO thin film possesses room temperature resistivity of $6.19 \times 10^3 \text{ } \Omega\text{-cm}$. The lowest value of room temperature resistivity $0.001 \times 10^3 \text{ } \Omega\text{-cm}$ is observed in Ag doped CuO thin film for the doping concentration $x=0.005$. Further increase in Ag doping concentrations increase the resistivity values, but not exceed room temperature resistivity of pure CuO. At lower level of Ag doping, the Ag ions are placed into the CuO lattice effectively and act as donors by supplying free electrons when they occupy the sites of Cu^{2+} ions. At higher doping concentration the excess of silver atom might have not occupied the correct places, instead occupy the interstitial positions and distort the crystal structure, which decreases the electronic mobility. The disorder produced in the lattice, increases the efficiency of scattering mechanism such as photon scattering, ionized scattering which in turn cause increase in resistivity [22, 23].

It is observed that the calculated activation energy has no significant variation upto doping concentration $x=0.01$ of Ag doping. However at higher doping concentrations $x=0.02$ and 0.03 the activation energy values are high 0.55 and 0.57 eV respectively. The increase of activation energy at higher doping concentration may be due to the structural imperfections that induce defects and impurities in the films that lead to an increase in activation energy. Usually less activation energy can be attributed to perfection in crystal structure.

4. Conclusion

Pure and Ag doped CuO thin films have been successfully deposited on glass substrates at 350 °C by the chemical spray pyrolysis technique. Doping concentration produced significant variations in structural, optical and electrical properties. XRD patterns showed the formation of single phase monoclinic structured film and this single phase was retained up to Ag doping concentration of $x=0.02$. At the higher doping concentration ($x=0.03$) the mixed phase of both CuO and AgO were obtained. The optical band gap of CuO remarkably increases from 2.5 to 3.4 eV with increasing Ag doping concentrations from $x=0$ to 0.01 and then decreased to 2.4 eV. The electrical conductivity and activation energy were measured and found dependent to the dopant concentrations. Lowest resistivity of about $0.0017 \times 10^3 \Omega\text{-cm}$ was observed in Ag doped CuO sample with $x=0.005$. From the obtained results it can readily be noticed that CuO thin films doped with a level of $x=0.005$ exhibited interesting properties of high transmittance and low resistivity that could be suitable for optoelectronic applications.

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