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Research Article

Influence of Annealing Temperature on Morphology and Electrical Properties of ZrO_2:CuO Thin Films Prepared by Pulse Laser Deposition

Nahida B. Hassan[Á*], Ghuson H. Mohamad[B] and Murtada M. Abd-Alkadum[Á]

[Á]Department of Physics, College of Science, University of Babylon
[B]Department of Physics, College of Science, University of Baghdad

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Abstract

Morphology and electrical properties of Zirconium Oxide (ZrO_2) pure and doped with (0,5,8 and 10) % copper oxide (CuO), prepared by using the pulsed laser deposition technique using a laser pulse with Nd:YAG wavelength (1064 nm), which enabled quality factor of a repetitive rate (6 Hz) and pulse duration (10 ns) and energy laser (1000 mJ) on the substrate of the glass with different annealing temperatures (RT,373,473)K. The morphology of the surface was examined by using an atomic force microscope (AFM). It can be found that the average grain size get to decrease with increasing of CuO content while increases with increasing of annealing temperature (T_a). The roughness results reveal increases with increasing of CuO content while decreases with increasing of annealing temperatures. D.C Conductivity measurements showed that there two transition mechanisms and there are two activate energies E_{a2} , E_{a1} for films ZrO_2:CuO with ratios (0,5,8 and 10) %. Hall effect measurements showed that all the films ZrO_2:CuO was kind of p-type for each ratios.

Keywords: *Zirconium Oxide, copper oxide, pulsed laser deposition technique.*

1. Introduction

Zirconia (ZrO_2) is an attractive material with its high dielectric constant (15–21) [Chang , 2001] , the lattice parameters of ZrO_2 are : a = 5.13Å, a band gap of 5.12 eV has been reported , while for sputtered thin films a value of 4.1 eV has been obtained [Jeon *et.al* 2001]. And good thermal stability against silicate formation on silicon [Hubbard and Schlom, 1996]. Thus, ZrO_2 thin films are well suited for many applications, e.g., as the buffer layer for high-T_c superconductors or for integration of ferroelectric thin films in nonvolatile ferroelectric memories [Choi *et.al*, 2001], as the gate dielectric for complementary metal oxide semiconductors [Cho *et.al* 2002], or oxygen sensors [Tan and Wu, 1998]. It is important for the various applications of ZrO_2 thin films to control their crystallinity, orientation, and surface morphology.

ZrO_2 films are widely used as optical coatings due to their excellent properties, such as a high refractive index, a broad region of high absorption from the near UV to the mid visible and a high pulse laser damage threshold [Gao , 2000]. In addition, they are currently used as thermal barrier coatings and buffer layers [Cassir *et.al* 2002 and Kim 2004].

Zirconia is one of the important ceramic which is used as a biomaterial that has a bright future because of its high mechanical strength and fracture toughness and has unique a characteristic called transformation toughening, which can give it higher strength and toughness compared with other ceramics. Also, Zirconia has unique properties such as electrical, mechanical, optical and thermal, which makes it a good choice for application such as: structural materials, thermal barrier coating, solid oxide fuel cell electrolytes, and semiconductor materials. Its stable photochemical properties make it directly applicable to photonics. As reported in literature, Zirconia can be catalyst in various reactions such as isomerization of alkanes, dehydration of alcohols, decompositions of nitrous oxide [Felora and Reza , 2011]. Zirconia implants are becoming increasingly important in the field of dental medicine because of their good mechanical properties, biocompatibility, and for aesthetic reasons. However, Zirconia is bioinert and this can lead to a poor fixation of the ceramic implant in the bone [Reshmi 2010].

2. Experimental

The preparation of bulk ZrO_2:CuO and their thin films on different substrates glass and p-Si using pulse laser deposition technique. The preparation plates of ZrO_2:CuO at different CuO contents (0,5,8 and 10) % were sintering to temperature of 1273K for three hour. Atomic Force Microscopy studies were recorded by using (Scanning probe Microscope type AA3000), supplied by Angstrom Advanced Inc. to determine the average grain size and roughness of ZrO_2:CuO on glass substrate and their statistical distribution. The electrical resistance has been

*Corresponding author: **Nahida B. Hassan**

measured as a function of temperature for ZrO_2:CuO films in the range (303–433)K. The measurements have been done using sensitive digital electrometer type Keithley 616 and electrical oven. The resistivity (ρ) of the films is calculated by using the following equation:

$$\rho = \frac{R.A}{L} \quad (1)$$

Where R is the sample resistance, A is the cross section area of the film and L is the distance between the electrodes. The conductivity of the films was determined from the relation:

$$\sigma_{d.c.} = \frac{1}{\rho} \quad (2)$$

The activation energies could be calculated from the plot of Lnσ versus $10^3/T$ according to equation (3).

$$\sigma = \sigma_o \exp(-E_a/k_B T) \quad (3)$$

Where σ_o is the minimum electrical conductivity at 0K, E_a is the activation energy which corresponds to $(E_g/2)$ for intrinsic conduction, T is the temperature and k_B is the Boltzmann's constant [Kireev, 1978]. Hall effect measurements have been done by Van der Pauw (Ecopia HMS-3000) Hall Measurement Systems. Measurements required four Ohmic contacts on the sample; it has been pleased in four point probe into this device. The principle Hall effect refers to potential difference (Hall voltage) on opposite sides of a thin sheet of conducting or semi-conducting material through which an electric current is flowing, created by a magnetic field (B=0.550 Tesla) applied perpendicular to the Hall element. The Hall coefficient (R_H) is determined by measuring the Hall voltage that generates the Hall field across the sample of thickness (t), by [Islam *et.al* 1998 and Gurumurthy *et.al* 1999]:

$$R_H = \frac{V_H}{I} \cdot \frac{t}{B} \quad (4)$$

From the Hall coefficient equation we can determine the carrier's concentration of the semiconductor, and the carrier type, since R_H is negative and positive for n– and p– type, respectively:

$$R_H = \frac{-1}{n.e} \quad \text{For} \quad \text{n-type} \quad (5)$$

$$R_H = \frac{1}{p.e} \quad \text{For} \quad \text{p-type} \quad (6)$$

Where (e) is the electron charge. If the conduction is due to one carrier's type e.g. electrons, we can measure the mobility as:

$$\mu_n = \frac{\sigma}{n.e} \quad (7)$$

$$\mu_n = \sigma |R_H| \quad (8)$$

i.e., by knowing σ , the mobility can be determined. We can calculate the carrier lifetime from the mobility values by using the following equation:

$$\tau = (\mu.m^*)/e \quad (9)$$

Where m* is the effective mass, and τ is the life time of the carrier.

The drift velocity could be calculated from the equation:

$$v_d = \mu.E_n \quad (10)$$

Where E_n is the applied electric field. Also the mean free path could be calculated using the following equation:

$$\ell = v_d . \tau \quad (11)$$

3. Results and Discussion

3.1 Atomic Force Microscopy (AFM) Analysis

The grain size (grain diameter) and average roughness of ZrO_2:CuO thin films with different CuO content (0, 5, 8 and 10)% prepared at R.T and annealing with different temperature (373, 473)K have been measured using AFM as shown in figs. (1, 2 and 3). The surface morphology of the ZrO_2:CuO thin films as observed from the AFM micrographs proves that the grains are uniformly distributed within the scanning area (10 μm ×10 μm).

It is obvious from Table (1) that the average grain size get to decrease with increasing of CuO content while increases with increasing of annealing temperature. The roughness results reveal increases with increasing of CuO content while decreases with increasing of annealing temperatures, indeed the grain size decreases with increasing of CuO content in the other hand the roughness decreases from 5.83 to 1.71 nm, from 6.24 to 1.95 nm , from 6.70 to 2.01 nm and from 15.8 to 2.18 nm when annealing temperatures increases from R.T to 473K respectively when CuO content increases from 0 to 10% these results are due to structure enhancement. This result agreement with Soo Ho Kim [Kim et.*al*. 2006].

Table (1): Average grain size and roughness for ZrO_2:CuO films with different CuO content and different annealing temperature

T_a (K)	CuO %	Average grain size (nm)	Average Roughness (nm)
RT	0	95.77	5.83
	5	92.24	6.24
	8	91.52	6.7
	10	87.55	15.8
373	0	133.6	2.54
	5	122.51	2.71
	8	109.15	5.3
	10	98.69	5.73
473	0	288.3	1.71
	5	187.36	1.95
	8	152.56	2.01
	10	136.52	2.18

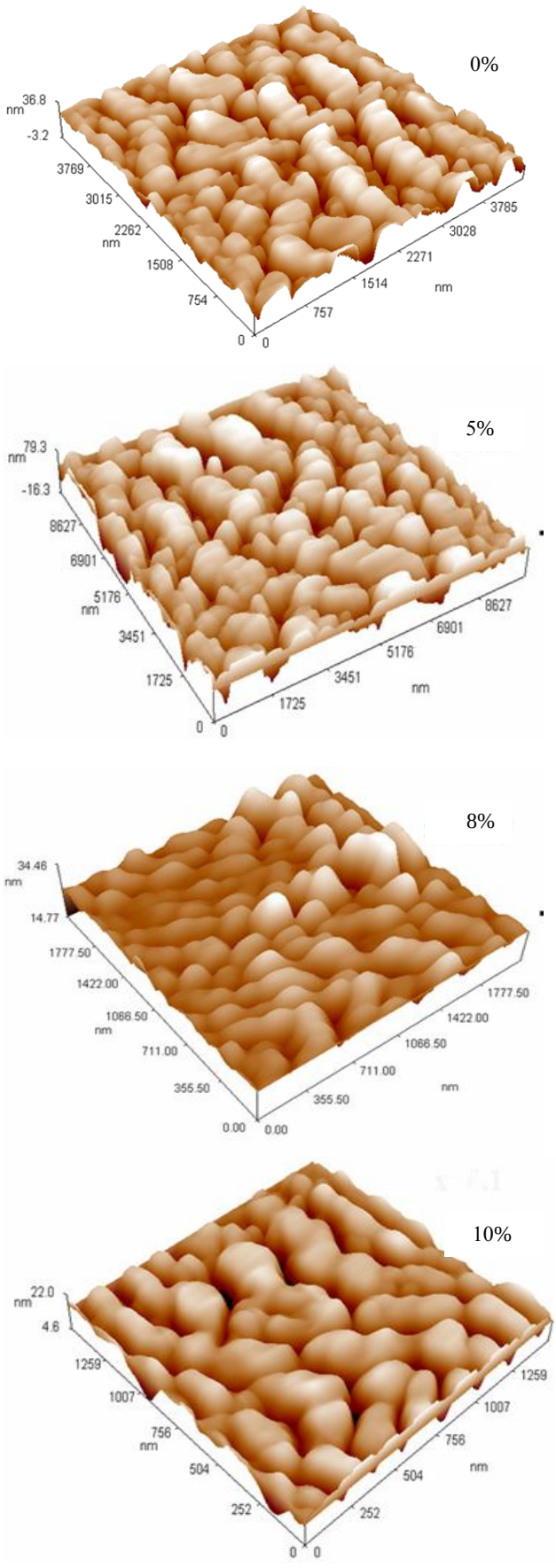


Fig. (1) AFM pictures for ZrO_2: CuO films at R.T with different CuO content (0, 5, 8 and 10) %

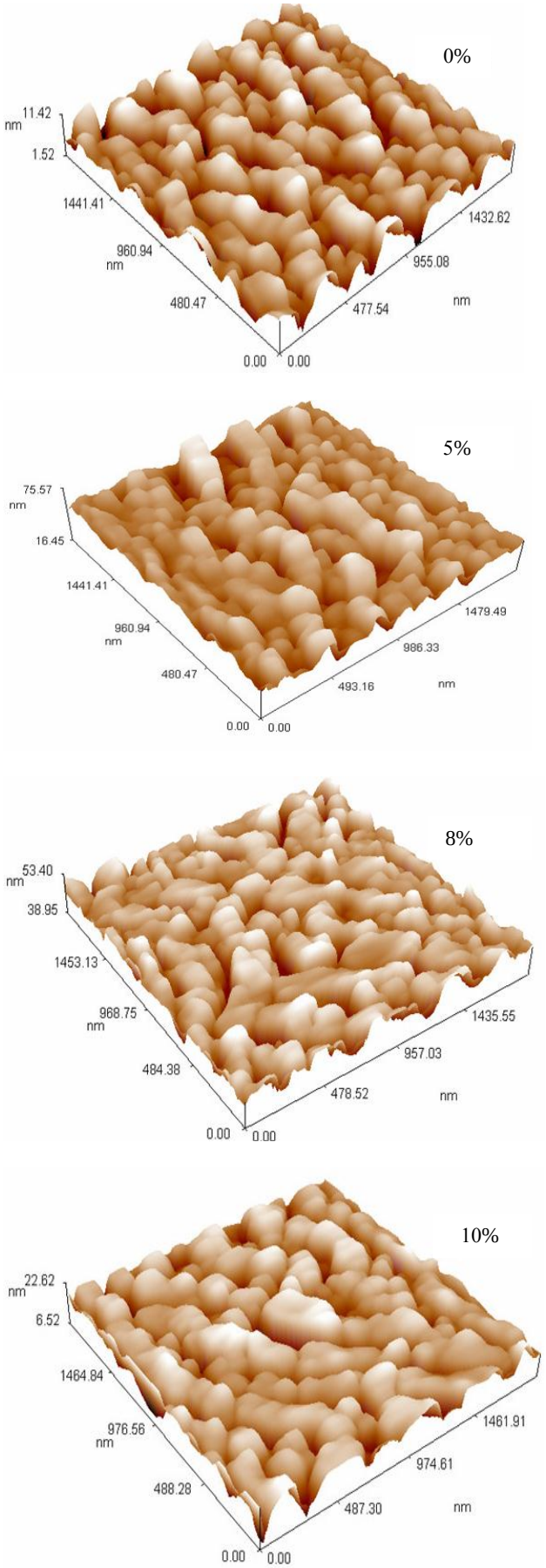


Fig. (2) AFM pictures for ZrO_2: CuO films at T_a= 373K with different CuO content (0, 5, 8 and 10) %

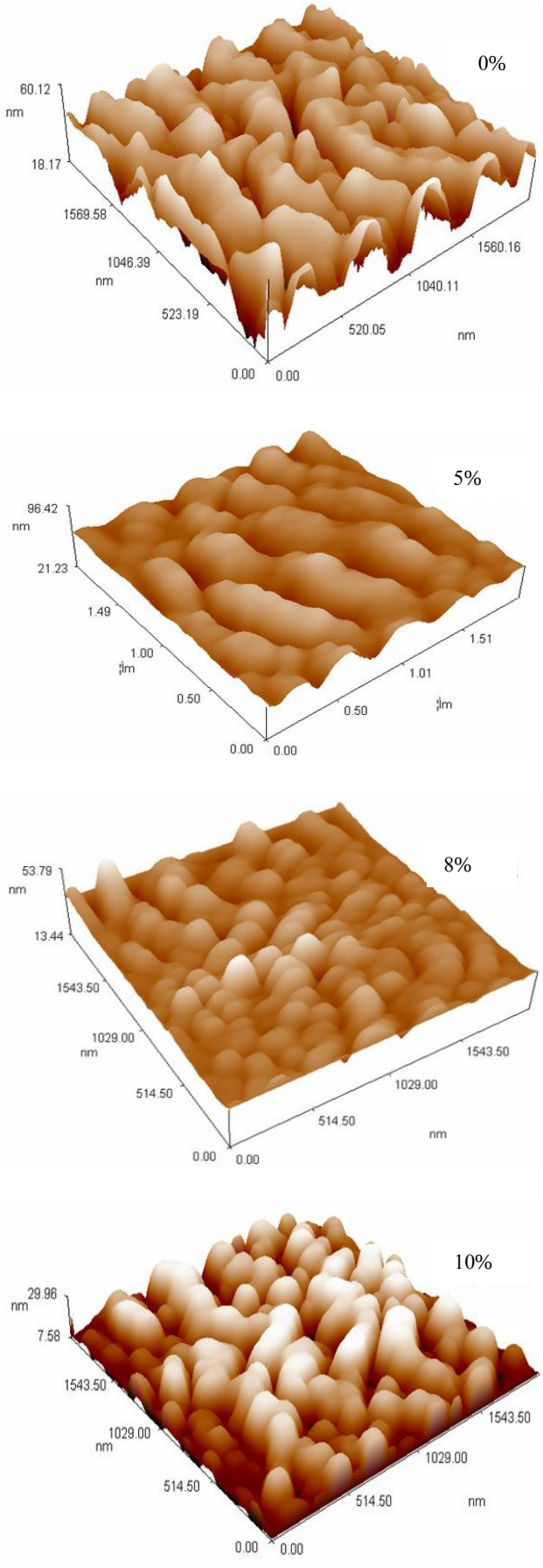
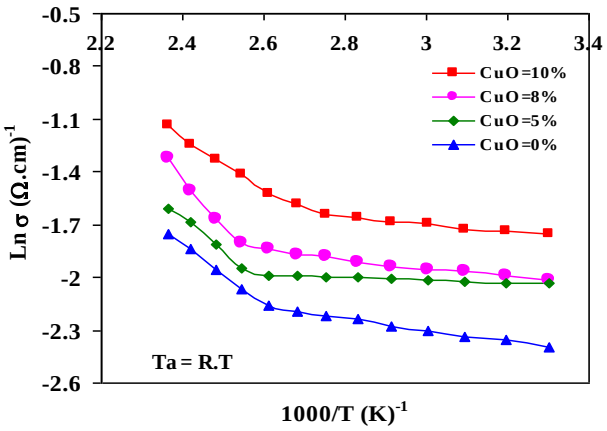


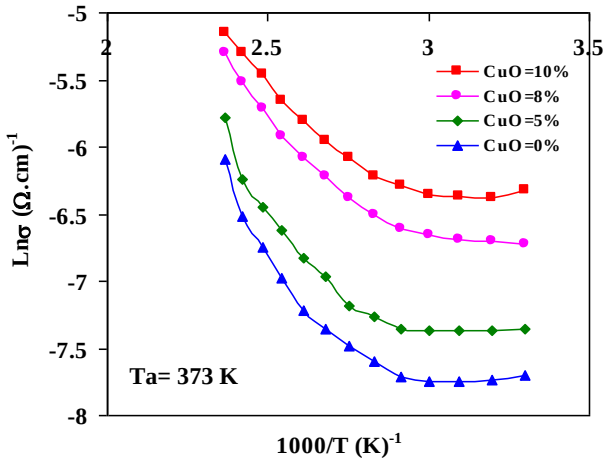
Fig. (3) AFM pictures for ZrO_2: CuO films at T_a= 473K with different CuO content (0, 5, 8 and 10)%.

3.2 D.C. Electrical Conductivity

It is very useful to determine in the extrinsic range the activation energies of impurity centers and in the intrinsic range the main energy gap. By using equation (3), plots the (Lnσ) vs. reciprocal of the absolute temperature (10^3/T), we can measure the activation energy by taking the slope of straight lines of (-ΔE/k).

Fig. (4) show the variation of $\ln\sigma_{d.c}$ versus 10^3/T for ZrO_2:CuO thin films at RT and different annealing temperatures (373 and 473) K with different CuO content (0,5,8 and 10)% within the range of (303-433) K .





From this figure, it is found that there are two stages of conductivity throughout the heating temperature range. The first activation energy (E_{a1}) occurs at higher temperature within range (373-433) K and this activation energy is due to conduction of the carrier excited into the extended states beyond the mobility edge, while the second activation energy (E_{a2}) occurs at low temperature within range (303-373) K and the conduction mechanism of this stage is due to carriers transport to localized states near the valence and conduction bands. These two conduction mechanism means there are two mechanisms of transitions. Also, it is seen that the conductivity decreases with decreasing of temperature range for all samples at different T_a and CuO content. This decreased means a negative coefficient of resistance, confirming the semiconductor behavior of ZrO_2:CuO thin films is non-linear with temperature.

Table (2) Values of E_{a1} and E_{a2} and these ranges for ZrO_2 films with different CuO and different annealing temperature

T_a (K)	CuO%	Ea_1 (eV)	Temp. Range (K)	Ea_2 (eV)	Temp. Range (K)	σ_{RT} $(\Omega.cm)^{-1}$
RT	0	0.0312	303-373	0.1076	373-423	0.09125
	5	0.0281	303-373	0.2288	373-423	0.13048
	8	0.0278	303-373	0.1442	373-423	0.13367
	10	0.0165	303-353	0.1133	353-423	0.17310
373	0	0.0123	303-333	0.2371	333-423	0.00043
	5	0.0026	303-333	0.2306	333-423	0.00072
	8	0.0244	303-343	0.2193	343-423	0.00120
	10	0.0058	303-343	0.1982	343-423	0.00180
473	0	0.0796	303-368	0.5325	368-433	0.00332
	5	0.0134	303-368	0.1014	368-433	0. 00233
	8	0.0084	303-368	0.1021	368-433	0. 00329
	10	0.0045	303-353	0.1904	353-433	0.00283

Table (3) Hall Effect measurements for ZrO_2:CuO film with different annealing temperature and different CuO content

T_a (K)	CuO%	R_H (cm^3/C)	n_H $(cm^{-3}) \times 10^{11}$	type	μ_H $(cm^2/V.s)$
RT	0	5.99E+06	3.9	p	213
	5	1.24E+06	5.6	p	206
	8	2.11E+06	29	p	38.1
	10	1.79E+06	34	p	21.3
373	0	5.67E+06	11	p	127
	5	3.39E+06	18.3	p	102
	8	1.08E+06	57.3	p	65.23
	10	1.29E+06	59.1	p	58.56
473	0	1.09E+06	19	p	747
	5	6.31E+06	6.5	p	178
	8	1.30E+06	6.08	p	13.9
	10	7.02E+06	8.8	p	7.21

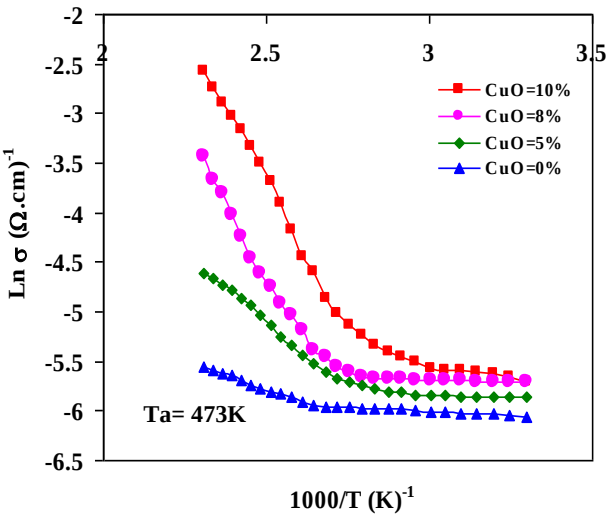


Fig. (4) Relation between Ln (σ) versus reciprocal of temperature for ZrO_2 films with different CuO content and different annealing temperature.

It is found that the conductivity at room temperature (σ_{RT}) increases with increasing of CuO content while decreases with increasing annealing temperatures. The increase in the conductivity with CuO content is obviously due to the increase in the carrier concentration as well as in the absorbance i,e decreases in the mobility while the explanation for decreasing in the conductivity with increasing of annealing temperature because of the rearrangement that may occur during annealing. Table (2) shows the effect of CuO content and annealing temperatures on activation energies for ZrO_2:CuO films. It is clear from this Table that the activation energies decrease with increasing of the CuO content but increase with increasing of annealing temperatures. The decrease of the activation energies with the increase of CuO content may be due to the increase of the absorption and the decrease of energy gap while increase in E_{a1} and E_{a2} with T_a refer to the elimination of some defects from the films as a result of annealing. The effect is shown clearly by the improvement in crystallinity during annealing [Yamamoto, 2000].

3.2 Hall Effect

The type of charge carriers, concentration (n_H) and Hall mobility (μ_H), have been estimated from Hall measurements. Table (2) illustrates the main parameters estimated from Hall effect measurements for ZrO_2:CuO thin films deposited at room temperatures and annealing at 373K and 473K with different CuO content (0,5,8 and 10)% .

The Hall coefficients R_H were determined from the average measured values of the Hall voltage V_H in V using the well-known equation (6).The obtained values of R_H for the deposited ZrO_2:CuO thin films and those annealed

at different annealing temperatures, indicated that all samples are p–type (i.e, the conduction is dominated by holes) and R_H decreases with increasing CuO contents and increases by increasing of annealing temperature.

The variation of carriers concentration (n_H) and Hall mobility (μ_H) with CuO content and annealing temperature of ZrO_2:CuO thin films is shown in Table (3). It is clear that the carrier's concentrations n_H increase and Hall mobility decreases with the increase of CuO content while n_H decreases and μ_H increases with increasing annealing temperature. The complete data of R_H , μ_H and n_H with T_a for all value of CuO content are tabulated in Table (3). Increases the density of charge carriers is essentially because increasing of the lowering the potential barrier. While the decreasing of mobility is come from the inverse relation between μ_H and n_H . Also, the explanation of increasing in μ_H with T_a is due to reduction of the scattering of the carrier from the surface as well as due to the elimination of the defects in the films the increase in crystallite size that decreasing the number of grain boundaries. The decrease in μ_H with the increasing of CuO content, the interpretation of this decrease is attributed to the increase in the localized state near band edge and also increase in carrier concentration then the effect of barriers scattering is predominate, this leads to decrease in μ_H.

From the Hall mobility measurements, we can calculate the drift velocity (υ_d), carrier life time (τ) and free mean path (l) from the results were listed in Table (4). It's found that these parameters are decreased with increasing of T_a but increased with increasing of CuO and the reason for this increment is the same which mentions previously.

Conclusions

The Morphology surface analysis by AFM measurements shows that increasing of the annealing temperature causes a decrease in the surface roughness on opposite with doping percentage. D.C conductivity measurements for all films showed that there are two mechanisms and thus two activate energies E_{a2}, E_{a1}. Hall measurements show that all the films are p-type. Hall mobility decreases with increasing of CuO content while n_H decreases and μ_H increases with increasing of annealing temperature.

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