Morphology and electrical properties of $Cu_X Zn_{1-X}O$ thin films prepared by PLD technique

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Abstract

$Cu_X Zn_{1-X}O$ films with different x content have been prepared by pulse laser deposition technique at room temperatures (RT) and different annealing temperatures (373 and 473) K. The effect of x content of Cu (0, 0.2, 0.4, 0.6, 0.8) wt.% on morphology and electrical properties of $Cu_XZn_{1-X}O$ thin films have been studied. AFM measurements showed that the average grain size values for $Cu_XZn_{1-x}O$ thin films at RT and different annealing temperatures (373, 473) K decreases, while the average Roughness values increase with increasing x content. The D.C conductivity for all films increases as the x content increase and decreases with increasing the annealing temperatures. Hall measurements showed that there are two types of conductance (n- type and p-type charge carriers). Also the variation of drift velocity (v_d), carrier life time (τ), and free mean path (l) with different x content and annealing temperatures were measured.

Key words

$Cu_XZn_{1-X}O$ thin films, Morphological properties, electrical properties, PLD technique.

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الخصائص التركيبية و الكهربائية للاغشية الرقيقة $Cu_X Zn_{1-X}O$ المحضرة بتقنية (PLD)

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الخلاصة

تم تحضير اغشية $Cu_X Zn_{1-X}O$ لنسب مختلفة من المحتوى x بدرجة حرارة الغرفة و بدرجات التلدين المختلفة (373 و473) كلفن. بتقنية الترسيب بالليزر النبضي. وقد تم دراسة تأثير نسب مختلفة من المحتوى x (0, 0.2, 0.4, 0.6, 0.8) على الخصائص التركيبية والكهربائية للاغشية $Cu_XZn_{1-X}O$. قياسات AFM اظهرت ان حجم الحبيبة للاغشية $Cu_XZn_{1-x}O$ عند درجة حرارة الغرفة و درجات التلدين المختلفة (373, 473) كلفن تقل بينما قيم معدل الخشونة تزداد بزيادة المحتوى x. التوصيلية الكهربائية للاغشية اظهرت ان هناك نوعين من حاملات الشحنة (n- type) و (p- type) كذلك تم حساب التركيز للحاملات و سرعة الانجراف (v_d) و زمن عمر الحاملات (τ) و معدل المسار الحر(l) لنسب المحتوى x المختلفة و درجات التلدين المختلفة.

Introduction

Zinc oxide (ZnO), which is one of the most important binary II-VI semiconductor compounds, has a hexagonal wurtzite structure and a natural n-type electrical conductivity with a direct energy wide band gap of 3.37 eV at room temperature and a large exciton binding energy (approximately 60 meV) [1].

The electrical conductivity of ZnO is mainly due to a zinc excess at interstitial sites. Its electrical properties can be modified by thermal treatment in different atmospheres such as hydrogen and nitrogen [2,3]. Zinc oxide (ZnO) is an important multifunctional material with applications such as varistors, gas sensors, transparent electrodes, catalysts etc. The various applications of ZnO are due to the specific chemical, surface and microstructural properties of this material. Copper Oxide (CuO) is a non toxic semiconductor that has a direct band gap of 2.17eV, which is ideal for use in multi junction cells or for photo-electrolysis of water [4] Copper Oxide is intrinsically a p-type semiconductor predominately due to copper vacancies, There are different methods to prepare $Cu_xZn_{1-x}O$ Thin films such as chemical method such as spray pyrolysis[5], chemical vapor deposition [6], Sol-gel [7] and physical method such as thermal evaporation[8], RF magnetron sputtering [9], Atomic layer deposition[10], pulse laser deposition (PLD). Among these, we will focus on PLD technique in this paper, In PLD method, it is very important to control the plume dynamics in order to obtain thin films or nano crystals with high quality [10]. PLD involves the stages of target heating, melting, evaporation, ionization, re-solidification/re-crystallization and condensation [11,12]. This technique was first used by Smith and Turner [13] in 1965 for the preparation of semiconductors and dielectric thin films and was established due to the work of Dijkkamp and coworkers [14] on high-temperature superconductors in 1987, this deposition technique has been intensively used for all kinds of oxides, nitrides, or carbides, and also for preparing metallic systems and even polymers or fullerenes. In this study, thin $Cu_xZn_{1-x}O$ films by Pulse laser deposition technique have been prepared and the effects of x content and annealing temperatures on the morphology and electrical properties have been studied.

Expermintal Part

Pure zinc oxide (ZnO) and copper oxide supplied with purity 99.5%, and 98% respectively, were used as start materials to prepare $Cu_xZn_{1-x}O$ films by pulsed laser deposition technique at different x content (0, 0.2, 0.4, 0.6, and 0.8) using Nd:YAG laser with λ=1064 nm, average frequency 6 Hz and puls duration 15 ns, these materials were mixed in gate mortar for one hour. After that, the mixture was pressed at 5 Ton to form a target with 2.5 cm diameter and 0.4 cm thickness. Finally, the targets were sintering at temperature 873K to ensure the homogenous of the materials. The target must be as dense and homogenous as possible to ensure perfect quality of the deposit. Glass substrates were used to deposit the films by laser ablation. Morphology of the thin films were determined by AFM with a (Digital Intruments, CSPM-AA3000). The electrical measurements include D.C conductivity and Hall effect for $Cu_X Zn_{1-X}O$ films with different x content. The electrical resistance has been measured as a function of temperature for $Cu_XZn_{1-X}O$ films in the range 293 – 473K. The measurements have been done using sensitive digital electrometer type Keithley 616 and electrical oven. Also Hall Effect has been done by Van der Pauw (Ecopia HMS-3000) Hall measurement Systems.

Results and discussion

Atomic Force Microscope (AFM)

AFM parameters (average size diameter, average roughness and Peak-Peak) of $Cu_xZn_{1-x}O$ films for different x contents (x= 0, 0.2, 0.4, 0.6 and 0.8) deposited on glass substrates have been determined using AFM analysis. Fig.1 shows 3D AFM images for $Cu_xZn_{1-x}O$ thin films at different x content at RT and annealed at different annealing temperatures. In general, It is observed that the grains uniformly distributed with homogenous structure. The AFM images also show that a good quality film over a large region can be grown by pulsed laser deposition technique. Also it is observed from Table 1 that average grain size diameter values for all samples decrease with increasing of x content and this is attributed to increasing of nanocrystaalline by increasing Cu content. In general, the average Roughness values increase with increasing x content. These results confirm with other researchers[15,16].

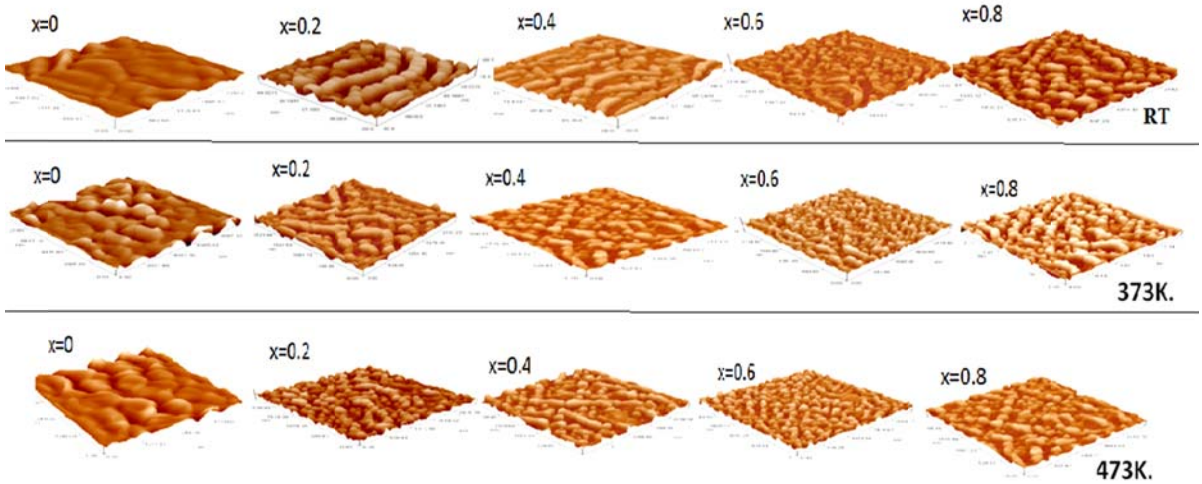

Fig. 1: AFM images for $Cu_xZn_{1-x}O$ with different x content at RT, 373K and 473K.

Table 1: Average grain size, average roughness and peak- peak for films with different x content at RT and (373 - 473) K.

T_s (K)	x	Ave. grain size (nm)	Ave. Roughness (nm)	Peak- Peak (nm)
R.T	0	350.16	0.478	5.16
	0.2	187.75	10.2	38.6
	0.4	103.28	1.83	10.3
	0.6	88.25	2.69	15.1
	0.8	108.98	5.76	28.7
373	0	644.4	2.84	28.7
	0.2	190.21	3.11	32.5
	0.4	96.45	4.51	38.3
	0.6	83.93	2.29	12.1
	0.8	98.43	7.4	40.9
473	0	230.12	1.46	17.5
	0.2	197.81	2.17	10.7
	0.4	102.53	2.7	13.1
	0.6	82.38	2.81	13.6
	0.8	99.33	4.33	23.8

Electrical properties

In order to study conductivity mechanisms, Fig.2 shows the plots of lnσ versus $10^3/T$ for $Cu_X Zn_{1-X}O$ films deposited at R.T and different annealing temperatures (373 and 473)K and different x content (0, 0.2, 0.4,0.6, and 0.8) in the range (302-473)K. From d.c measurements It is noticed that the conductivity ($\sigma_{d.c}$) increases with increasing of x content. Also from the same figures and Table 2, it is observed that the conductivity ($\sigma_{d.c}$) decreases with increasing T_a, and this attributed to rearrangement that may occur during annealing at temperatures higher than substrate temperatures which produce an irreversible process in the conductivity ($\sigma_{d.c}$) [17]. Also, Fig.2 shows that all films have two activation energies E_{a2} and E_{a1}. The conduction mechanism of the activation energy (E_{a2}) occurs at the higher temperatures range (443-473) K, while the activation energy (E_{a1}) occurs at the lower range of temperatures 303-433 K. The effect of x content and annealing temperature on both activation energies E_{a1} and E_{a2} for $Cu_XZn_{1-X}O$ films is cleared. It is observed that the activation energies decrease with increasing of x content but increase with increasing of annealing temperatures. The decrease in the activation energy is due to creation of defect states, resulting in an increase of the electron density in the conduction band and this leads to reduce in the energy requires to transport the carriers from Fermi level to the conduction band [18, 19].

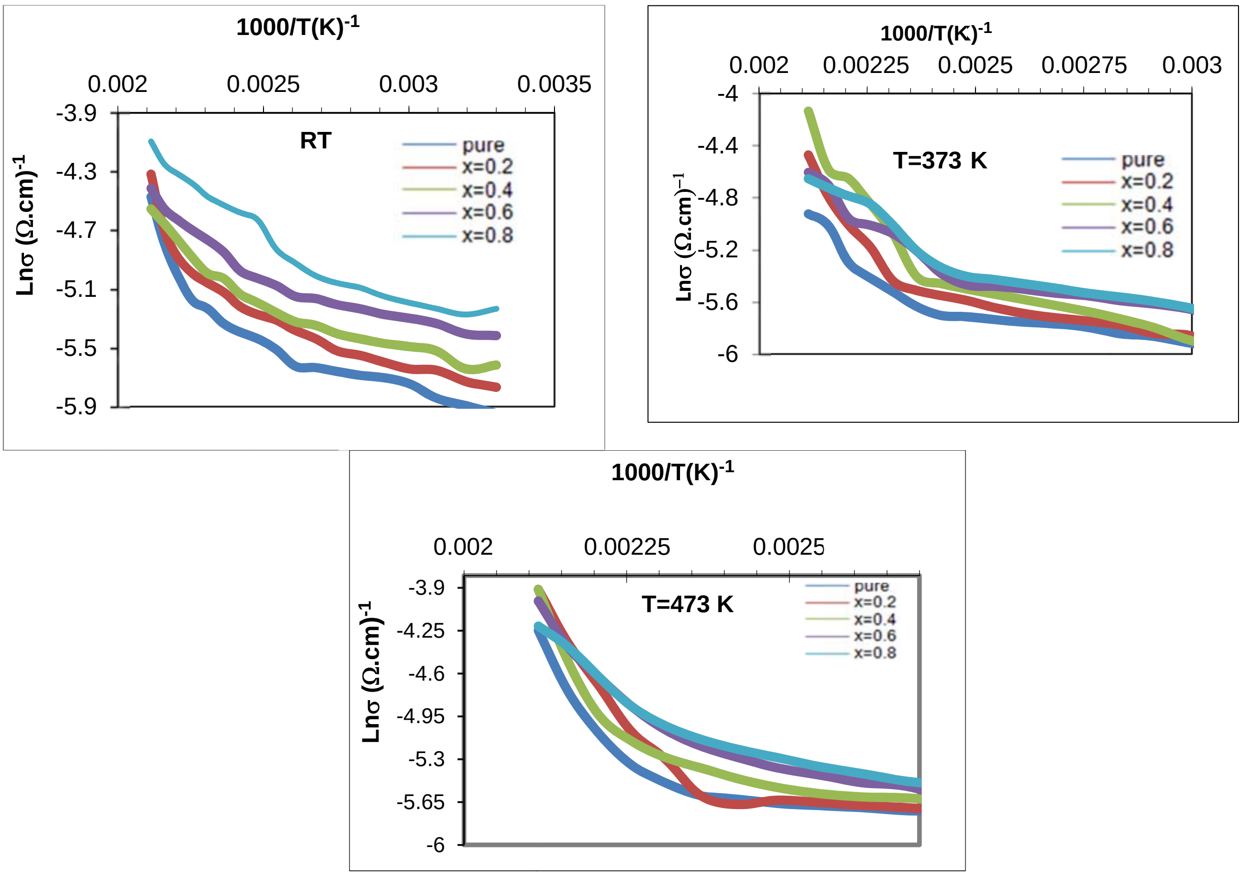

Fig. 2: Ln σd.c versus 1000/T for $Cu_XZn_{1-X}O$ films at different x content and annealing temperatures.

Table 2 shows that the activation energy E_{a1} at RT decreases from 0.056 to 0.040eV with increasing of x content from (0 to 0.8). Also the activation energy E_{a2} decreases from (0.42 to 0.12) eV with increasing of x content from (0 to 0.8), also, the similar behaviour will be appears for annealed films (373 and 473) K.

Table 2: D.C. conductivity parameters for $Cu_x Zn_{1-x}O$ films at different x content and annealing temperatures.

T_a (K)	x content	$\sigma_{d.cR.T}$X10^{-5} $(\Omega.cm)^{-1}$	E_{a1} (eV)	Temp. Range (K)	E_{a2} (eV)	Temp. Range (K)
RT	pure	2.61	0.056	303-433	0.42	443-473
	0.2	3.12	0.055	303-423	0.31	433-473
	0.4	3.63	0.050	303-423	0.20	433-473
	0.6	4.44	0.041	303-413	0.14	423-473
	0.8	5.33	0.040	303-383	0.12	393-473
373	pure	1.69	0.061	303-383	0.59	393-473
	0.2	2.06	0.059	303-423	0.4	433-473
	0.4	2.45	0.056	303-403	0.36	413-473
	0.6	2.72	0.046	303-393	0.20	403-473
	0.8	3.10	0.043	303-383	0.17	393-473
473	pure	1.78	0.064	303-443	0.60	443-473
	0.2	2.02	0.062	303-403	0.51	413-473
	0.4	2.26	0.059	303-403	0.40	413-473
	0.6	2.64	0.051	303-393	0.35	403-473
	0.8	3.07	0.048	303-413	0. 33	423-473

Figs.3a, b, c, d and e show (n_H) for $Cu_XZn_{1-X}O$ thin films at different x content and different annealing temperatures. The $Cu_XZn_{1-X}O$ films have a negative Hall coefficient (n-type) at (x=0-0.4), and then it changes to (p-type) conductivity at (x=0.6-0.8) for all annealing temperatures as shown in Table 3. This is attributed to that Cu is trivalent, then the conductivity change to p-type with increasing cu content. The carriers concentrations were increase with increasing x content. This may be due to increasing of the trapping centres which increases the number of charge carriers and then decreases their mobility. Also, we notice that the carriers concentration decreases with increasing of annealing temperatures as shown in Fig. 3a, while the Hall mobility increases with increasing of annealing temperatures as shown in Fig. 3b. It is clear that drift velocity, life time and mean free path approximately decrease with increasing of x content and increases with increase of annealing temperatures as shown in Fig. 3c ,d ,e and Table 3.

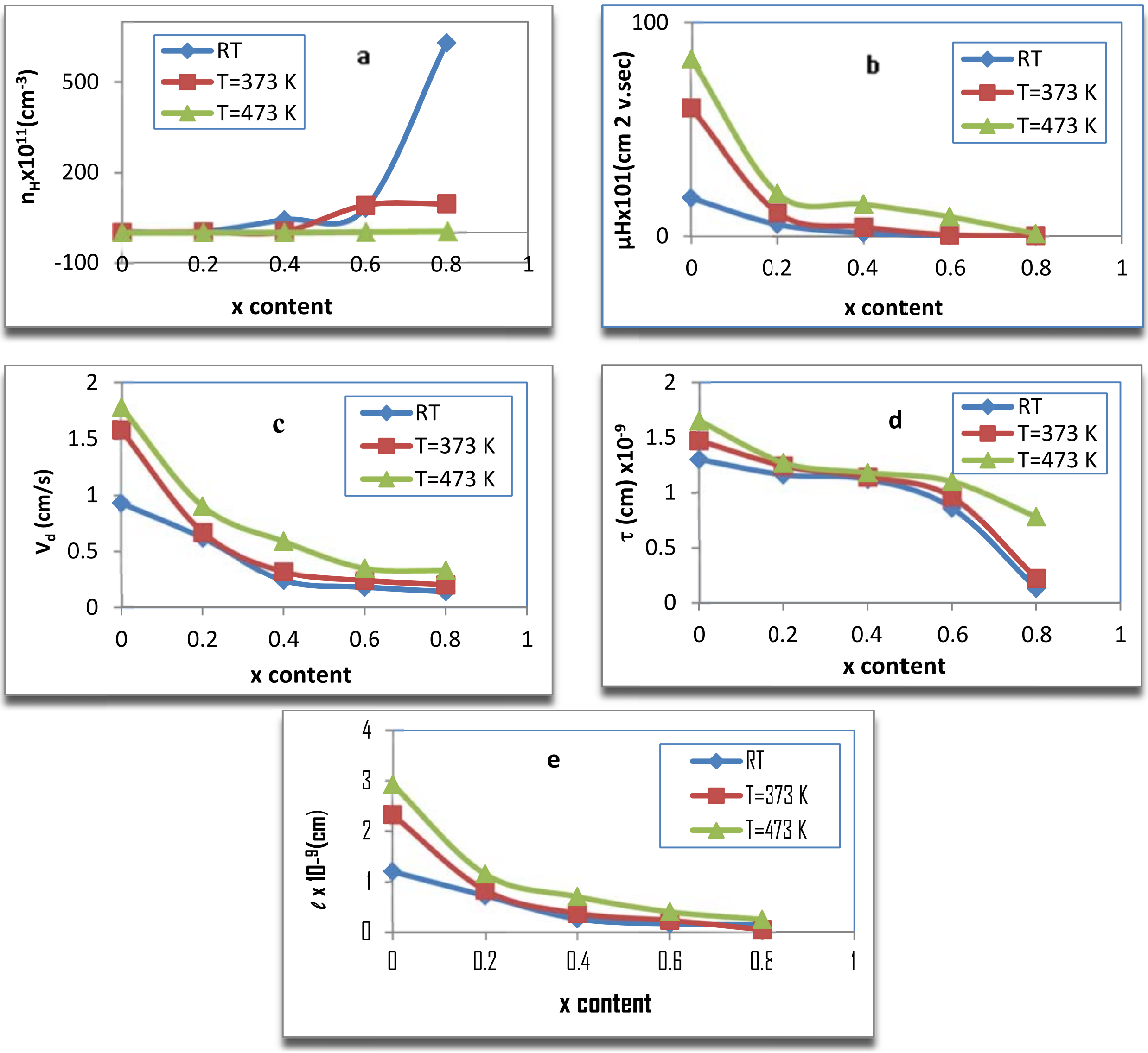

Fig. 3: Hall parameters of $Cu_X Zn_{1-X} O$ thin films a-concentration (n_H) b –Hall mobility(μ_H) c-drift velocity (V_d) d- Lifetime (τ) e-mean free path (ℓ)

Table 3: Hall parameters for $Cu_xZn_{1-x}O$ films at different x content and annealing temperatures.

T_s (K)	x	$n_H\times10^{11}$ (cm^{-3})	$\mu_H\times10^{1}$ (cm^2/V.sec)	V_d (cm/s)	τ(s)$\times10^{-9}$	l × 10^{-9} (cm)	type of conduct.
273	0	2	18	0.93	1.30	1.20	n-type
	0.2	3	5.5	0.62	1.16	0.72	n-type
	0.4	41.9	1.5	0.24	1.12	0.26	n-type
	0.6	80	0.24	0.18	0.86	0.16	p-type
	0.8	630	0.093	0.14	0.13	0.14	p-type
373	0	0.13	60	1.58	1.47	2.33	n-type
	0.2	2.1	11	0.67	1.24	0.83	n-type
	0.4	3.5	4.3	0.32	1.14	0.37	p-type
	0.6	90	0.55	0.24	0.96	0.23	p-type
	0.8	95	0.15	0.20	0.22	0.045	p-type
473	0	0.01	83	0.03	1.65	2.93	n-type
	0.2	0.02	20	0.34	1.27	1.15	n-type
	0.4	0.25	15	2.4	1.18	0.70	n-type
	0.6	1.9	9.1	0.35	1.10	0.4	p-type
	0.8	4	1.1	0.33	0.78	0.25	p-type

Conclusions

$Cu_X Zn_{1-X}O$ thin films have been prepared successfully on glass substrate by pulsed laser deposition technique at RT and different annealing temperatures (373 and 473)K. AFM measurements showed that the average grain size values decrease with increasing x content. While the average Roughness values increase with increasing x content.

From the electrical properties, the D.C conductivity is increasing with increasing x content and decreases with increasing annealing temperatures. Hall measurements showed that there are two types of carrier change from n- type to p-type with increasing x content. Also the carrier concentration increases with increasing x content and decreases with increasing annealing temperatures, whereas mobility, drift velocity, carrier life time, and free mean path decrease with increasing x content and increases with increase of annealing temperatures.

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