Effect of additive of CuO and annealing on the Morphological and Electrical Properties of TiO_2 by pulse laser deposition

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Dr. Sabah N. Mazhir,
Collage of Science for woman ,University of Baghdad/ Baghdad
Dr.Ghosoun Hamid Ahmed
Collage of Science,University of Baghdad/ Baghdad
Noha. H. Harb
Collage of Science for woman ,University of Baghdad/ Baghdad
Emial: nohaharb2009@yahoo.com
Dr.A.Abdallah.A
Collage of Science for woman ,University of Baghdad/ Baghdad

Abstract

In this paper, Nano crystalline TiO_2 and CuO additive TiO_2 thin films were successfully deposited on suitably cleaned glass substrate at constant room temperature, and different concentration of CuO (0,5,10,15,20)% wt using pulse laser deposition(PLD) technique at a constant deposition parameter such as : (pulse Nd:YAG laser with λ=1064 nm, constant energy 800 mJ ,with repetition rate 6 Hz and No. of pulse (500).The films were annealed at different annealing temperatures 423K and 523 K. Effect of annealing on the morphological and electrical were studied. Surface morphology of the thin films has been studied by using atomic force microscopes (AFM). AFM measurements confirmed that the films have good crystalline and homogeneous surface. The Root Mean Square (RMS) values of thin films surface roughness are increased with the increase of annealing temperature. Also, The grain size increases with the increasing of concentration of CuO and annealing. The temperature dependence of the electrical conductivity and the activation energy at temperature ranging from (293-473)K of the as-deposited and films annealed at different annealing temperatures have been studied. The results show that as the film concentration of CuO and conductivity increases, while the activation energy(Ea_1,Ea_2) decreases. Both, the annealing and composition effects on Hall constant, R_H, charge carrier concentration (N_H), Hall mobility. Hall Effect are studied. Hall Effect measurements show that all films have n- type charge carriers and the concentration and annealing increases carriers concentration while the mobility decreases .

Keywords: TiO_2, pulse laser deposition technique, Morphology, Electrical properties.

تأثير التراكيز و التلدين على دراسة طبوغرافية السطح و الخواص الكهربائية لأغشية التيتانيوم المطعمة بأوكسيد النحاس النانوية ذات التركيب النانوية المحضرة بتقنية ترسيب الليزر النبضي PLD

الخلاصة:-

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

في هذا البحث, رسيب مادة (TiO_2) المطعمة بمادة (CuO) على ارضيات زجاجية منظفة بشكل مناسب بدرجة حرارة الغرفة وبتراكيز مختلفة من مادة wt% (0,0.5,0.1,0.15,0.2) CuO بطريقة تقنية ترسيب الليزر النبضي (PLD) باستخدام ليزر النيدميوم ياك النبضي بمعلمات ترسيب ثابته وهي الطول الموجي 1064nm عند طاقة ثابتة 800m ,معدل تكرار 6Hz وكان عدد النبضات المستخدمة (500) وقد لدنت بدرجات حرارة مختلفةK (423K , 523).تم استقصاء تأثير التلدين على طبوغرافية السطح و الخصائص الكهربائية. تم دراسة طبوغرافية السطح باستخدام مجهر القوى الذرية (AFM). اكدت مقاييسَ (AFM) بأنّ الأفلامَ لَها سطحُ بلّوريُ متجانسُ جيدُ وان قيم (RMS) للأغشية الرقيقة والخشونة تزداد بزيادةِ درجةِ حرارة. وأيضاً زيادة حجمَ الحبوبَ بزيَاْدَة تركيزِ CuO والتلدين. كما درست تأثير درجة الحرارة للأفلام المترسبة بدرجات حرارة مختلفة على التوصيلِ الكهربائيِ وطاقةِ التنشيطَ والتي كان مداها k(293-473).وكانت النتيجة زيادة التوصيلية الكهربائية وقلت طاقة التنشيط مع زيادة تراكيز مادةCuo ودرجات الحرارة .و درست تأثيرات التركيبَ والتَلْدين على ثابت هول ، R_H ،تركيز ناقلات الشحنة (N_H)و التحركية . وقد تبين كُلّ الأفلام لها حاملات شحنة من النوع السالب n وبزيادة التركيز و التلدينات تزداد حاملات الشحنة بينما تَنْقصُ قابليةَ الحركة.

الكلمات المرشدة: ثنائي اوكسيد التيتانيوم ،تقنية الترسيب بالليزر النبضي ،الطبوغرافية ،الخصائص الكهربائية.

INTRODUCTION

Nano materials are now become available and useful in all the man daily life applications such as in: medicine, solar cells, water purification, pharmaceutical and catalysts [1].

TiO_2 is a multifunctional material with remarkable chemical, electronic, and optical properties. TiO_2 membranes have been extensively studied because of their potential for application as antireflective and protective coatings for optical elements [2], filters [3] photo catalyst [4], dielectrics in thin-film capacitors, and solar cells[5]. Crystalline (TiO_2) occurs in three different structures: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [6] . The anatase phase is especially adequate for those applications due to its crystal structure and its higher band gap of 3.2 eV compared to the 3 eV in rutile [7] .

Copper (II) oxide has application as a p-and n-type semiconductor, because it has a narrow band gap of 1.2 eV [8]. It is an abrasive used to polish optical equipment, produce dry cell batteries, wet cell batteries as the cathode, etc. [9]. It has been widely used for growing oxide films because of the simplest and low cost method needed to grow oxide films, also it allows for stoichiometry of the synthesized material. PLD technique was successfully applied for growing quality Tio_2:Cuo thin films. In this paper, the effect of the concentration and thermal annealing on the structure and electrical properties of TiO_2:CuO thin film deposited by (PLD) technique is studied. The (PLD) pulse laser deposition technique was used because of its simplicity and relative cost[10]. In recent years, many studies on the co-doping effect of transition metal and non-metal elements have been carried out and have given considerable enhancements on visible light absorption and photocatalytic properties of TiO_2 [11]. simulated the co-doping process of C–Cr and C–Mo. The results showed that the energy band gap of the material decreased depending on the metal and non-metal ion pairs. In the case of co-doping of C–Mo and C–Cr pairs the TiO_2 band gap can be reduced by 0.9 and 1.2 eV, respectively. Many experimental studies on the modified TiO_2 by co-doping C, Mo and Bo have also been carried out and reported [12].

Experimental

TiO_2: CuO nanoparticles growth

During this work pulse laser deposition (PLD) is used to prepare TiO_2:CuO nanoparticle's. Using the Nd: YAG Laser for the deposition , the targets were ablated with a laser of wavelength λ= 1064nm and no. of shot (500) at a repetition rate of 6 Hz and energy pulse 800mJ and TiO_2(99.99%) and CuO(99.999%) targets were pressed under 5 ton to prepared the pellet which were sintered to temperature 973K for 1hour.The distance between the target and the substrate was set to 10 cm. Thermal annealing at 423K and 523 K under vacuum of 3×10^{-3} m Torr The annealing vacuum oven were utilized for an one hour to anneal the thin film using glass slides substrate of 3 x 2 cm^2 area. The glass slides were cleaned with dilated water using ultrasonic process for 15 minute to deposit the films. Also work mask is a piece of aluminum foil having (width: 2mm, distance between electrodes 2mm) with the same size of the substrate.

These masks are put on glass substrates to deposit the aluminum using (Tungsten W) boat material by using vacuum thermal evaporation technique of type (Balzers-BAE370) under pressure (10^{-5} mbar). Various shapes of masks were used to determine electrical properties as shown in fig (1). The effect of annealing temperatures and concentration on morphological the electrical properties such as Dc conductivity and Hall measurements were studied for TiO_2:CuO thin films.

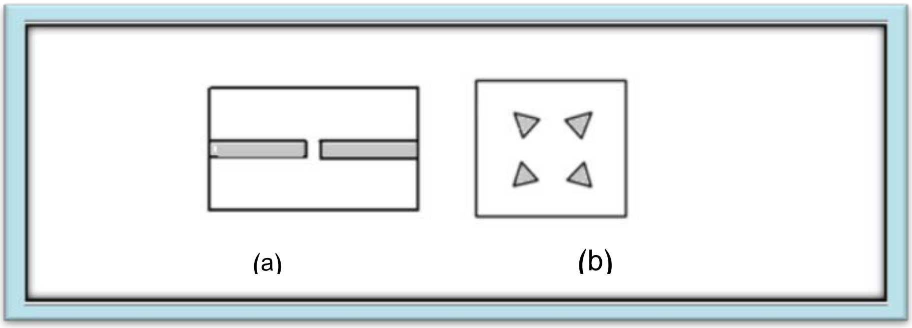


Figure (1) Masks of different shapes and purposes. (a) D.C conductivity electrodes. (b) Hall effect electrodes.

Theoretical calculation

The D. C conductivity in crystalline semiconductors depends on the presence of free electrons and free positive holes. The conductivity (σ) of TiO_2 samples are obtained via using equation[13] :

$$\sigma=q(n\mu_n+p\mu_p) \quad ....(1)$$

results obtained from Hall effect which indicate that the pure TiO_2 and TO_2:Cuo thin films were (n-type), The hall coefficient (R_H) is determined by measuring the Hall voltage that generates the Hall field across the sample of thickness (t), by[14]:

$$R_H=(V_H/I)(t/B) \quad ....(2)$$

where I is the current in A passing through the sample, t is the thickness of the film in cm and B is the magnetic field strength
The n_H and R_H was calculated by using the the relation[15].

nH=(-1\qR) for electron ….(3)

Hall's mobility (μ_H) can be written in the form[16]
$\mu_H=\sigma/n.q$ …… (4)
Where q is the charge of electron and μ_H is Hall mobility measured with (cm^2/V.s)

Results and discussion

atomic force microscopy (AFM)

Figure (2,3 and 4) shows the AFM images for TiO_2:CuO thin films deposited on glass substrate at RT and different annealing temperatures 423K and 523 K, with thickness 250 ± nm. Average grain size ,surface roughness, Root mean square values were listed in Table (1). From the topographic images, The RMS roughness increased with increasing annealing temperatures, and the average grain size increases with increasing of T_a and concentrations, This improvement occurs because after the annealing process. The increase in roughness is due to the existing of larger grain size of nanostructured of TiO_2:CuO thin film,also the film species at high temperatures have enough kinetic energy to collide strongly with each other and simultaneously re-evaporate because of the low melting point of CuO compared to the temperature of the PLD plume.

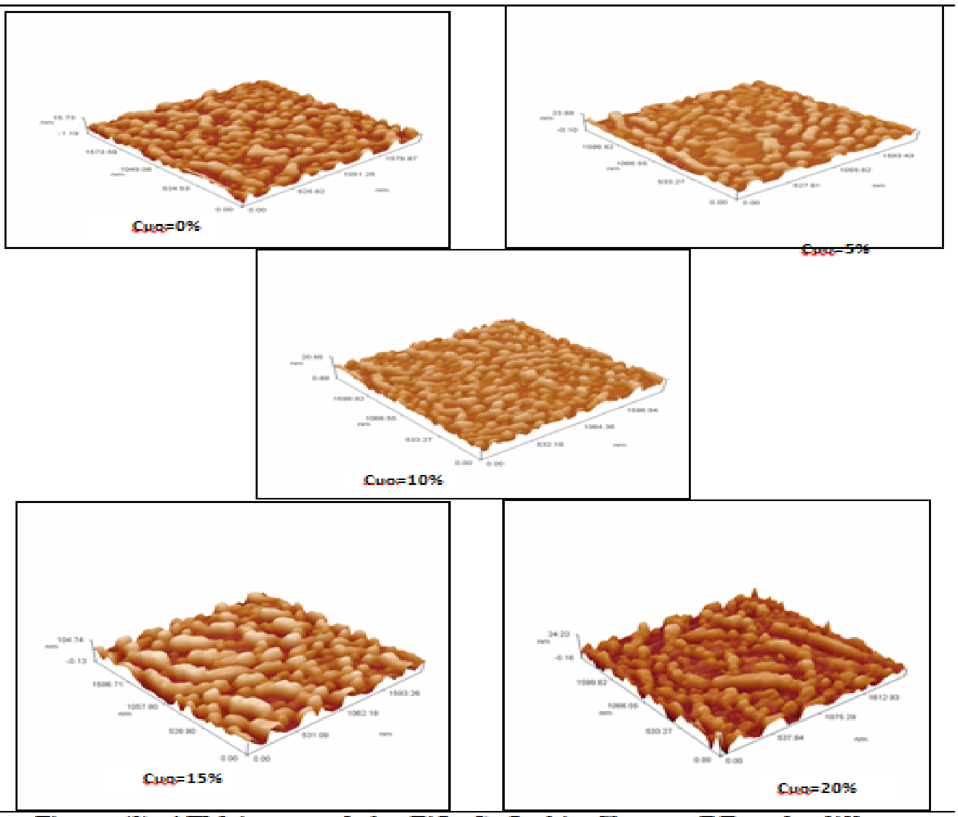


Figure (2) AFM images of the TiO_2:CuO thin film at RT and different concentration

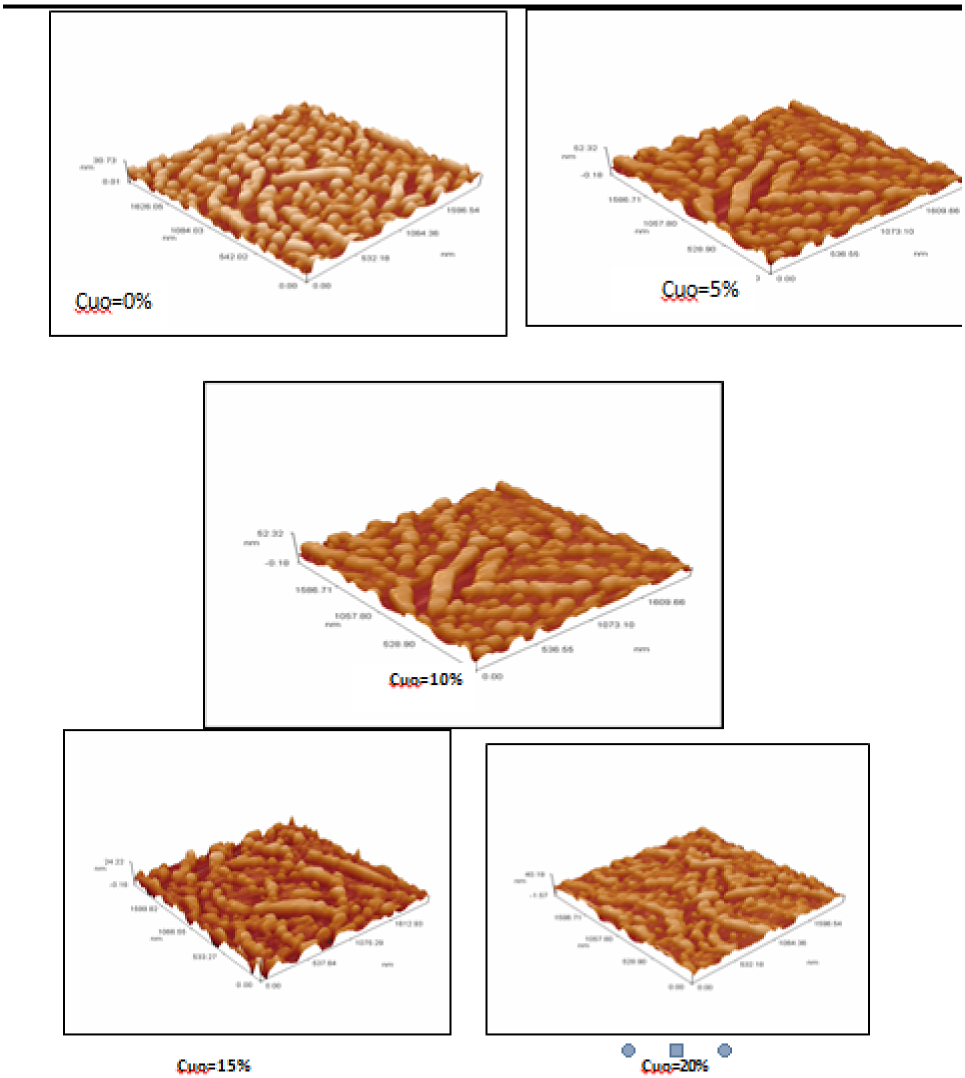


Figure (3) AFM images of the TiO2:CuO thin film at 423k and different concentration

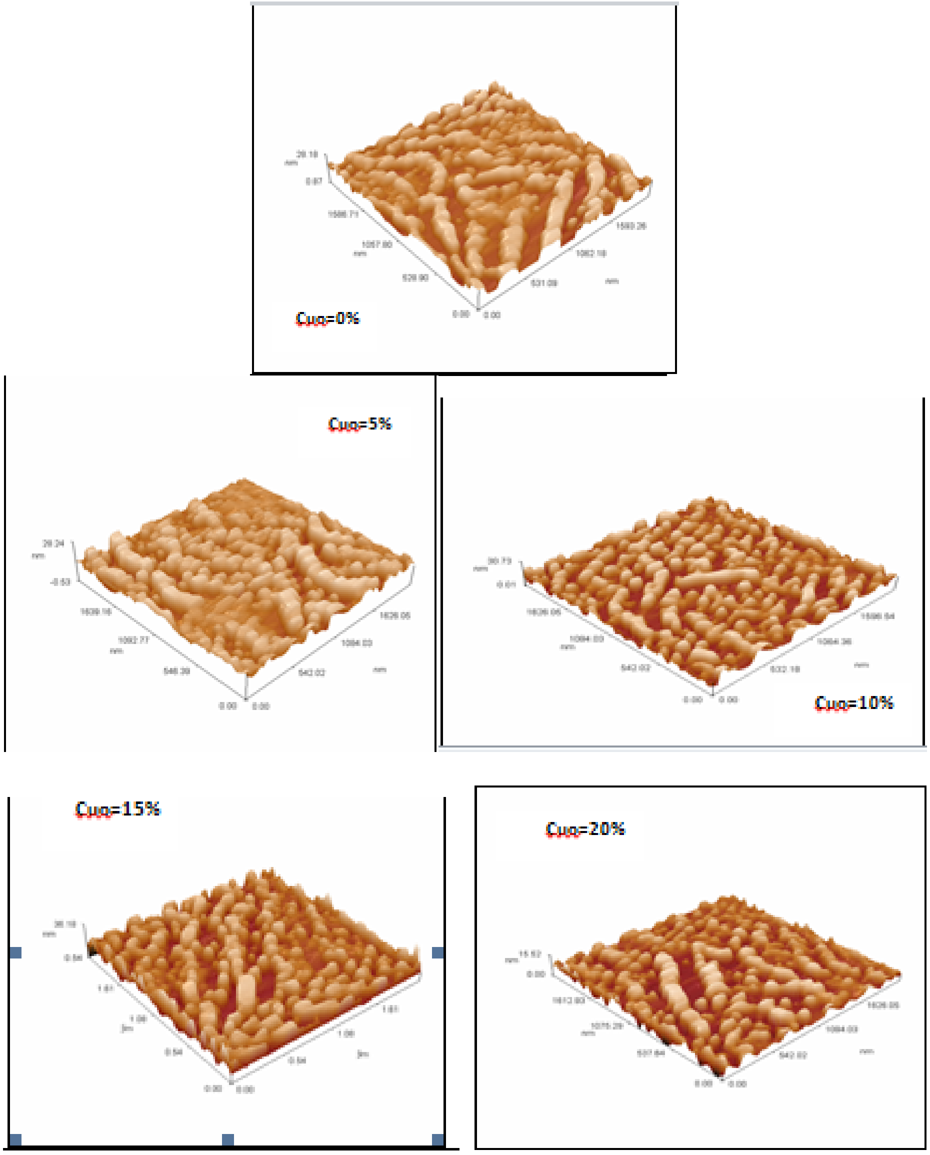


Figure (4) AFM images of the TiO_2:CuO thin film at 523k and different concentration

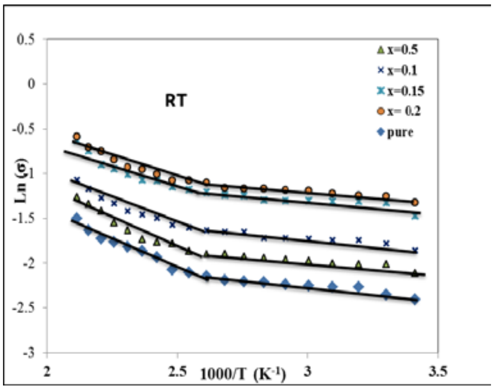
Table(1)AFM parameters of TiO_2:CuO thin film.

Cu0% Wt	Annealing	Roughness (nm)	Rotmean square (nm)	Average grain size (nm)
0	RT	3.76	4.46	85.42
	423k	4.42	5.05	93
	523k	16.7	19.3	96.22
5	RT	2.15	2.46	88.78
	423k	2.21	2.61	98.98
	523k	2.65	3.16	99.79
10	RT	1.95	1.7	90.72
	423k	2.77	3.33	93.97
	523k	10.6	12.2	95.76
15	RT	2.21	1.91	94.06
	423k	2.21	2.61	95.77
	523k	2.31	2.82	98.22
20	RT	2.85	3.3	92.98
	423k	4.89	5.61	98.77
	523k	4.99	5.64	98.81

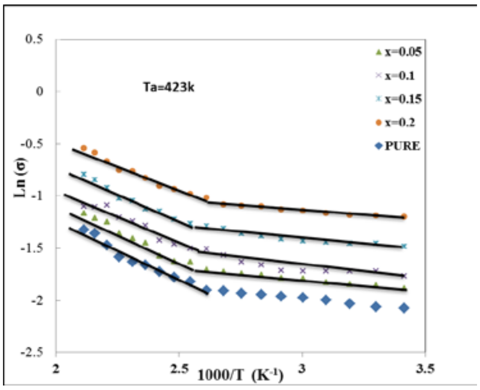
DC Conductivity

Figure's (5 - a,b and c) shows the variation of d.c. conductivity for pure and doped TiO_2 with different CuO concentration at the average thickness (250) nm. There are two stages of d.c conductivity mechanism throughout the temperature range (293-473K).The first activation energy (E_{a1}) occurs at higher temperature (293-373K) due to conduction of the carrier excited into the extended states beyond the mobility edge and the second activation energy(E_{a2}) occurs at low temperature (373-473K) due to the carriers transport to localized states near the valence and conduction bands. Whereas the values of E_{a1} and E_{a2} decrease with the increasing of content of CuO% as in Table (2) and figure (6) and figure (7) but with slight change at all annealing temperature, we conclude the increasing in CuO content leads to decrease in activation energy leading to saturate the dangling bonds, i.e. there is reduction in the density of state which occurs at Fermi level which caused to the transfer from conductivity near Fermi level to the thermal activation conductivity at band gap .

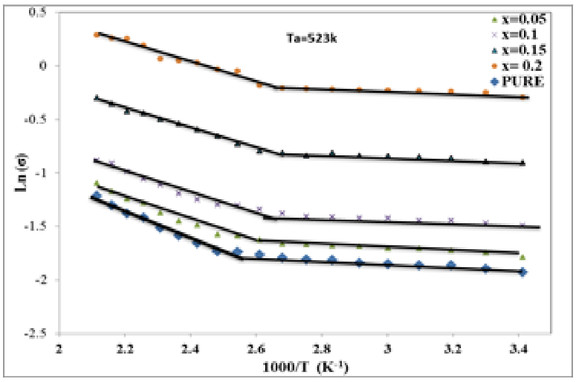
Figure (8)show that the conductivity increases with increasing the temperature, It this may be due to the reason where after annealing process, the good crystallinity and nanostructure surface area obtained after the annealing and it promises much surface for electron passes through from one grain to another grain within the TiO_2:CuO thin film. Table (2) demonstrates that as the film concentration of CuO and conductivity increases, while the activation energy(E_{a1},E_{a2}) decreases .This increases in the conductivity can be attributed to the increase in the density of charge carriers due to the decrease of energy gap values .



(a)



(b)



(c)

Figure (5-a,b and c) Variation of Ln(σ) with reciprocal temperatures for TiO_2:CuO thin films at (300,423,523)k with at different Cuo dopant ratio(o,5,10,15,20)wt% .

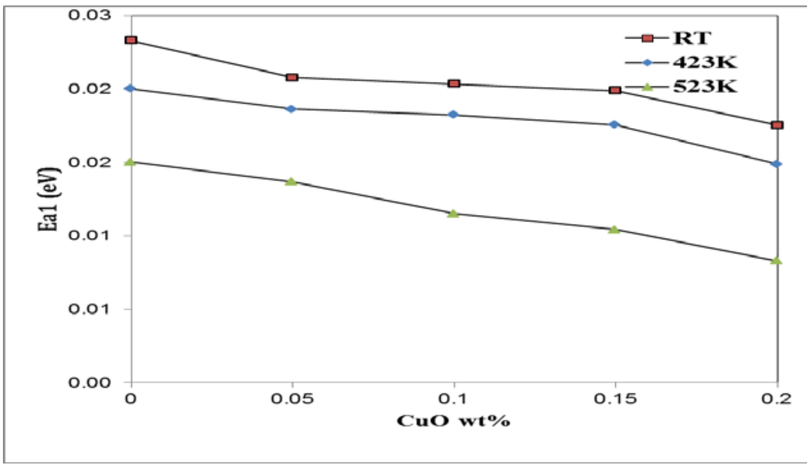


Figure (6) Variation of DC activation energies E_{a1} with CuO dopant ratio TiO_2 films with different annealing temperature.

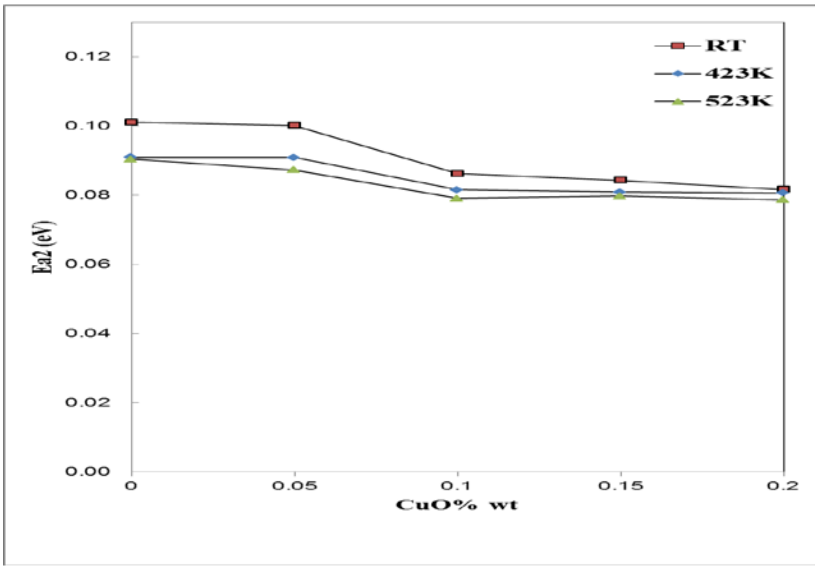


Figure (7) Variation of DC activation energies E_{a2} with CuO dopant ratio TiO_2 films with different annealing temperature.

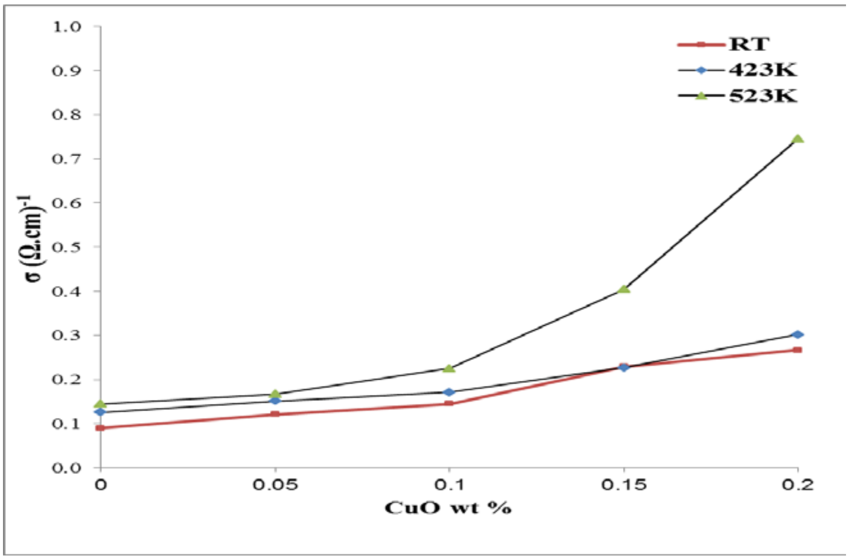


Figure (8) Variation of DC Conductivity at room temperature with CuO dopant ratio TiO_2 films and different annealing temperature.

Table (2): D.C conductivity parameters for TiO_2:CuO thin films at different concentration of CuO doped and different annealing temperature

T_a (K)	Cuo% wt	$\sigma_{d.cR.T} X10^{-5}$ $(\Omega.cm)^{-1}$	E_{a1} (eV)	E_{a2} (eV)
RT	0	9.01E-02	0.0233	0.1011
	5	1.21E-01	0.0208	0.1001
	10	1.45E-01	0.0203	0.0862
	15	2.29E-01	0.0199	0.0843
	20	2.67E-01	0.0175	0.0817
423	0	1.26E-01	0.0200	0.0910
	5	1.52E-01	0.0186	0.0909
	10	1.71E-01	0.0182	0.0816
	15	2.27E-01	0.0176	0.0809
	20	3.02E-01	0.0149	0.0807
523	0	1.45E-01	0.0143	0.0904
	5	1.67E-01	0.0137	0.0873
	10	2.25E-01	0.0115	0.0790
	15	4.04E-01	0.0104	0.0798
	20	7.45E-01	0.0083	0.0786

Hall Effect

From the Hall Effect measurements, the resistivity (ρ), charge carrier concentration (N_H) and carrier Hall mobility (μ_H) values were calculated and is given in table (3). .Figure (9) observed that the carries concentration decreases with increase of annealing temperature due to improving the crystallite size, and the recrystallization occurring due this treatment leads to a growth of the main crystallite size. It is also figure(10) found that the mobility decreased sharply with the increasing concentration of CuO due to increase the carriers concentration. This is typical of many polycrystalline thin films and is due to the existence of potential barriers in the grain boundaries.

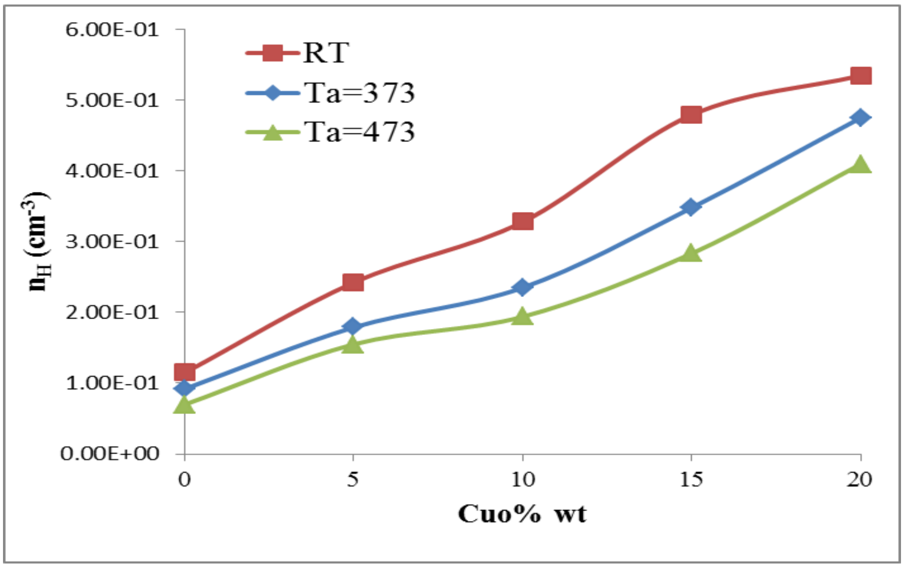


Figure (9) Variation of carrier concentration (n) with dopant ration for different annealing temperature.

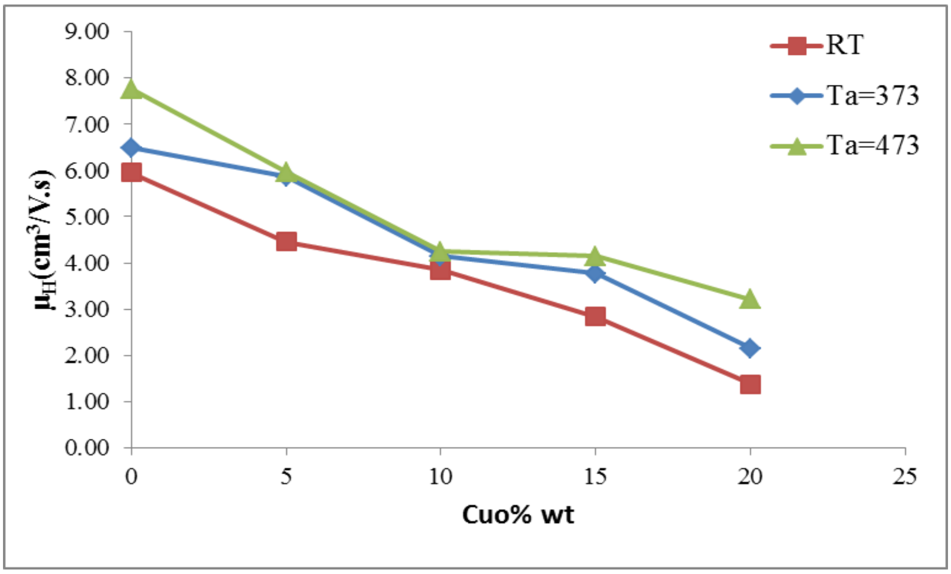


Figure (10)Variation of mobility (μ_H) with dopant ration for different annealing temperature.

Table (3) Hall measurement of Tio_2:Cuo thin films prepared at different Cuo dopant ration and different annealing temperature.

T_a (K)	Cuo%	ρ (Ω.cm)*10^{-6}	n_H $(cm^{-3})*10^{10}$	μ_H $(cm^2.V^{-1}.s^{-1})$ *103	RH *10^9	type
RT	0	1.496	0.115	5.956	5.601	n
	5	1.660	0.2423	4.454	2.579	n
	10	2.320	0.468	3.851	1.335	n
	15	2.428	0.4792	2.839	1.304	n
	20	3.431	0.5346	1.377	1.169	n
423	0	1.642	0.092	6.491	6.786	n
	5	1.942	0.179	5.863	3.481	n
	10	2.421	0.225	4.151	2.771	n
	15	2.640	0.468	3.769	1.334	n
	20	3.701	0.475	2.148	1.317	n
523	0	1.945	0.08	7.754	7.185	n
	5	2.126	0.175	5.96	3.569	n
	10	2.732	0.194	4.251	3.22	n
	15	3.511	0.2833	4.15	2.206	n
	20	4.161	0.4095	3.213	1.526	n

Conclusion

Nanoparticles of TiO_2:CuO were grown by PLD technique from the synthesize pellete at different concentration of CuO at substrate temperature (300,423,523)k. The morphology, roughness and grain size were investigated by atomic force microscopy (AFM). The result obtained of AFM showed the average grain size less than100nm, The RMS roughness also increased with increasing annealing temperatures. The electrical conductivity and Hall effect were measured for films with average thickness (250) nm. The analysis of the d.c. conductivity There are two stages of d.c conductivity mechanism throughout the temperature range (293-473K) decreases while conductivity increases with concentration of Cuo and annealing . also from Hall Effect measurements show that all films have n- type charge carriers and the concentration and annealing increases carriers concentration while the mobility decreases .

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