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Influence of concentration on the structural, optical and electrical properties of TiO_2: CuO thin film Fabricate by PLD

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***Abstract**: In this work, Titanium oxide thin films doped with different concentration of CuO (0,5,10, 15,20) %wt were prepared by pulse laser deposition(PLD) technique on glass substrates at room temperature with constant deposition parameter such as : pulse (Nd:YAG), laser with λ=1064 nm, constant energy 800 mJ , repetition rate 6 Hz and No. of pulse (500). The structure , optical and electrical properties were studied . The results of X-ray diffraction(XRD) confirmed that the film grown by this technique have good crystalline tetragonal mixed anatase and rutile phase structure, The preferred orientation was along (110) direction for Rutile phase. The optical properties of the films were studied by UV-VIS spectrum in the range of (360-1100) nm. The optical transmission results show that the maximum transmission over than ~ 48% for pure TiO_2 films and decreases to ~ 30% with increasing the CuO content to 20%wt .The optical energy for pure TiO_2 film was about 3.212eV and decreases to 3.13eVwith increasing of concentration. The results of PL emission at RT shows that there are two peaks positioned around 386 nm and 396 nm for predominated peak and795 nm and 810 for the small peaks. DC measurements show that as the increasing of film concentration lead to increase the conductivity , while the values of activation energy (E_{a1},E_{a2}) decrease. Hall effect measurements show that all films have n- type charge carriers and the carriers concentration increases while the mobility decreases with increasing the CuO content.*

***Keywords:** Titanium oxide, pulse laser deposition technique, optostructural propertied, electrical properties.*

I. Introduction:

After the invention of the first ruby laser, We appreciate that the use of pulsed lasers as a directed energy source for evaporative film growth (now termed PLD).

Smith and Turner utilized a pulsed ruby laser to deposit the first vacuum deposited thin films in 1965 for the preparation of semiconductors [1]. shares some process characteristics common with molecular beam epitaxy and some with sputter deposition[2]. A typical set-up for PLD is schematically shown in Figure(1a) , It consists of a target holder and a substrate holder housed in a vacuum chamber, The idea of (PLD) is simple. A pulsed laser beam is focused onto the surface of a solid target. The strong absorption of the electromagnetic radiation by the solid surface leads to rapid evaporation of the target materials. The evaporated materials consist of highly excited and ionized species. They presented themselves as a glowing plasma plume immediately in front of the target surface if the ablation is carried out in vacuum[3]. The pulsed laser deposition (PLD) technique is probably the most versatile method for the fabrication of oxide thin films because of its unique features a high pulse deposition rate and the controllable kinetic energy of the deposited particles. one of the metal oxides, which is Titanium dioxide (TiO_2) that has a white solid inorganic substance and which thermally stable, a cheap, non-flammable, poorly soluble, and not classified as hazardous, also TiO_2 occurs naturally in several kinds of rock and mineral sands. Titanium is the ninth most common element in the earth's crust [4]. Crystalline (TiO_2) occurs in three different structures: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [5,6]. Copper (II) oxide or cupric oxide (CuO) is the higher oxide of copper. As a mineral, it is known as tenorite. It is a black solid with an ionic structure, which melts above 1200 °C with some loss of oxygen. Copper forms two well-known stable oxides, which are cupric oxide (CuO) and cuprous oxide (Cu_2O) ,These two oxides have different physical properties, colors, crystal structures and optical properties [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].

II. Experimental

2.1TiO2:CuO nanoparticles growth

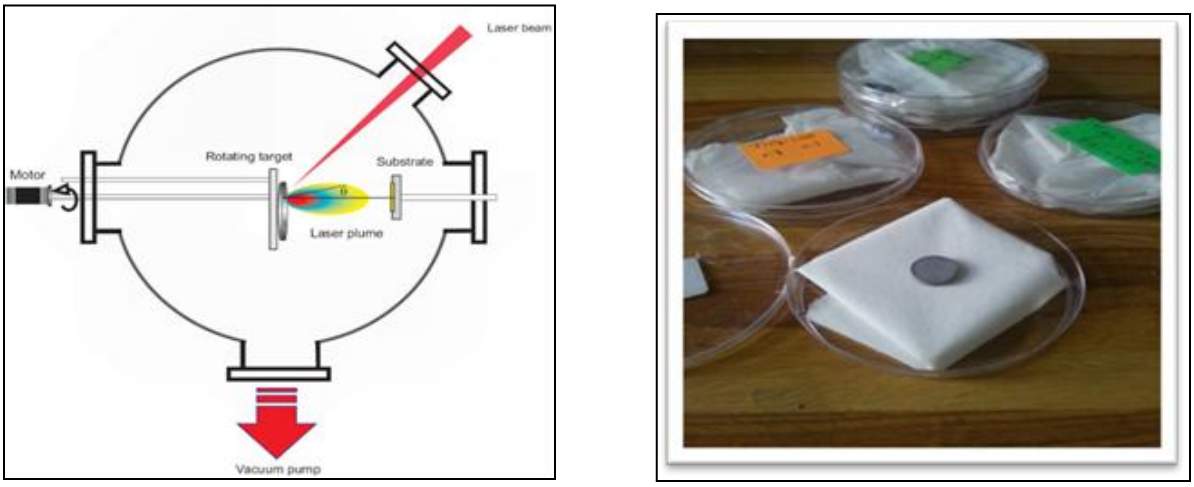
Thin films of approximately (5,10,15,20) at. % CuO-TiO_2 thin films, were deposit on glass substrate by pulsed laser deposition (PLD) technique using Nd:YAG laser operating at 1064 nm and constant parameter such as : constant energy 800 mJ, repetition rate 6 Hz and No. of pulse (500) on glass .The set up of our PLD system was illustrated in Fig.(1a) . The doped TiO_2 with CuO target was prepared from high purity TiO_2 (99.999%)-and CuO(99.999%).The powders were mixed together for 1 hour using agate mortar then press into disk with

(1.5)cm in diameter and(3)cm thick using hydraulic type (SPE CAC) as shown in Fig (1 b) under pressure of 5 Ton. Finally the pellets were sintered in air at Temperature (873) K for 1 hour .The glass slides substrate of 3 x 2 cm^2 area were cleaned with dilated water using ultrasonic process for 15 minute to deposit the films. Also ,a mask was prepared from a piece of aluminum foil having width: 2mm and distance between electrodes 2mm) with the same size of the substrate. These masks are put on glass substrates to deposit the electrodes of aluminum using Tungsten (W) boat material using vacuum thermal evaporation technique of type (Balzers-BAE370) under pressure (10^{-5} mbar).

2.2Characterization

The crystalline structure of TiO_2 thin films was determined by using > θ−2θ scans were recorded using Cu Kα radiation of wavelength of 1.5405 Å from 20^o to 60^o with a step size of 0.05.the optical properties were measured using UV-VIS spectrometer in the range (200-1100)nm .Photoluminescence emission spectra were recorded on a type fluorescence spectrophotometer over a wavelength range of 3600–900 nm.

The DC conductivity was measured over the range of temperature from 293k to 473k using sensitive digital electrometer type keithley (616). The Hall coefficient (RH) is determined using four probe technique.



(a) **(b)**

Fig (1) (a) Schematic of PLD [10],(b) palette of TiO_2:CuO

III. Results and discussion

Fig(2) shows the X-ray diffraction patterns of TiO_2:CuO thin film prepared at RT with different concentration of CuO (0,5,10,15and 20)%. It is clear from this figure that the preferred orientation was along (110) direction for Rutile phase. The XRD data of thin films coincides with that of the known tetragonal. Also, it was noticed that the peaks intensities increase with increasing of the doping ratio from 5 to 20%.

The value of crystallite size and the experiment and the standard peaks from International Centre for Diffraction Data(ICDD) for anatase and Rutile TiO_2 was listed in table (1). The average crystallite size D measured in direction perpendicular to the surface of the specimen is calculated using the Debye- Scherer formula [11].

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad \text{……………………………………………………} (1)$$

Where D is the mean crystallite size, λ is the X-ray wavelength in nanometer (nm), θ is the degree of the diffraction peak, and β is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians and K is a constant related to crystallite shape, normally taken as 0.9.

It is cleared from the tables (1) that d_{hkl} and grain size increases with increasing of CuO content This implies that Cu partially substituted for Ti in TiO_2 structure. However, copper may exist in the sample with a quantity so low that the x-ray shoulder around 800 nm in the case of the sample doped by Cu with a concentration of 5 at% that attributed to the absorption concerned with the transitions between states created by doping Cu in TiO_2,This result is in agreement with the result of N. Tai Ly, et al. [12].

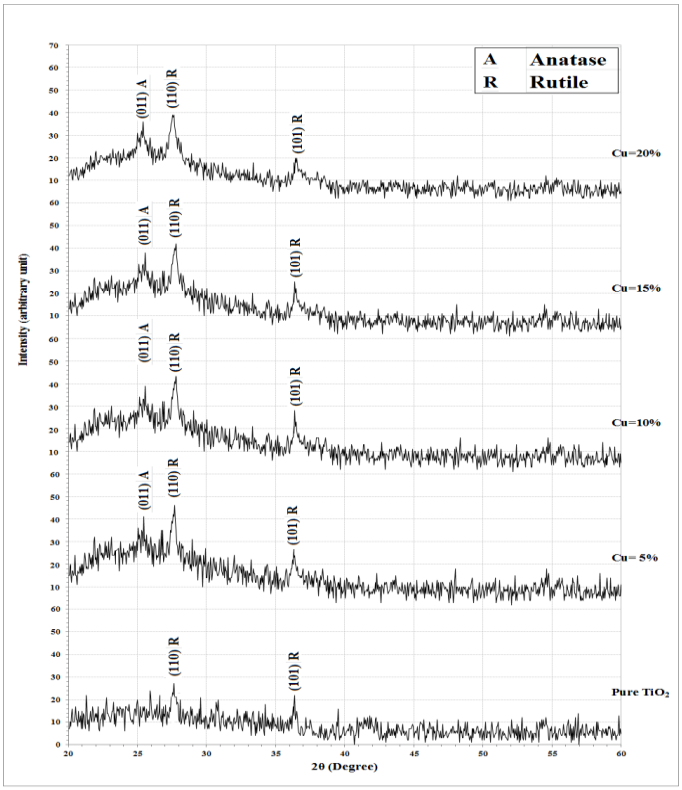


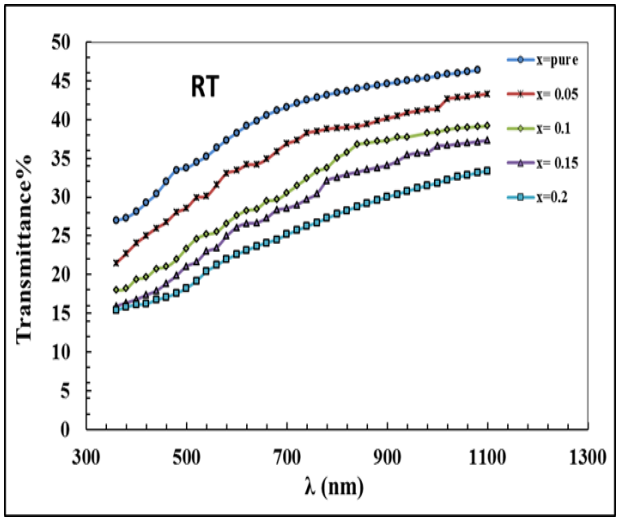
Fig. (2) X-ray diffraction patterns of as deposited TiO_2 films at 423K with different CuO doping ratio (0, 5, 10, 15 and20) % wt

Table (4-1) The obtained result of the XRD for TiO_2:CuO at RT

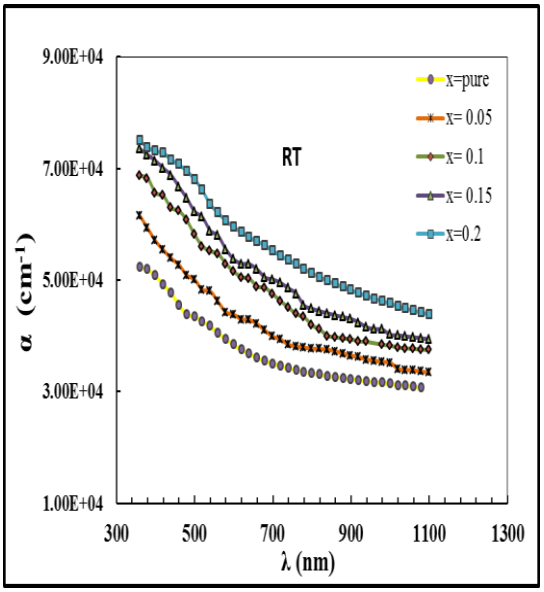
Cu %	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std. (Å)	Hkl	Phase	card No.
0	27.7255	1.0673	3.2150	7.7	3.2483	(110)	Rutile	96-900-9084
	36.3659	0.9657	2.4685	8.7	2.4871	(101)	Rutile	96-900-9084
5	25.3367	0.9149	3.5124	8.9	3.5372	(011)	Anatase	96-900-8217
	27.5222	0.7624	3.2383	10.7	3.2483	(110)	Rutile	96-900-9084
	36.3151	0.8207	2.4718	10.2	2.4871	(101)	Rutile	96-900-9084
10	25.4892	0.7116	3.4918	11.4	3.5372	(011)	Anatase	96-900-8217
	27.7255	0.6607	3.2150	12.4	3.2483	(110)	Rutile	96-900-9084
	36.3659	0.7116	2.4685	11.8	2.4871	(101)	Rutile	96-900-9084
15	25.5400	0.5591	3.4849	14.6	3.5372	(011)	Anatase	96-900-8217
	27.7764	0.5743	3.2092	14.2	3.2483	(110)	Rutile	96-900-9084
	36.3659	0.6607	2.4685	12.7	2.4871	(101)	Rutile	96-900-9084
20	25.3875	0.5091	3.5055	16.0	3.5372	(011)	Anatase	96-900-8217
	27.6239	0.5191	3.2266	15.8	3.2483	(110)	Rutile	96-900-9084
	36.4168	0.5285	2.4652	15.8	2.4871	(101)	Rutile	96-900-9084

Figures (3) shows the optical transmission spectrum for pure and doped TiO_2 with different concentration of CuO (5,10,15 and 20)wt% prepared at RT. It is clear from this figure that the transmission decreases with increasing of CuO content and this is may be due to the increased in the absorption value due to Cu has substituted Ti inTiO_2 structure and/or incorporated in the form of Cu_xO with TiO2. Figure (3) shows the variation of (α) as a function of wavelength . From this Figures, it can be seen that the absorption coefficient (α) decreases with increasing of wavelength. One can see from these figures that the absorption coefficient of the TiO2:CuO films is characterized by strong absorption at the shorter wavelength region between 300nm -600nm with sharp edge on the long wavelength side from 600nm–1100nm. The absorption coefficient exhibits high values of α ($\alpha > 10^4$) which means that there is a large probability of the allowed direct transition . In general, it can be observed from these figures that the absorption coefficient increases with increasing of CuO content and annealing temperatures.. This can be linked with increase in grain size and it may be attributed to the light scattering effect for its high surface roughness, or also corresponds to the density of absorbing centers such as impurities absorption, excitation transition, and other defects in the crystal lattice dependent on the conditions of sample preparation. From figure (4) It can be observed that the energy gap decreased with increasing of CuO content. This result confirmed an incorporation of TiO_2 with Cu_xO and the overlapping of their energy bands.

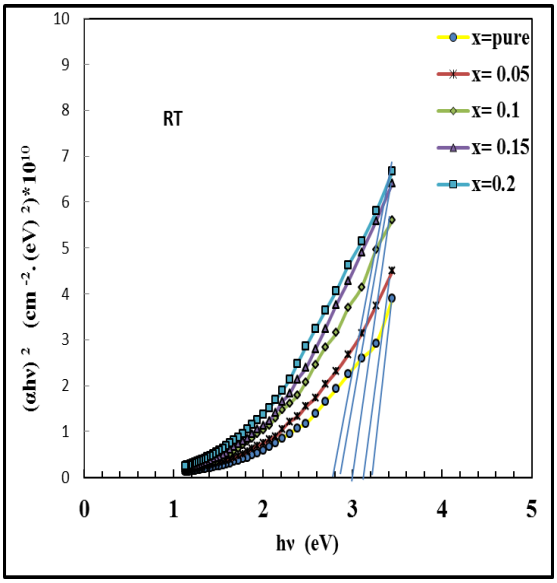
The experimental evidence proved again that Cu has substituted Ti in TiO_2 structure, also annealing process lead to increase levels of localized near valence band and conduction band and these levels ready to receive electrons and generate tails in the optical energy gap and tails is working toward reducing the energy gap, or can be attributed decrease energy gap to the increased size of particles in the films and such variation in the optical band gap has been observed earlier with the results of other workers N. Tai Ly, et al [12].



Figure(3) The variation of transmittance with wavelength for TiO_2:CuO films at RT with different concentration of CuO (0, 5, 10, 15 and20) % wt.



Figure(4) The variation of with absorption coefficient wavelength for Tio_2:Cuo thin films at RT with at different of CuO (0,5,10,15,20) % wt .



Figure(5) The variation of $(\alpha h\nu)^2$ versus photon energy of (hv) for Tio_2:Cuo thin films at RT with at different of CuO (0,5,10,15,20) % wt .

Figure (6) presents the PL measurements for TiO2:CuO deposited at room temperature It can be seen that the samples have a stronger emission peak positioned are around 386 nm and 396 nm for peak 1 and a weaker emission peak at around 795 nm and 810 nm for peak 2. From Figure 6, it is clear that the relative intensity of the emission spectra of TiO2 has the greatest relative intensity, which means that electrons and holes of TiO2 are easy to recombine .The intensity of these two peaks 1 and 2 increases with increasing of concentration of Cuo ,due to the large exaction bending energy of TiO2. Usually for semiconductor Nano crystals, two emission peaks can be observed, the exaction and the trapped luminescence .The exaction emission peak is sharp while the trapped emission peak is broad. The emission bands shown in the spectra can be attributed to band gap emission; the strong band gap emission demonstrates the high crystalline nature of the as-

synthesized particles[13]. That there were shifts between the peaks of all concentration which may be attributed to the difference between band gaps for the content. Table (2) shows the peak values and the intensity of the luminescence spectrum of all samples

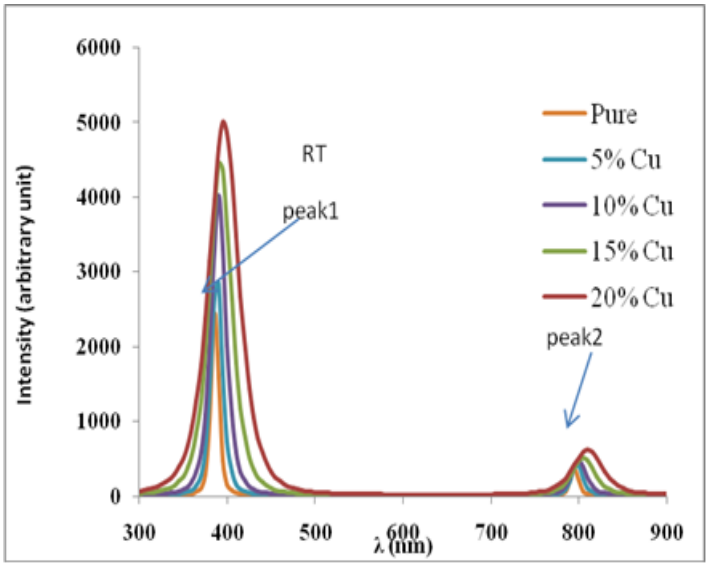


Fig (6): Room temperature photoluminescence spectra of the TiO_2:CuOthin film at different concentration of CuO

Table (2) The obtained result of the Photoluminescence for TiO_2:Cuo thin films

Cu%	Wavelength (1) (nm)	Energy (1) (eV)	Wavelength (2) (nm)	Energy (2) (eV)
pure	386	3.212	795	1.560
5	388	3.196	798	1.554
10	390	3.179	800	1.550
15	392	3.163	805	1.540
20	396	3.131	810	1.531

Figure (7) shows the variation of d.c. conductivity for pure and doped TiO2 films with differeny concentration of CuO. There are two stages of mechanism d.c conductivity throughout the temperature range (293-473K).The first activation energy (Ea1) occurs at higher temperature (373-473)K due to conduction of the carrier excited into the extended states beyond the mobility edge and the second activation energy(Ea2) occurs at low temperature (293-373)K due to the carriers transport to localized states near the valence and conduction bands. From d.c measurement we can see that the conductivity increases with increasing of CuO content, as show in Figure(8) and Figure (9and 10) shows the variation of (Ea1,Ea2) as a function of CuO content .Table (3) demonstrates that as the film concentration increases leads to increase in the conductivity while decreases in the values of activation energy(Ea1,Ea2). We conclude that the excess CuO will act as the donor impurities may occupy shallow donor levels in the film, resulting in the reduction of conduction activation energy .Also ,This increasing in the conductivity can be attributed to the increase in the carrier concentration in the layers .

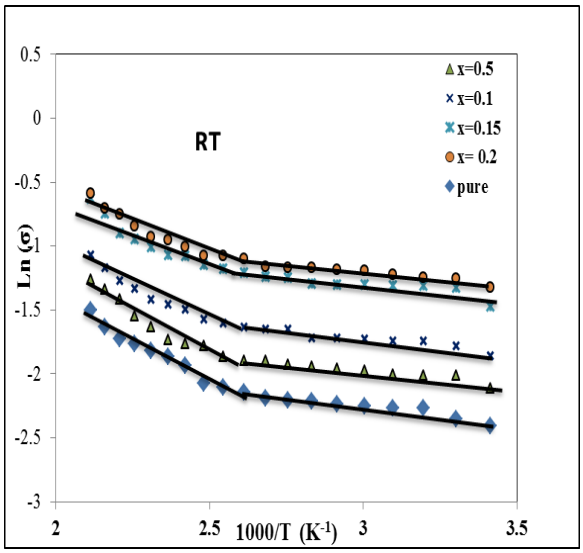
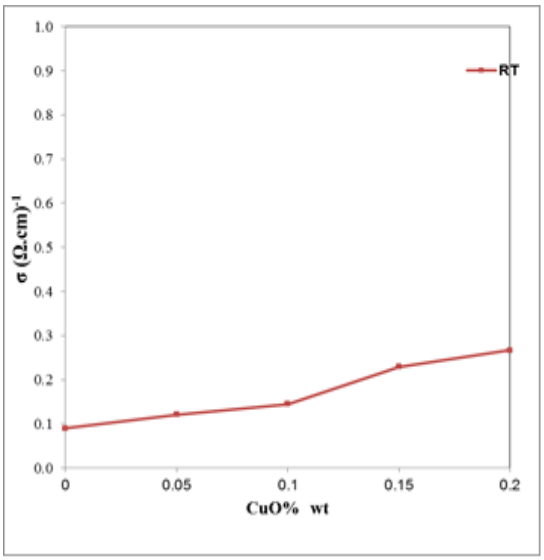
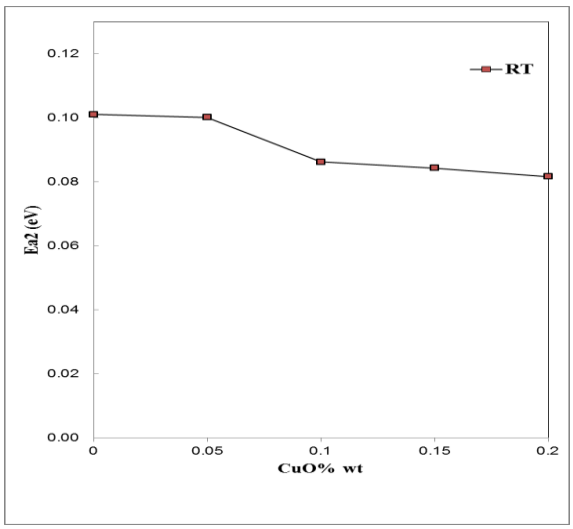


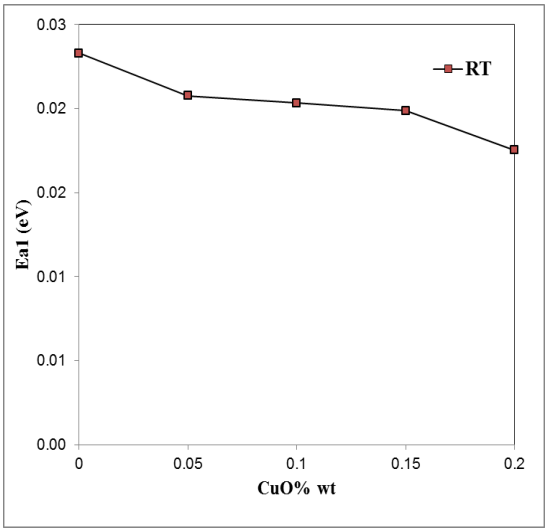
Fig (7) Variation of Ln(σ) with reciprocal temperatures for Tio_2:Cuo thin films at RT with at different concentration of Cuo (o,5,10,15,20) % wt .



Fig(8) Variation of DC Conductivity at RT with CuO for Tio_2:Cuo thin films at RT with at different concentration of Cuo (o,5,10,15,20) % wt .



Fig(9)Variation of E_{a2} at different concentration of Cuo (0,5,10,15,20)%wt



Fig(10)Variation of E_{a1} at different concentration of Cuo (0,5,10,15,20)%wt

Table (3): 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

Hall effect measurement system can actually be used to determine quite a few material parameters, but the primary one is the Hall voltage (V_H). Other important parameters such as carrier mobility, carrier concentration (n), Hall coefficient (R_H), resistivity, magneto resistance(R), the mobility of the majority carrier and the conductivity type (n or p) are all derived from the Hall voltage measurement[14].

The Hall coefficient (R_H) is determined by measuring the Hall voltage generated by the Hall field across the sample of thickness (t), given by[15]:

$$R_H = \frac{V_H}{I}.\frac{t}{B} \quad \text{……(2)}$$

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

Carriers concentration can be determined by using the relation[16]

$$n_H = \frac{-1}{qR_H} \quad \text{…….…. for electrons (3)}$$

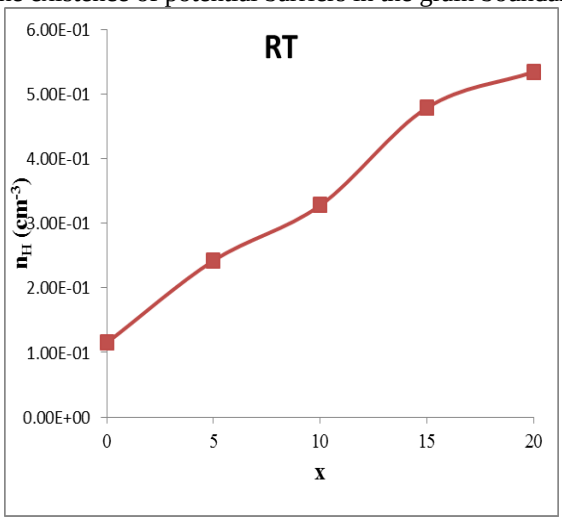
Hall's mobility (μ_H) measured with (cm2/V.s) can be written in the form[17]

$$\mu_H = \frac{\sigma}{n.q} \quad \text{……...(4)}$$

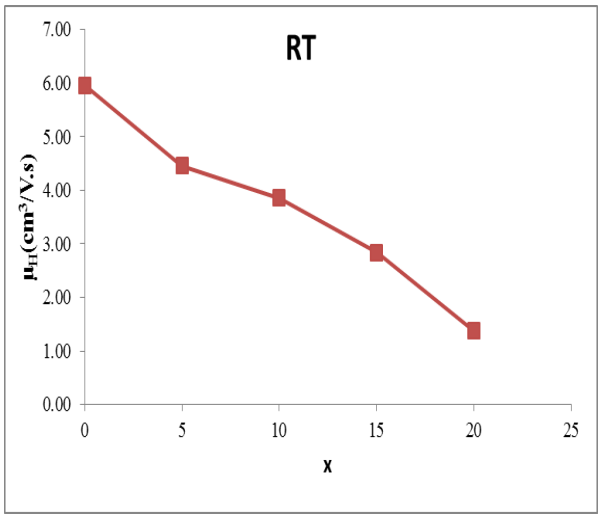
where q is the charge of electron.

From the Hall Effect measurements, the resistivity (ρ), charge carrier concentration (NH) and carrier Hall mobility (μH) values were calculated and is given in table (3) and figure(10 and 11). The results obtained from the Hall effect indicated that the pure doped TiO2 thin films with CuO have negative Hall coefficient (n-type) conductivity i.e Hall voltage decreases with increasing of the current .

It is seen from these figures that the carries concentration increases with increasing of CuO content such behavior is expected as a result of the substitution doping of CuO creating one extra free carrier in the process .As the doping level is increased, more dopant atoms occupy lattice sites of Ti atoms resulting in more charge carriers. Thus, the conductivity increases with increasing of CuO content. In contrast with the Hall mobility, it is decreased sharply with increasing of concentration of CuO The decreasing of mobility is come from the inverse relation between μH and nH This is typical of many polycrystalline thin films and is due to the existence of potential barriers in the grain boundaries.



Figurer(10)Variation of carrier concentration(n_H) with different concentration of CuO (0,5,10,15,20) % wt.



Figurer(11)Variation of mobility (μ_H) with different concentration of CuO (0,5,10,15,20) % wt

Tabel(3) Hall measurement of TiO_2:CuO thin films prepared at different concentration of CuO .

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

IV. Conclusion

Nanoparticles of TiO_2:CuO were grown by PLD technique from the synthesize palate at different concentration of CuO at RT. XRD results Increasing in d_{hkl} and grain size with increasing of CuO content can be attributed that Cu partially substituted for Ti in TiO_2 structure. This work presents a simple and a general strategy to improve the growth of TiO_2 doped Cuo at different concentration of Cuo with a wide optical band gap directly on glass substrates, providing an opportunity to integrate them in optoelectronic devices, e.g. for UV light detection or solar cell applications. 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 . also from Hall Effect measurements show that all films have n- type charge carriers and the concentration increases carriers concentration while the mobility decreases .

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