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ALL OPTICAL INVESTIGATIONS OF COPPER OXIDE FOR DETECTION DEVICES

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A High quality high transparent conductive copper dioxide (Cu_2O) thin film was prepared by reactive pulsed laser deposition method. The prepared samples were analyzed and measured using the UV-visible and the photoluminescence. The Optical properties shows a high transparency reached to about (62 and 66) % and decreases sharply with the decreasing of annealing. Optical band gab of prepared film at optimum condition is about 2.62-2.67 eV. The optical investigations and constant of the energy band gap, the refractive index, and the extinction coefficient were also elaborated.

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1. Introduction

Copper oxides are semiconductors that have been studied for several reasons such as the natural abundance of starting material copper (Cu); [1, 2]. It has a cubic crystal structure with a lattice parameter are a= 4.6837A°, b= 3.4226A°, c= 5.1288Aand this material is suitable for solar cell applications [3, 4]. As a solar cell material, has the advantages of low cost and great availability. It is very attractive as a photovoltaic material because of its high absorption coefficient in visible regions, nontoxicity, abundantly available starting material (Cu) on earth, low cost to produce, and the theoretical energy conversion efficiency being in the order of 20% [5, 6].The easiness of production by Cu oxidation; their non-toxic nature and the reasonably good electrical and optical properties by Cu_2O [7].Copper oxide commonly crystallizes in three forms such as cupric oxide or tenorite, for Cu_2O range from 2.10-2.6 eV, whilst values of 1.3-2.1 eV, for CuO, and 1.4 -2.5 eV energy band gap values for (Cu_4O_3),and all the tenorite and cuprite were p-type semiconductors[8, 9]. Cu_2Ofilms are reported to have high transparency, with a slightly yellowish appearance and absorb usually at wavelengths below 600nm, [10,]

Several methods of deposition techniques have been used to prepare Copper Oxide films, such as the anodic oxidationof copper through a simple electrolysis process [11], the thermal oxidation method [12], thermal vacuum evaporator [13], spraypyrolysis [14], R.f. magnetron sputtering [15], reactive evaporation [16], sol-gel method [17], chemical vapor deposition [18], plasma evaporation [19],thermal evaporation [20], electro deposition [21], pulsed laser deposition [22],dip coating [23], simple electrolysis based oxidation of metals [24], molecular beam epitaxy [25], chemical bath deposited[26] Electrolytic Method [27] activated reactive evaporation [28] reactive and conventional evaporation [29] reactive magnetron sputtering [30] thermal evaporation and electroplating [31]

Copper oxide can be used as a many of applications depend on its properties like, in the fabrication of gas sensing devices because of the conductivity changes induced by the reaction of gases with surface adsorbed oxygen.[32]. It been used as electrode materials for lithium batteries, in lithium primary cells and lithium-copper oxide electrochemical cell [33].

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Thin films can also be used in p-type field effect transistors and CO gas sensors [34]. Photo sensor applications [35], photo thermal application [36]. CuO thin films could be employed in solar cells [37]. High temperature super conducting materials [38, 39].A range of direct optical band gap energies has also been reported for Cu_2O and CuO (3) semiconductor films in the literature, depending on the method of fabrication and stoichiometry photocatalytic activities using LED lamps as cold light sources [40], field emission devices [41], etc.

In this work, we report on the growth and characterizations of the CuO_2 thin films on glass substrates by the reactive PLD method. High purity cupper target and very simble and cheep Nd-Yag Laser tatto removal was used to deposite the CuO_x films. The research continued to study and analyze the effect of Laser fluincy on the growth mechanism of the material and, thereafter, transmission, reflection, bandgap and refractive index are presented and discussed deeply.

2. Experimental

The un doped CuO_2 thin films were deposited on a cleaned slide of glass as a substrate using tattoo removal Nd: YAG laser, Fig. 1 shows the PLD system that will be used to deposit the nanostructure thin films. The pulse duration of the Q-switched Nd: YAG laser is 7 ns (FWHM) with wavelength= 1.064 nm, the laser beam was focused through a lens with a focal length=10 cm spotted on a cooper target (99.999% provided from Fluka com.). The targets spin at a rate of one cycle per minute. The energy density of a pulse laser at the target surface was maintained within the range 500-1000 mJ/cm^2. All prepared thin films were created by 50 laser shots at the temperature of the substrate is 150 C^o. The optical properties such as the transmittance of the prepared films were investigated at spectral range (300–1000) nm using UV-VIS Shimatzu double beam spectrophotometer.

The value of the incident energy of photon was studded as a function of (λ) depending on the formula [42-44]

$$E_g(eV)=1240/\lambda(nm) \tag{1}$$

where λ is wavelength. The energy gaps are dependence on the value of the absorption coefficient (α) and the excitation of the transition could be described depending on the Tauc formulas [45, 46]

$$(\alpha h\nu)=B\ (h\nu-E_g)r \tag{2}$$

where the B is a constant inversely proportional to amorphous, r is a constant = 2, 3, etc… depending on the raw used materials and the type of the optical transition $\alpha h\nu$. If the straight part of the plot of the $(\alpha h\nu)^{1/r}$ against ($h\nu$) is extrapolated to $(\alpha h\nu)^{1/r}$ =0, the intercept gives the energy gap value. The value of the absorption coefficient (α) for all wavelengths was examined by [47, 48]:

$$\alpha=2.303(A/t) \tag{3}$$

where A is absorbance and t is the thickness of nanophotonic films. Equation (4) relates the absorption coefficient (α) with the excitation ratio (K) [49, 50]:

$$K = \alpha\ \lambda / 4\pi \tag{4}$$

All other constants such as refractive index (n), the ε_r and ε_i which they relate to the real and imaginary parts of the dielectric constants, the conductivity (σ) are used to calculated from equation (5) [51, 52]:

$$n = \{[4R / (R-1)]-K^2\}^{1/2} - [(R+1) / (R-1) \tag{5}$$

Note that R represents the reflectance which can be found from (R = 1-T-A), or it can be obtained from equation (6) [53, 54]:

$$n=n_s\left(\frac{1+\sqrt{R}}{1-\sqrt{R}}\right)^{1/2} \quad (6)$$

where n_s denotes to the substrate refractive index. It is an important to mention that the refractive index of the quartz substrate is considered to be 1.51, and the total dielectric constant (ε) is [55, 56]:

Fig.1 The PLD system set-up.

3. Result and discussion

The transmission of the deposited thin film and prepared under different laser energy conditions are present in Fig. (2). In general, a slight decrease in the optical transmission as a function of energy of laser wavelength could be recognized with increasing with laser energy due to the increase in laser ablation efficiency and amount of ablated material. These value of the transmission peaks have as lightly red shift as the laser energy will be increased (increase in particle size), this result agrees with other work [51], implying that the deposited films at the low value of laser energy have a much smaller size. The spectral characteristic of the semiconductor has been shown to vary with the effects of quantization.

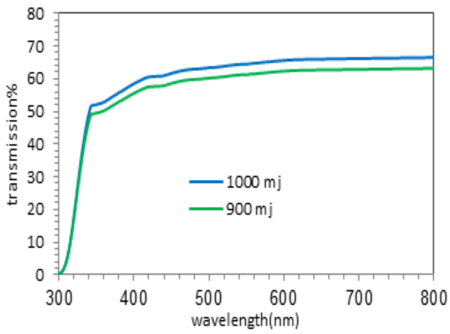

Fig. 2. Optical transmission spectra of Cu2O at two different laser energy.

The values of the energy band gap (ΔE) vary with the radius values of the particles (d).

$$\Delta E = \left(\frac{h}{2me^*}\right)\left(\frac{\pi^2}{d^2}\right) \quad (7)$$

where ΔE (energy shift or optical band gap shift with respects to bulk band gap value (3.35 ev) and d is the size of the particle, h the constant of Planck's and me^* is the electron reduced mass thus with the decrease in the value of the particle size.

Indeed the increase in the laser energy means transfer more of the laser energy and indicate to ablating the larger amount of the raw materials. It was observed that the increase of the energy of the used laser produce the plume of the plasma become denser and could become more intense and this gives an indication that the large particles will be produced due to the two fact, the first fact is due to the longer time of growth and the other fact as a result of the high probability of clustering. The alteration of the $(\alpha h\nu)^2$ value with the values of the photon energy (hν) are present in figure (3), the value of the optical band gap (E_g) of Cu_2O are calculated from the extrapolating of linear part of $(\alpha h\nu)^2$ as a function of photon energy (hν) plot on x-axis. The values of the optical band gap (Eg) are found to be varied from (2.62-2.66) eV with the effect of laser energy.

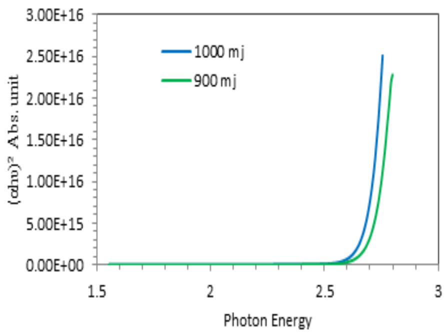

Fig. 3. The optical band gap (E_g) of Cu_2O.

The value of the prepared films reflectance (R %) were testing by using the double-beam UV-vis instrument and presents in Fig. 4, the reflectance spectra of the deposited films as a function of (λ) range of 300-800 nm. It's clearly observed that optical reflection decrease with the increasing of the Laser energy and this increasing as a result due to the fact that when the beam of the light effects on the thin layer of the film the light beam is slightly reflected and then transmitted, depending on the energy of the incident photon, the thickness of the films and the size of the deposit particles since the deposited material consists of the charged particles, the bounds and the loose electrons, and the ionic elements, etc.

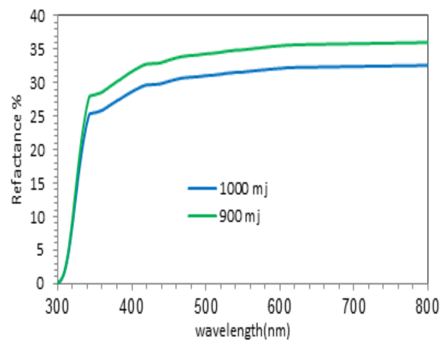

Fig. 4. The reflectance of Cu_2O.

The value of the refractive index was calculated using the transmittance spectrum values in the range of 300-800 nm. There is a tangible change in the refractive index (n) value in the visible range; according to estimates and found to be about 2.3 – 2.37 at 330 nm as present in Fig. 5 and is tabulated in Table 1. The decreasing in the particle size values results in overall causes increasing of the refractive index; this due to the result of increasing the transmission value as the thickness decreases. The value of the (n) changes a bit after 310 nm to 800 nm wavelength. It could be showed that the n decreases with the laser energy, this behavior may be attributed to a decline of the film thickness which resulting in low reflection, the elevated value of the refractive index is good for an optoelectronic device.

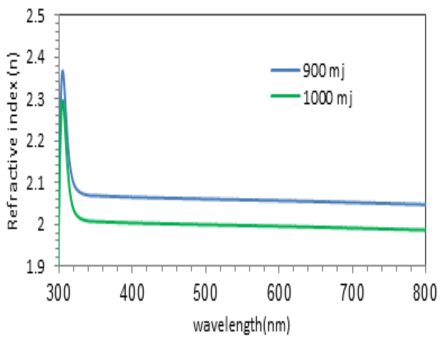

Fig. 5. The refractive index of Cu_2O.

The value of the extinction coefficient K is a very important physical parameter related to microscopic atomic interactions. The extinction coefficient is shown in Fig. 6 as a function of photon energy, has high value at lower Laser energy.

It shows that the extinction coefficient is high in the region of the low energy photon and it will decrease with increasing of the photon energy. The stronger absorbing medium present high extinction coefficient [49]. The loss of the energy of the electromagnetic radiation out of the medium is examined using the extinction coefficient value of a special substance. The value of extinction coefficient is inversely associated with the value of the spectra of the transmittance [50], therefore the low value of T% gives a high value of extinction coefficient.

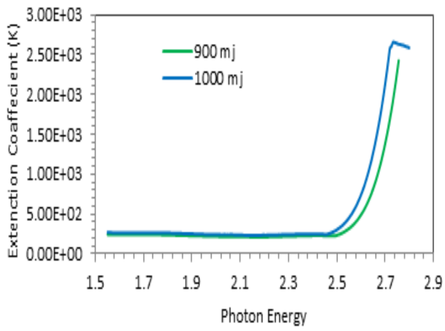

Fig. 6. The extinction coefficient of Cu_2O.

Table 4.1. The energy band gaps, refractive index and optical dielectric constant corresponding to molarity concentration of $LiNbO_3$ nanostructures.

Laser Energy (mj)	E_g measured (eV)	E_g (eV) exp.[a]	*n* measured	*n* exp [b]	*T* %
900	2.62	1.66- 3.6	2.3	1.9-3.5	62.7
1000	2.66		2.37		65.4

4. Conclusion

Cu_2O Films have been deposited using PLD technique. It was found an approximate match between the value of the energy band gap that calculated by UV. The maximum value of the transmission was found to be about 65%. The value of the refractive index showed the highest value of 2.30, while 2.37 that is appropriate for optoelectronic applications.

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