Synthesis, characterization, and optical properties of copper oxide thin films obtained by spray pyrolysis deposition

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Abstract

Copper oxide thin films were synthesized by using spray pyrolysis deposition technique, in the temperature around 400°C in atmosphere from alcoholic solutions. Copper (II) chloride as precursor and glass as a substrate. The textural and structural properties of the films were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD). The average particle size determined from the AFM images ranged from 30 to 90 nm and the roughness average was equal to 9.3 nm. The XRD patterns revealed the formation of a polycrystalline hexagonal CuO. The absorption and transmission spectrum, band gap, film thickness was investigated. The films were tested as an optical limiter. The experiments were performed using Q-switched Nd:YAG laser at 532nm and 1064 nm at different intensities. Copper oxide thin films appear to be attractive candidates for optical limiting application and sensor application.

Key words
Copper oxide, AFM, spray pyrolysis deposition.

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تحضير و دراسة الصفات الضوئية لغشاء من اوكسيد النحاس المحضر بطريقة الترسيب بالرش الحراري

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الخلاصة

حضرغشاء رقيق من دقائق اوكسيد النحاس النانومترية بواسطة استخدام طريقة الترسيب بالرش الحراري في درجة حرارة مقاربة ل 400 م ° بالهواء الجوي لمحلول كحولي. في حين استخدم كلوريد النحاس (الثنائي التكافؤ) كمادة خام وشريحة من الزجاج كمادة اساس. درست الصفات التركيبية للشريحة المحضرة بأستخدام تقنية (المجهر الذري) وتقنية حيود الاشعة السينية ووجد ان معدل حجم الدقائق هو 90-30 نانومتر كما تم قياس خشونة السطح والتي تساوي 9.3 نانومتر.
وكذلك تم دراسة اطياف الامتصاص والنفاذية، وفجوة الطاقة، وسمك الغشاء. كما اختبرت العينة كمحدد بصري. التجارب اجريت بأستخدام ليزر النديميوم - ياك عند الاطوال الموجية 532 نانومتر و1064 نانومتر وباستخدام طاقات مختلفة. وقد اظهرت الدراسات امكانية استخدام دقائق اوكسيد النحاس النانومترية كمحدد بصري ومتحسس.

Introduction

Materials have emerged as attractive alternatives to conventional materials by virtue of their prominent electronic, optical and chemical properties [1]. Copper have attracted considerable interest because of their optical, catalytic, mechanical and electrical properties, resulting in a wide range of applications in the field of metallurgy, catalysis, and optoelectronics. Consequently, a wealth of preparation methods have been developed and range from wet phase preparations, hydrothermal, sonochemical or chemical reduction to gas phase processes [2]. Copper oxide-based

materials are of interest on account of their potential uses in many technological fields. CuO and Cu_2O materials are known to be p-type semiconductors in general and hence potentially useful for constructing junction devices such as pn junction diodes. Apart from their semiconductor applications, these materials have been employed as heterogenous catalysts for several environmental processes, solid state gas sensor heterocontacts, and microwave dielectric materials. Their use in power sources has received special attention. Thus, in addition to photovoltaic devices, copper oxides have been used as electrode materials for lithium batteries. The earliest studies in this area focused on their potential use as cathodes in lithium primary cells[3].

The linear optical constants (refractive index -n- as well as the absorption coefficients - α, Extinction coefficient (K) and Real and Imaginary part of dielectric constant ε_1 andε_2) can be found from transmittance spectrum of the films by the following equations:

$$\alpha = \frac{2.303 \times A}{t} \quad (1)[1]$$

where A is absorbance spectrum

t is thickness of thin films

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (2)[4]$$

Where R is reflectance and it equal R=1-T-A

$$K = \alpha \lambda / 4\pi \quad (3)[5]$$

where

λ is wavelength.

$$\varepsilon_1 = n^2 - k^2 \ldots \quad (4)[6]$$

$$\varepsilon_2 = 2nk \ldots \ldots \quad (5)[6]$$

A common geometry for optical limiting studies is illustrated in Fig. 1. Laser beam is focused into a nonlinear refractive material and then collected through a finite aperture in the far field. At high irradiance the far field beam distortion arising from the self action of the laser beam inside the medium will result in the limiting of the transmitted light through the aperture[7].

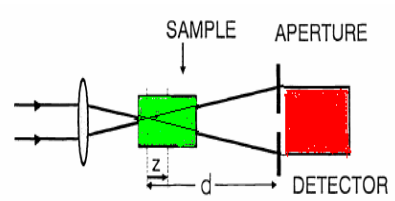


Fig.1: Schematic of the limiting geometry where Z is the distance between the focal plane in free space and the center of the sample, and d is the distance from this plane to the aperture plane[8]

Clearly, an optical sensor requires high linear transmittance, T_L, at low input light levels, while for higher inputs the limiter must clamp the transmitted energy below some maximum value, E_{max}, up to the maximum energy the limiter can withstand, E_D. This is usually the energy damage threshold for the limiting material itself [7].

The ideal optical limiter has the characteristics shown in Fig. 2 it has a high transmittance for low input fluence or energy.

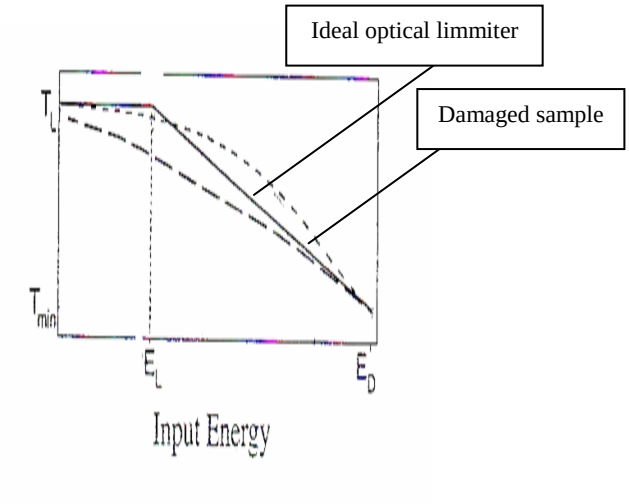


Fig.2: Transmittance output of an ideal optical limiter as a function of the input fluence or energy[7] .

From the above figure the dynamic range D.R can be calculated, the dynamic range is defined as D.R = E_D/E_L (6).

For the ideal limiter the D.R is equivalent to the FOM, by plotting of the nonlinear transmittance versus the input fluence as shown in Fig. 2.

FOM is an important quantity which is represented the performance of a limiting system or device is characterized by some type of figure of merit (FOM) .Commonly FOM is equal to[7]:

$FOM = T_L/T_{min}$ (7)

Which states that a large linear transmittance combined with a low minimum transmittance is desirable.

From Fig. 2 one can estimate the O.D which is defined as the optical density which is equal to[7] :

$OD = \log_{10} (T_L/T_{min})$ (8)

Experimental

Spray pyrolysis method was used to prepare the CuO coatings. An alcoholic solution (Ethanol) of 0.05 M $CuCl_2 .2H_2O$ was used as precursor. The solution was pumped into the air stream in the spray nozzle at a rate of 50 ml. h^{-1} by means of a syringe pump, for a preset time of 30 min. An air stream of 25 L min^{-1}, measured at 1.25 bar, was used to atomize the solution. Glass sheet with (2.5×2.5) cm^2 were used as substrate. They were kept at temperature over the range of 400 C. The amount of oxide attached to the a substrate was determined by weighting the substrate before and after deposition using a Sartorius microbalance with a sensitivity of ±1µg.

After CuO thin films were prepared, some measurement had be done involve linear optical properties measurement, optical limiting properties measurement.

X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 X-ray diffractometer, using Cu Ka radiation and graphite monochromator. Topographic AFM examinations were performed by using a Nanoscope IIIa contact-mode AFM (Digital Instruments). Type NP cantilevers (Digital Instruments) with Si_3N_4 tips and a spring constant of 0.58 $N.m^{-1}$ were employed. In order to avoid exposure to the air, a series of precautions were adopted in recording the AFM images of the film.

CuO thin films were tested using UV-VIS spectrophotometer type (SP3000, Optima, and Japan) for measuring the transmission (T).

Results and Discussion

The film thikness was found 11.6 nm. Fig.3 showed XRD abstracted a polycrystalline hexagonal structure with the narrow peaks that indicate large grain size. The analysis is demonstrated the reflection surfaces at (101), (102), (103), (006) and (110). All patterns reveal peak at (103) directions, which corresponds to typical CuO (covellite) with lattice constant of a=3.792 A° and c=16.344 A°. This means that this plane is suitable for crystal growth.

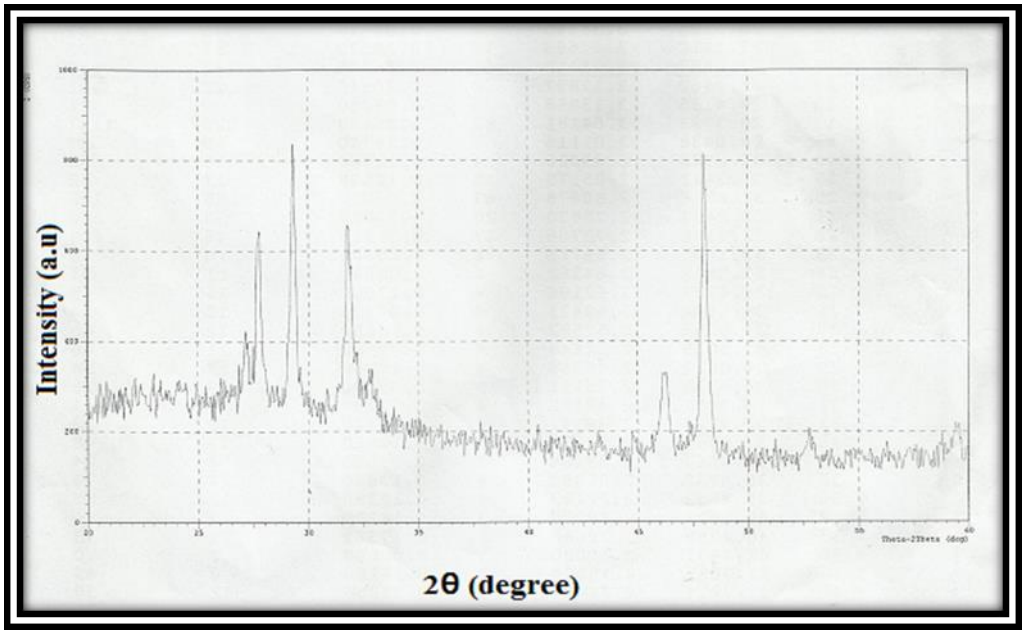
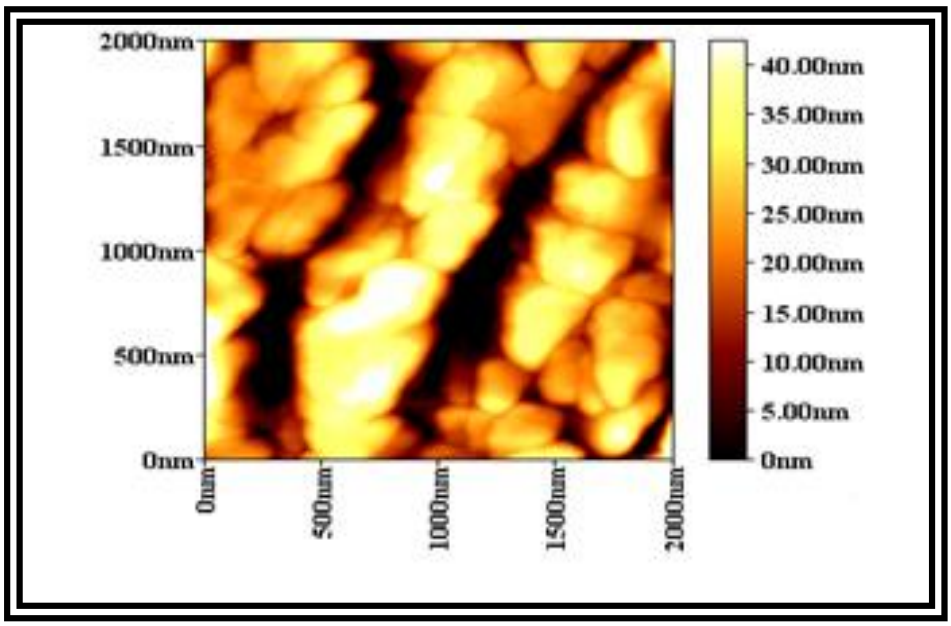
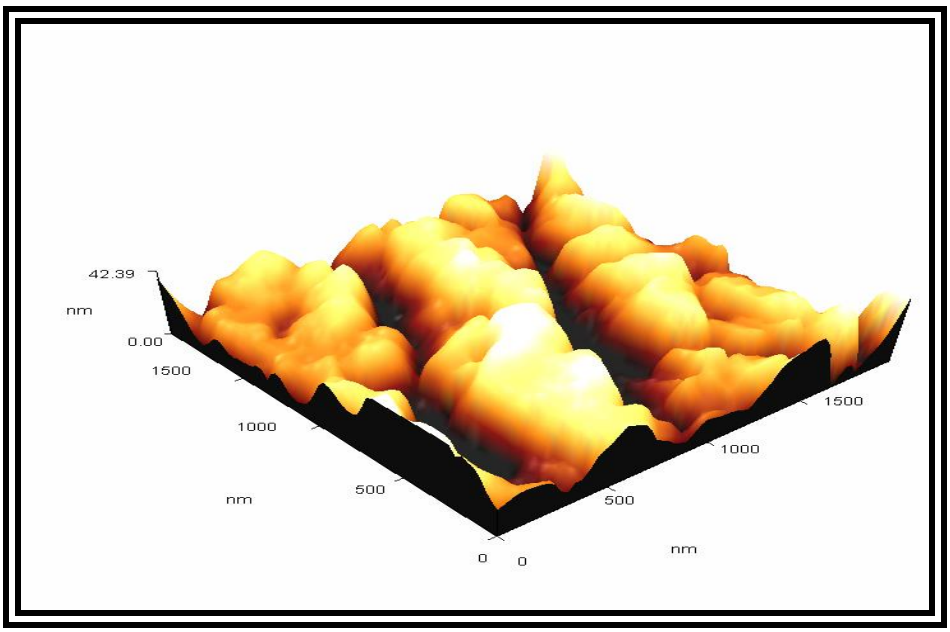


Fig.3: X-ray diffraction pattern of of copper oxide thin film.

Complementary information of the film morphology was obtained from AFM images (Figs.4a, 4b), which also exposed the high uniformity of the films obtained with all the treatments and revealed that they resulted from the agglomeration of round-shape (see Fig. 4b). Particle size was calculated by averaging the results of several AFM observations in different regions of the film to be equal to 90 nm and from CSPM Imager surface roughness analysis the Sa (roughness Average equal to 9.3 nm.



Fig(4a): AFM Topography image of copper oxide thin film.



Fig(4b):3D AFM Image of copper oxide thin film.

Fig.5 shows the optical transmittance spectra of CuO thin film. Thin film is not highly transparent in the visible region of the electromagnetic spectrum.

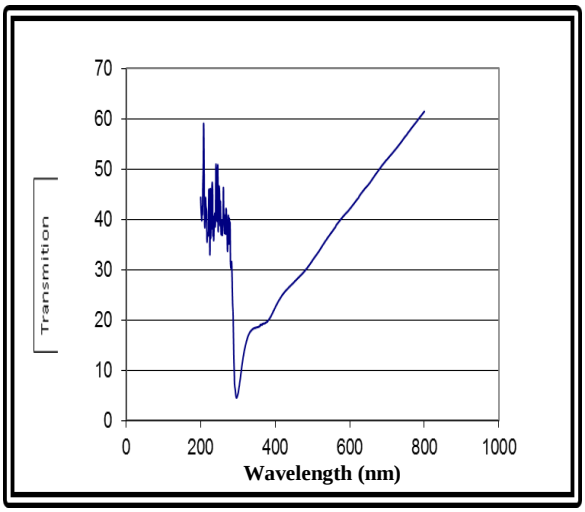


Fig. 5: UV-VIS transmition spectrum of copper oxide thin film.

Fig.6 shows the variation of (α) with photon energy $(h\nu)$ for (CuO) thin film. From this figure, it can be seen that the absorption coefficient (α) increases with increasing photon energy for investigated thin film. It can evidently see that absorption coefficient having values $(\alpha > 10^4 cm^{-1})$ which leads to increase the probability of occurrence direct transition. This can be linked with the formation stage and with increase in grain size and density of layers and it may be attributed to the light scattering effect for its high surface roughness. Also the extinction coefficient as a function of λ takes the same behavior of α as a function of hυ (eV).

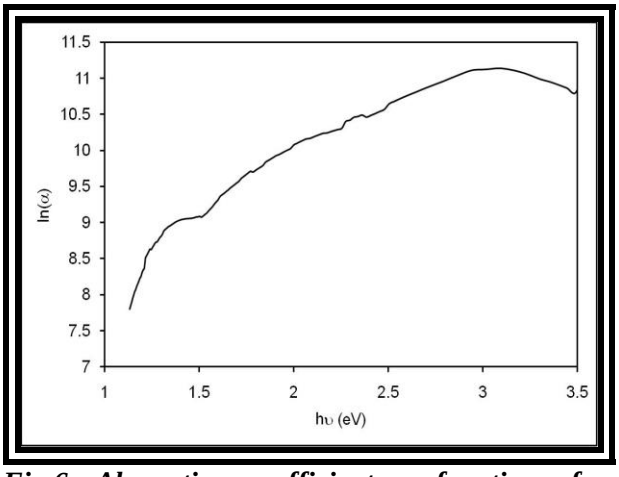


Fig.6: Absorption coefficient as function of energy photon of copper oxide thin film.

From Fig.7 the behavior of refractive index with photon energy $(h\nu)$ is the same of reflectance as a function of photon energy $(h\nu)$ curve as shown in Fig.8. Linear refractive index were increased directly with photon energy$(h\nu)$, afterward, they are slowly decreased.

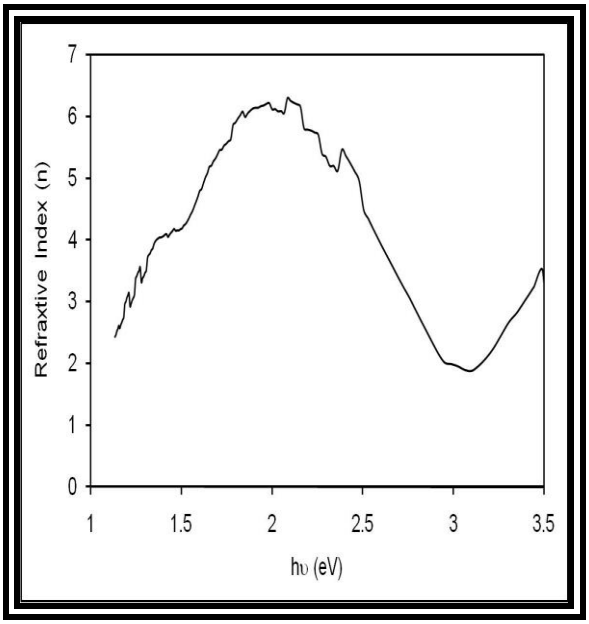


Fig.7: Refractive index as function of energy photon of copper oxide thin film.

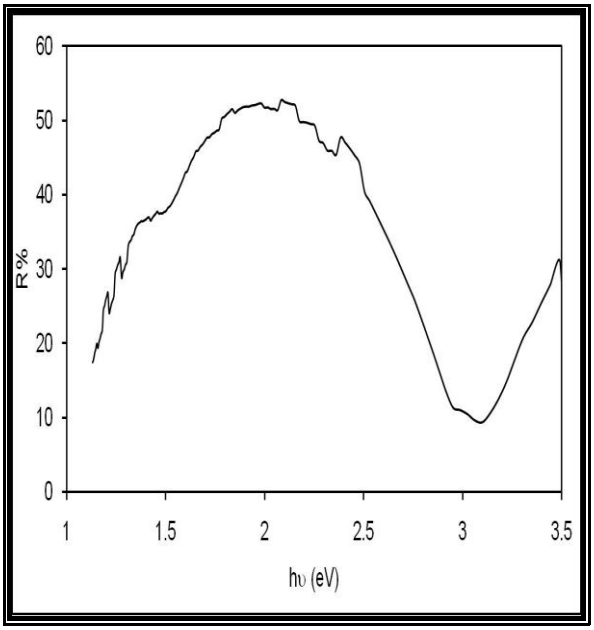


Fig.8: Refractivty as function* of *energy photon of copper oxide thin film.

The variation of ε_1 and ε_2 versus photon energy $(h\nu)$ are shown in Fig.9 and Fig. 10. The variation of ε_1 and ε_2 with the increase of the wavelength of the incident radiation is due to the change of reflectance and absorbance. The behavior of ε_1 is similar to that of the refractive index because of the smaller value of k^2 compared with n^2, while ε_2 mainly depends on the k value, which are related to the variation of absorption coefficient. ε_2 represents the absorption of radiation by free carriers.

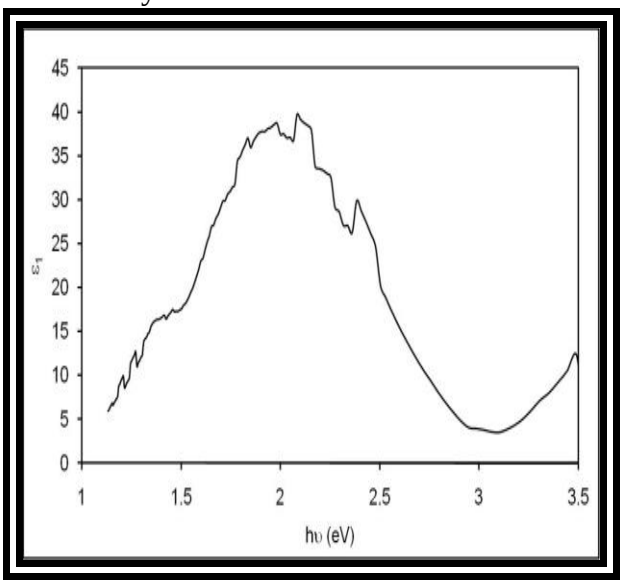


Fig.9: Real dielectric constant (ε_1) of copper oxide thin film.

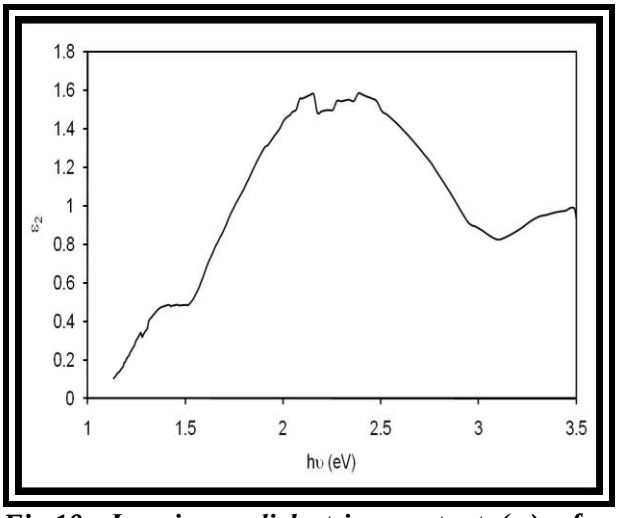


Fig.10: Imaginary dielectric constant (ε_2) of copper oxide thin film.

Fig.11 show the direct energy gap.

$$\alpha h\nu = B\left(h\nu - E_g{}^{opt.}\right)^{\frac{1}{2}} \quad (9)$$

The coefficient B (taus slope) in the equation (9) has been obtained from square of the slope of straight line of Fig.11 and the value of E_g is 1.51 eV.

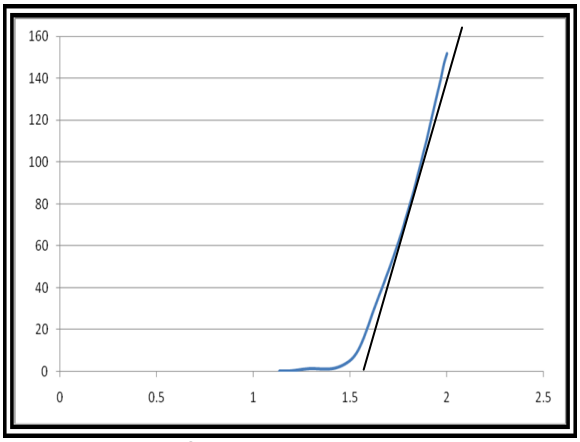


Fig. 11: $(\alpha h\nu)^2$ as function of energy photon for different thickness of copper oxide thin film.

The limiting behavior of copper oxide was performed. The output energy was plotted versus the input energy as measured for varoius input energy. The limiting energy was measured at the focusing of a Gaussian beam and the beam waist.

The output energies are increased as the incident energies increased until the limiting threshold energy where the output energy is constant inspite of the incident energies increasing as shown in Figs.(12, 13).

These energies are 81.2 mJ at 532 nm and 97.25 mJ at 1064nm for the sample. The limiting energy is equal to 100mJ at 532 nm and at 1064 nm it is equal to 120 mJ. These energies values represent the optical limiting threshold energy for the samples as listed in the Table 2.

Conclusions

In this work, we report the preparation and characterization of CuO thin films by spray pyrolysis of an alcoholic solution of copper chloride a simple preparation method that requires no sophisticated equipment.

An ideal optical limiter is one which is perfectly transparent at low intensities up to a predetermined intensity level, above which the transmitted intensity remains clamped at a constant value.

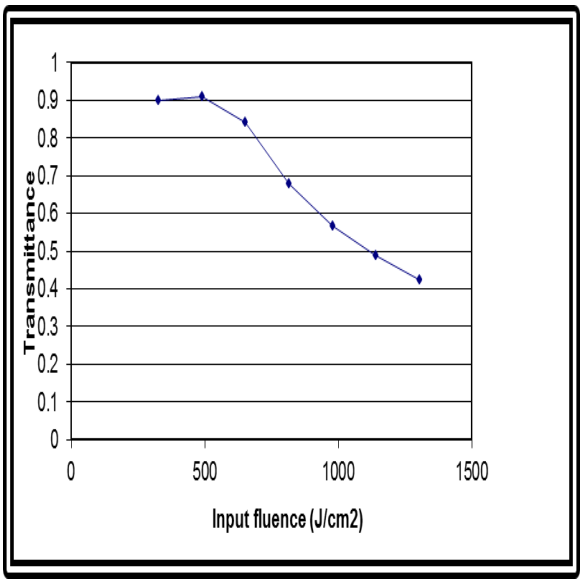


Fig.12: The optical limiting behavior of nanostructure copper oxide thin film. At 532nm

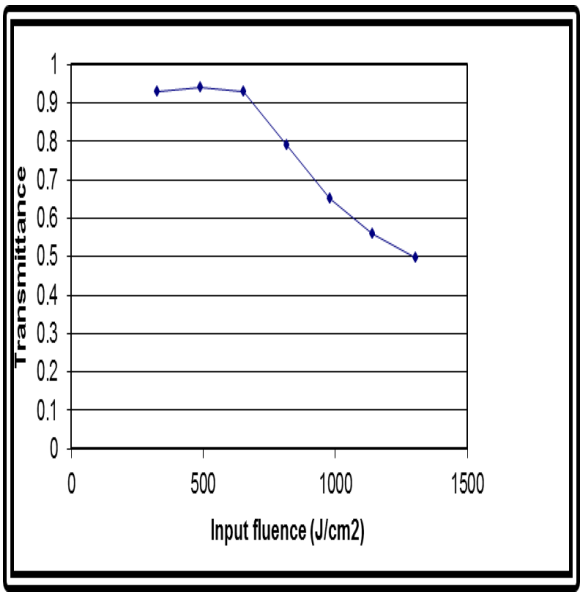


Fig.13: The optical limiting behavior of nanostructure copper oxide thin film. At 1064 nm

Table 1: The E_L , $E_{clamping}$, and D.R values of the CuO at 532 nm and 1064 nm.

Material	E_D (mJ)	E_L (mJ)	$E_{clamping}$ (mJ)	*D.R*
nanostructured CuO At 532 nm	110	100	81.2	1.20
nanostructured CuO At 1064 nm	160	120	97.25	1.33

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