Investigation on the Chemical Mist Deposited of Polyethylene Glycol (Peg-400) Assisted Cuo Thin Films

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***Abstract*—CuO is technologically an important material and in the present study it has been synthesized by forming mist from an aqueous solution of cupric nitrate with PEG-400 using ultrasonic nebulizer sprayed onto glass substrates kept at elevated substrate temperature. The X-ray diffraction study shows the formation of CuO as dominant phase in film samples. The scanning electron microscope images reveal dispersing nature of surfactant that helps to improve porosity in the material. The film sample deposited at substrate temperature of 400℃ comparatively higher response among all samples. The maximum sensitivity was found to be about 6.83% for light impulse of 27800 lux of 40 seconds duration. The sample also shows a repeatable behaviour in response when exposed to a light impulse of 2 seconds. The response of the films for light is almost follows a linear behaviour with time.**

***Keywords*— Photosensor, mist deposition, CuO**

I. INTRODUCTION

A photosensor is a device that detects the presence of light energy. Most of the photo sensing devices consist of semiconductor material have ability to possess called photoconductivity in which the electrical conductance of the material varies depending on the intensity of radiation. The most common types of photosensor are the photodiode, the bipolar phototransistor, and the photosensitive field-effect transistor. Photosensors are used in a great variety of electronic devices, circuits, and systems, including fiber optics, optical scanners, wireless LAN, automatic lighting controls, machine vision systems, electric eyes, optical disk drives, optical memory chips, remote control devices.

Thus to synthesize photoactive metal oxide nanoparticles has been attracted considerable attention in last decade. There are various fields where these materials find important applications such as catalyst [1], window material [2], photosensor [3] and gas sensor [4, 5]. CuO being a p-type semiconductor material with a band gap of 1.25-1.51 eV having wide range of applications which makes it promising material in research. This material in the form of nanoribbons [5], nanowires [6, 7], mesoporous dandelion structure [8], urchin-sheet like structure [9], hollow microsphere [10] and nanoneedles [11] etc. has attracted considerable attention due to utilization in diverse technological areas. In the form of a film, it is mainly used in devices like solar cell, window material for solar cell [2], photosensor[7], catalytic sensor [12] and gas sensor [13].

Variety of synthesis techniques like chemical [14], polymer precursor [15], and hydrothermal [16] etc. have been used widely for the preparation of nanocrystalline CuO powder. However, despite the excellent progress in afore mentioned techniques, there is one or more drawback sassociated in their procedure. As no sophisticated instrument is required in chemical precipitation and sol–gel methods and simple processing route, so these methodologies drawn considerable attention [17, 18].High quality CuO films have been deposited by various techniques such as thermal evaporation [19], thermal oxidation [20], spray pyrolysis [21, 22], sol-gel dip coating [23, 24]etc. Among these the spray pyrolysis is preferred over the others routes due to several advantages such as cost effective, easily controllable parameters and most important no vacuum is required [21, 22, 25-28].

Surfactant molecules are widely used for controlling size, shape of grains and acts as polymer which plays an important role in synthesizing self assembled nano as well as micro structures. The surfactant molecules absorb on specific crystal planes and initiate an anisotropic grain growth. PEG as non-ionic surfactant has been widely used in fabricating nanostructured materials by different routes in interesting morphologies with improved properties [29-35]. In its molecules the hydrophilic oxygen atoms are easily linked with the free hydroxyl ions on the surface of colloid particles by hydrogen bonds. The properties of material can be tailored by selecting different types of PEG series. Reference [35] has successfully deposited hexagonal ferrites using PEG 2000 by adopting self propagating combustion technique. Reference [34] have deposit PEG assisted grown ZnO thin films by dip coating method. However as far as the data available, PEG has been widely used in the synthesis of various materials in the powder form but there is no report available related to the deposition of PEG assisted CuO films by using ultrasonic spray pyrolysis technique.

In this paper, the PEG assisted CuO thin films have been synthesized by ultrasonic spray pyrolysis techniques respectively. The samples are systematically characterized and obtained film sample has been tested for white light sensing properties.

II. EXPERIMENTAL

A. Material

All the chemicals (LobaChemie Mumbai) of analytical reagent grade are used as precursors. The solutions are prepared in doubly distilled water. Corning 7059 borosilicate glass slides (2x4 cm^2) are used as substrates and cleaned by standard procedure prior to use.

B. Synthesis process (Ultrasonic spray pyrolysis technique)

The precursor solution for aerosol generation is prepared by dissolving the required amount of $Cu(NO_3)_2{\cdot}3H_2O$ in water to form0.2 M, 100 mL solution. To it10 mL of 0.5M PEG-400 solution is added drop wise with vigorous stirring. The preparative parameters of the ultrasonic spray setup such as nozzle to substrate distance, solution concentration, solution spray rate etc., are optimized to obtain, pin hole free, adherent films and are kept constant in all experiments. The substrate temperature is varied from 300 to 400˚C, in steps of 50˚C using electronic temperature controller (Model DTC303, Selec make) with accuracy of ± 3 ˚C. The substrates are heated to required temperature by a specially designed electrical heater, and the temperature is measured using K type (chromel–alumel) thermocouple. The distance between the nozzle and the substrate after optimization is maintained at 25 cm. The spray rate is fixed at 1 mL per minute. The aerosol is generated using ultrasonic nebulizer (Omron NE-U17), and subsequently passed through glass nozzle using air as carrier gas onto preheated glass substrate. The detailed procedure of film deposition has been already discussed in detail previously [39]. The spray deposited films are named as per terminology indicated in Table I.

TABLE I. Sample codes for the PEG doped CuO thin films

Material powder/film	Substrate temperature	Code
CuO thin film (0.5M PEG-400)	300 ± 3 ˚C	F_1
CuO thin film (0.5M PEG-400)	350 ± 3 ˚C	F_2
CuO thin film (0.5M PEG-400)	400 ± 3 ˚C	F_3

C. Structural analysis

The phase identification of the powder and thin film samples is analyzed by X-ray diffraction (XRD) pattern, taken using X'PertPanlytical diffractometer with Cu Kα radiation (λ = 1.5405 Å , 30mA , 40 kV) in 2θ range from 30-80˚.

Texture coefficient for the thin films is calculated using the equation given as [38, 39]

$$T(hkl)=\frac{I(hkl)}{I_o(hkl)}\left[\frac{1}{n}\sum_{i=1}^{n}\frac{I(hkl)}{I_o(hkl)}\right]^{-1} \quad (1)$$

where I_0 represents the standard intensity, I is the observed intensity of the (hkl) plane and n is the reflection number.

The average crystallite size (D) is obtained from the most prominent peak using Scherrer's formula [36]

$$D=\frac{0.9\lambda}{\beta\cos\theta} \quad (2)$$

where β is the FWHM of the powder, θ the Bragg angle, λ the wavelength of X-ray used.

Lattice parameters ($a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$ for monoclinic structure) and the volume of unit cell for the CuO films are calculated using the formulas given below

$$\frac{1}{d^2}=\frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2}+\frac{k^2\sin^2\beta}{b^2}+\frac{l^2}{c^2}-\frac{2hl\cos\beta}{ac}\right) \quad (3)$$

$$V=abc\sin\beta \quad (4)$$

To study the surface topography films, field emission scanning electron micrographs (FESEM) are taken on a JEOL JSM-6700F with a beam voltage of 20 kV.

The film samples have been tested for their response toward white light of different flux by measuring conductance Keysight34410A multimeter. Sensitivity (S %) is defined as the percentage change in conductance when CuO film was exposed to light.

$$S(\%)=\frac{C_l-C_d}{C_d}\times 100 \quad (5)$$

where C_l and C_d are the CuO film conductances measured in light and dark respectively.

III. RESULTS AND DISCUSSION

XRD diffractograms of USP deposited films shown in Fig. 1indicates the film F_1 deposited at substrate temperature of 300 ˚C is found to be amorphous whereas rise in substrate temperature to 350 and 400 ˚C shows characteristic CuO peaks. The strong and sharp diffraction peaks corresponding to CuO phase of(002) and (111)atomic planes appeared at 2θ value of 35.5˚ and 38.7˚ respectively. No peak corresponding to Cu_2O phase has been noticed in the diffraction patterns .It has been noticed that addition of PEG strongly affects the crystallinity of CuO films. Findings from this work suggested that the crystalline CuO films with PEG are successfully deposited at substrate temperature of 350 ˚C. Further characterization of films results for the F_2 and F_3 films are calculated and co-related.

The values of texture coefficient for the F_2 and F_3 are recorded in Table 2. Its value greater than one for the peak located at 35.5˚ and 38.7˚ reveals the preferential orientation of the film. Texture coefficient value for the (002) plane is significantly higher in comparison to (111) plane. This result reveals that CuO particles are anisotropic in shape (non-spherical) [31] and deposited grains tend to possess facet like morphology as directed by the templating nature of surfactant.

TABLE II. Values of the texture coefficient T(*hkl*), lattice constant, *a* (Å), *b* (Å), *c* (Å), *β* (Degree), cell volume (Å^3), crystallite size (*D*) from XRD, particle size from FESEM, F_2 and F_3 samples

Property/ Sample code	**F_2**	**F_3**
T(*hkl*), (002):(111)	2.072:1.928	2.191:1.809
a (Å)	4.699	4.669
b (Å)	3.427	3.420
c (Å)	5.121	5.090
β (Degree)	99.639	97.709
cell volume (Å^3)	81.088	81.062
average Crystallite size (nm) XRD	38	43
SEM (average particle size, nm)	400	160

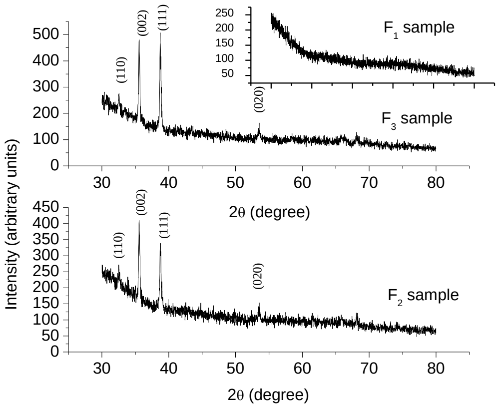

Fig. 1 XRD pattern of the spray pyrolysis deposited CuO thin films of F_1, F_2 and F_3samples

Using Scherrer's formula, average crystallite size of samples has been calculated (Table II) and in case of thin film F_3sample it is 43 nm. The lattice parameters of samples (F_2 and F_3) have been calculated (Table II) and found to be in good agreement with ICDD data card 41-254. The variation in values of lattice parameters and unit cell volume of samples indicates the evidence of strain. The values of lattice parameters for the samples have been found to be lower in magnitude as compared to one those reported for bulk CuO in literature. This implies that lattice structure in spray pyrolysis deposited CuO films having more number of defects.

Fig 2 shows FESEM images of spray deposited F_2 and F_3 films which exhibit uniform, compact, crack free and nano-sized particle agglomerates. Randomly distributed trapezium shaped grains of size 400 nm have been observed in F_2 film sample. F_3 film sample shows comparatively smooth morphology and possess more number of pore channels and possess an interesting morphology on the 100 µm scale, in which spherically shaped particles aggregated to form coin like structures. A numbers of coins appeared on different locations film on the micrograph. The transformation of facets like morphology of particles to spherical might be due to templating nature of the non-ionic, polymer type PEG surfactant used in the synthesis of several porous materials [35]. PEG assisted spray deposited CuO samples shows relatively higher specific surface area, which promises its potential applications.

PEG-400 is a nonionic surfactant and able to acts as a dispersing agent in the reaction. It is one of the most flexible water soluble polymer which has hydrophilic and hydrophobic radicals on the long carbon chains. In aqueous medium its flexible ether linkage makes it less sterically hindered and causing more oxygen atom on polymer chain to combine with the metal ion. The dispersing nature of the surfactant keep the sol particles separated due to long chain of molecules. The surfactant addition causes a reduction in surface tension and slows down growth rate of sol particles. Reference [30] have discussed same concept of the PEG-2000 molecules on the synthesis of ZnO particles by using zinc nitrate and citric acid. Reference [31] observed the similar effect of PEG-600 along with cetylytrimethylammonium bromide (CTAB) in the hydrothermal synthesis of hydroxyapatite.

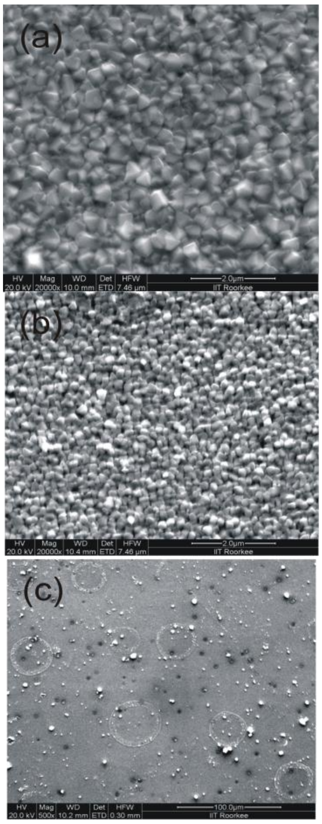

Fig. 2 FESEM images of spray pyrolysis deposited CuO thin films (a) F_2 and (b, c) F_3samples

The PEG assisted CuO thin film has been exposed toward white light from LED source at room temperature (300 K). The time resolved measurements were performed on the F_2film sample when exposed to light of 3420 lux for 2 seconds repeatedly and change in conductance of the film has been observed. The response curve as shown in Fig. 3 shows that F_2 sample after light exposure did not recover its dark conductance and sensitivity was found to be 0.37%. The F_3 sample when exposed to light of 3420 lux it regains its conductance in dark and comparatively higher sensitivity of 0.47 %. Thus F_3 sample explored for photosensing properties for light of 12960 and 27800 lux. The obtained response curves for F_3 samples have been shown in Fig. 4. The sensitivity has been calculated and the maximum sensitivity has been found to be1.62% for light of intensity of 27800 lux.

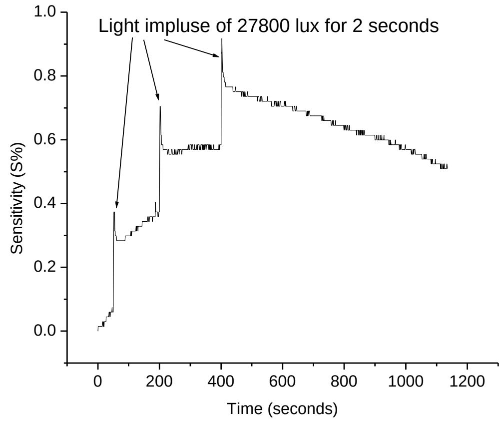

Fig. 4 Response of spray pyrolysis deposited CuO thin film $F_2$for light impulse of 2 seconds for 3420 lux

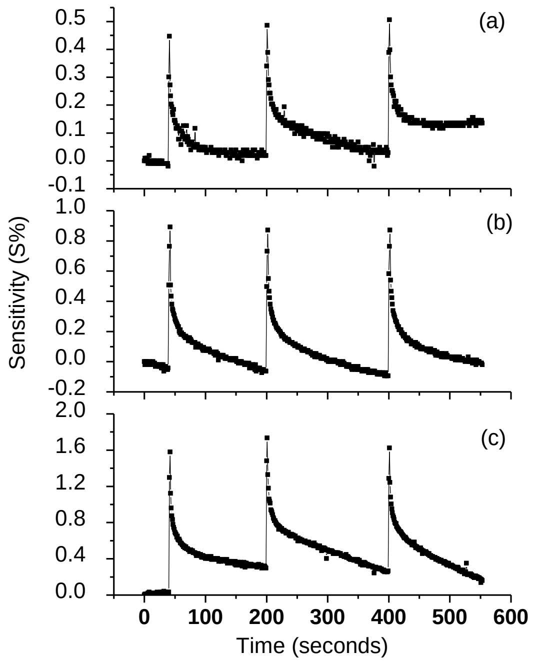

Fig. 4 Response of spray pyrolysis deposited CuO thin film $F_3$for light impulse of 2 seconds for (a) 3420, (b) 12960 and (c) 24900 lux

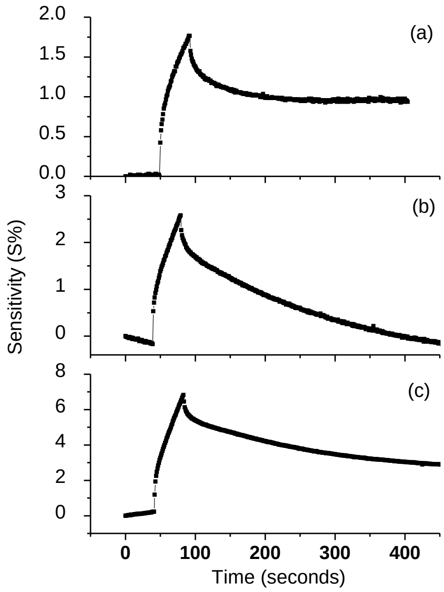

Fig. 4 Response of spray pyrolysis deposited CuO thin film $F_3$for light impulse of 40 seconds for 27900 lux

The F_3film sample has been tested for light impulse of time 40 seconds and obtained response curves are shown in Fig. 5. The calculated sensitivity values for samples F_2 and F_3 for light impulse of 40 seconds is shown in Table III.

The film sample shows almost linear response with light intensity and the corresponding equations for the change in conductance of film in light (C_l) and dark (C_d) with time are tabulated in table 3. The room temperature appreciable light response in case of surfactant assisted thin film sensor may be attributed to the large specific surface area as depicted by FESEM.

TABLE III. Response (*S*) of samples for light impulse of 40 seconds having different intensity and change in conductance in the light and in dark for F_3 sample

Property	**Light intensity (lux)**	**F_2**	**F_3**
Response (%) for light impulse of 40 seconds	3420	0.80	1.76 $C_l = 0.0167t - 0.689$ (R^2=0.97) $C_d = -0.002t + 0.7241$ (R^2=0.96)
	12960	1.99	2.58 $C_l = 0.0438t - 1.973$ (R^2=0.99) $C_d = -0.0012t + 1.86$ (R^2=0.92)
	27800	2.27	6.83 $C_l = 0.0519t - 2.42$ (R^2=0.99) $C_d = -0.002t + 2.14$ (R^2=0.94)

C_l and C_d correspond to the conductance of the film during light exposure and in dark respectively.

IV. CONCLUSIONS

NanocrystallinePEG-400 doped CuO mist deposited thin films are synthesized by using ultrasonic spray pyrolysis techniques. The average crystallite size has been found to be 43 nm in thin film samples. The lower value of the lattice constants as compared to standard data indicates that the CuO nanocrystallites are subjected to considerable defects in thin film. The defects provide the more active favourable sites for the light capturing. The facets like grains were uniformly distributed on the entire surface of substrate in case of thin film. As a light sensor PEG doped CuO thin films show an appreciable sensitivity of 6.83% at room temperature.

ACKNOWLEDGEMENT

Authors wish to thank UGC for providing financial support in the form of Minor research project, Director IIT Roorkee, STIC, Kochi and RSIC, Panjab University, Chandigarh for providing FESEM, EDAX and XRD facilities. We also gratefully acknowledge Mr. Gurpreet Singh, for his kind assistance in the electrical characterization of the samples.

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