

Dalila Tabli^{1*}, Nassim Touka¹, Kamel Baddari¹, Nourddine Selmi²

¹Laboratory of Materials and Sustainable Development, University of Bouira, Faculty of Sciences and Applied Sciences, Department of Physics, Bouira, Algeria

²Nuclear Research Centre of Birine, Algeria

*d.tabli@univ-bouira.dz

Pb-DOPED CuO THIN FILMS SYNTHETIZED BY SOL-GEL METHOD

ABSTRACT

The physical properties of pure CuO and Pb doped CuO thin films, deposited on glass substrates by a sol-gel method, were investigated. Structural analysis revealed the polycrystalline nature of the pure CuO and Pb:CuO composite films with a monoclinic structure, the crystallite size decreased and ranged from 36.78 nm to around 21.5 nm. The SEM images of the CuO thin films showed that the Pb doping concentration affects the surface morphology of the Pb:CuO composites. The absorbance of the Pb:CuO composites is higher than that of the undoped CuO thin films. The optical band gap energies of undoped CuO and Pb doped CuO thin films were estimated to 1.9 (pure), 2.17(5%) and 2.74 (7%)eV, and found that the band gap energy (E_g) increases with the Pb concentration. This blue shift is due to the quantum confinement induced by the reduction in the size of the crystallites.

Keywords: CuO; Pb; physical properties; sol-gel; thin films

INTRODUCTION

Scientific research focuses on the importance of nanotechnology in the field of the manufacture and study of materials at the nanometric scale and offers a look at new applications, due to their unique properties with respect to bulk materials. This has prompted the development of nanomaterials and nanocomposites, as well as different production techniques. Currently considerable efforts are concentrated on metal oxide semiconductors (TiO₂, SnO₂, ZnO, CuO...), has been the subject of numerous research studies and they have aroused great interest in academia and industry because they show a remarkable improvement in material properties compared to micro and conventional macrocomposites. The development of these materials is linked to their interesting physical properties and their advantages over other materials (stable, non-toxic, low cost). These materials are good candidates for applications in different technological sectors.

Copper oxide thin films semiconducting have attracted considerable attention in recent years, due to its unique properties. They find wide applications in solar cells as an absorber material [1-2] in gas sensors [3], biosensors [4], in catalysts [5] and as negative or positive electrode of lithium-ion batteries [6]. Copper oxide appears with two oxidation, cupric oxide (CuO) and cuprous oxide (Cu₂O), both of them are p-type semiconductors with optical direct

band gaps at the range of 1.3-3.7 eV and 1.8-2.5 eV successively [7-8]. Several techniques have been used to elaborate copper oxide, such as chemical vapor deposition [9], spray pyrolysis [10], thermal oxidation [11], pulsed laser deposition [12], electro-deposition [13], molecular beam epitaxy [14] and sol-gel [15]. Among these, the sol-gel technique has several advantages, such as deposition of high purity, homogeneous, large-area films at relatively low temperatures and low cost [16].

The doping of copper oxide films affects their physics properties, which allow to adapting them for a variety of applications. Although many research works have already been carried out on doped nanostructured films, there are still today demands for thin films of doped copper oxide with properties tailored for each application. When the copper oxide is doped with rare earth elements they tend to possess a narrow band gap which lies in the visible region leading to a higher optical activity.

In this paper, we present a simple and low cost sol-gel spin coating method for growing and modifying the properties of copper oxide thin films. Therefore, the aim of this work is also to introduce lead (Pb) into the CuO lattice at two distinct concentrations (5 and 7%). The properties of the obtained thin films were studied as a function of the Pb concentration.

MATERIALS AND METHODS

The precursor solutions for both undoped and Pb doped CuO were prepared by the sol-gel method using copper (II) chloride anhydrous (CuCl_2) (98%, Biochem) and lead (II) acetate anhydrous [$(\text{CH}_3\text{COO})_2\text{Pb}$] (98%, Sigma Aldrich) as the starting materials.

The details of the preparation of the undoped solution have been described elsewhere [17] except that in this work the quantity of the solvent methanol (CH_3OH) is 15 ml. Pb doping solution was prepared by dissolving lead (II) acetate anhydrous in undoped solution, we dissolve the necessary masses of this white powder in 15 ml to obtain the mass doping levels of 5% and 7%. The solution becomes homogeneous after stirring at 60 °C for 10 min.

Before deposition, the glass substrates were successively cleaned with acetone, ethanol, and deionized water in an ultrasonic bath. Undoped and Pb doped CuO thin films were deposited on the glass substrates by spin coating technique at room temperature, with a speed of 2800 rpm for 30 s. After each spin-coating process, the films were kept on a hot plate at 100 °C in air for 10 min to remove the organic contaminants. This cycle of the coating and drying process (one layer) was repeated to produce undoped and Pb doped CuO thin films with a thickness corresponding to three layers. Finally, all the films were annealed in air, at 350 °C for 2 h.

The structural properties of the films have been studied by X-ray diffraction using a Panalytical X'Pert PRO Diffractometer by scanning through 2θ angle of 25-60° with $\text{CuK}\alpha$ irradiation ($\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$). Raman spectra were recorded using a LabRAM HR Horiba Jobin Yvon spectrometer equipped with a HeNe laser providing an excitation wavelength of 632 nm. The surface morphologies of the deposited films were characterized by field emission scanning electron microscopy (JSM-7610F Plus). The vibrational bands of the synthesized thin films were analysed using Perkin Elmer Fourier transform infrared spectrometer in the range of 4000–400 cm^{-1} . The optical absorption spectra were recorded using an UV-Vis-NIR spectrophotometer (Shimadzu, UV-3101 PC) in the wavelength range 300-800 nm. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Structural analysis

The properties of the Pb:CuO thin films have been investigating for two different Pb concentration values 5 and 7%. The XRD patterns presented in figure 1 show the effect of Pb on the structural properties of CuO thin films. The observed peaks for undoped films at the positions $2\theta = 31.82^\circ$, 35.55° and 38.75° were assigned to (-110), (002) and (111) crystallographic planes, respectively, for Pb doped CuO films we observe the disappearance of the peak located at $2\theta = 31.82^\circ$, and we note the appearance of a new peak located at $2\theta = 49.0^\circ$ assigned to (-202) crystallographic plane.

The obtained XRD spectra revealed that all samples belong to the C2/c space group of the monoclinic CuO structure with lattice parameters, $a = 4.6853 \text{ \AA}$, $b = 3.4257 \text{ \AA}$, $c = 5.1303 \text{ \AA}$ and $\beta = 99.5490^\circ$ according to the JCPDS N°. 00-045-0937.

It is noted that the intensities and the full width at half maximum (FWHM) of the peaks are different according to the doping concentration. Consequently, the Pb^{2+} ions seem to substitute for the Cu^{2+} ions into the CuO matrix without modifying the monoclinic structure of the film. Any peak belonging to metallic Pb and its oxidation forms is found in the samples. As the ionic radius of the Pb^{2+} dopant ($1.2 \text{ \AA}$) is greater than that of Cu^{2+} ($0.73 \text{ \AA}$), the difference in the ionic radii of the host and the dopant atom causes a lattices strain and leads to changes in the lattice parameters of the system as the dopant concentration increases. The presence of Pb ions in the CuO matrix is correlated with the observed peak shift in the XRD patterns towards a lower angle [16]. The intensity of the (002) and (111) planes on the XRD spectra of the Pb:CuO films appears with a large increase in intensity; this peak increase indicates a crystallinity improvement of the composite film.

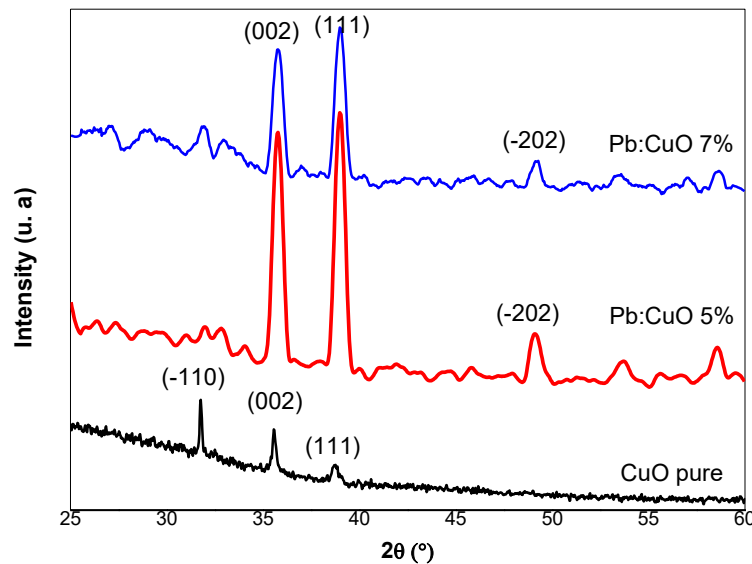


Fig. 1. X-ray diffraction pattern of Pb doped CuO thin films for 5% and 7% Pb concentrations

The structural parameters, such as grain size (D), FWHM (β), strain (ϵ), lattice spacing (d) and dislocation density (δ) of Pb:CuO films were estimated from the XRD patterns. The average value of the grains size was estimated from the XRD peaks, according to Debye Scherrer's formula [18]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where D is the crystallite size, $\lambda = 1.5418 \text{ \AA}$ is the X-ray wavelength, β the FWHM of the peak, and θ is Bragg's angle. Several reasons are responsible for the peak broadening in the XRD spectra including variation in the crystallite size, lattice structure, and internal strain (ε) which occur during the film preparation owing to non-uniform displacements of the atoms based on their reference-lattice positions [19]. The following equation was used to determine the strain values [20]:

$$\varepsilon = \frac{\beta}{4 \tan(\theta)} \quad (2)$$

Bragg's equation was used to calculate the lattice spacing (d) values for all films:

$$2d \sin \theta = n\lambda \quad (3)$$

Where n is the order of diffraction, λ is the radiation wavelength and θ is the angle of diffraction.

The density of defects in CuO films which is the dislocation density (δ) was calculated using the equation (4), dislocation density is inversely proportional to the square of crystallite size and therefore, the higher the δ is the smaller the D is which in turn suggests the presence of the defects in the samples [21].

$$\delta = \frac{1}{D^2} \quad (4)$$

The lattice parameters were calculated using the monoclinic structure equation [22]:

$$\frac{1}{d^2} = \frac{1}{(\sin \beta)^2} \left[\frac{h^2}{a^2} + \frac{k^2 (\sin \beta)^2}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right] \quad (5)$$

where d is the inter-planer distance and h, k, and l are Miller indices for the particular Bragg reflection.

Table 1. Structural parameters for undoped CuO and Pb doped CuO

Sample	2 θ (°)	β (°) FWHM	D(nm)	d (Å)	$\delta \times 10^{+4}$ (nm ⁻²)	$\varepsilon \times 10^{+3}$ (line ⁻² .m ⁻⁴)	Lattice constant (Å)		
							A	b	c
Pure CuO	31.77	0.13744	60.14	2.8165	2.7645	2.1073			
	35.60	0.23714	35.21	2.5218	7.3922	3.2228	4.8540	3.3825	5.1283
	38.75	0.38305	22.00	2.3237	18.9365	4.7527			
Pb:CuO 5%	35.18	0.38445	21.69	2.5509	19.4065	5.2913			
	38.44	0.43184	19.50	2.3415	24.0292	5.4048	4.5979	3.4360	5.0958
	49.08	0.43271	20.20	1.8561	22.4613	4.1353			
Pb:CuO 7%	35.18	0.43075	19.36	2.5509	24.3624	5.9285			
	38.45	0.40437	20.82	2.3412	21.0613	5.0595	4.6370	3.4320	5.1006
	49.15	0.40698	21.48	1.8536	19.8588	3.8831			

The (002) plane was used as a reference to compare the structural parameters of undoped and Pb doped CuO thin films (Table 1). The crystallite size was found to be decreased and the FWHM increased with the increase of Pb content. The dislocation density in the crystal structure increased from 7.3922×10^{-4} to 24.3624×10^{-4} with an increase in Pb concentration. The corresponding lattice spacing (d) slightly decreased and unchanged with the Pb doping concentration, this slight decrease may be attributed to the evidence of strain in Pb-doped CuO films. There is also an increase in the strain in the doped films. Therefore, it can be said that a decrease in the crystallite size is correlated with an increase in strain. The estimated values of lattice parameters a, b, and c are shown in Table 1; these values are in agreement with JPCDS card no. 00-045-0937.

Figure 2 represents the surface morphologies of samples of thin films of pure CuO and doped with Pb (5% and 7%) obtained by successive deposition of three layers. In general, it can be concluded that the morphology of the films is largely influenced by the introduction of the dopant, in particular by the size of the grains which has decreased compared to the pure CuO film. The films show the presence of grains (indicating a polycrystalline nature) and exhibit a relatively dense surface structure composed of crystallites of spherical and cubic shapes of various sizes, which are coherently dispersed on the glass substrate. However, we observed the presence of islands enveloping nanometre-size grains, these islands becoming more intense in the case of the doping rate of 7%; consequently, the particles become less dense to form agglomerations of grains.

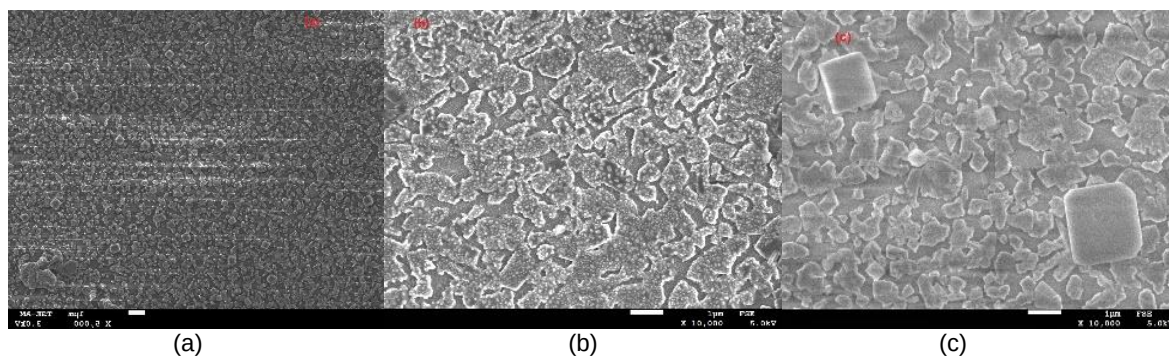


Fig. 2. SEM images of (a) undoped CuO thin film, (b) Pb doped CuO 5% and (c) Pb:CuO 7%

Raman analysis

Raman spectrometry is an important tool to analyze the phase of a prepared material. The copper oxide CuO has 12 phonon branches because there are four atoms in the primitive cell, three acoustic modes ($A_u + 2B_u$), six infrared active modes ($3A_u + 3B_u$) and three Raman active modes ($A_g + 2B_g$) [19]. It is well known that pure CuO nanoparticles have bands at A_g (296 cm^{-1}), $B_g(1)$ (346 cm^{-1}), and $B_g(2)$ (631 cm^{-1}) [19]. Figure 3 shows room temperature Raman spectra of CuO and Pb:CuO thin films. The Raman spectrum of CuO thin films shows peaks at 294.5 cm^{-1} , 342.7 cm^{-1} and 637 cm^{-1} , corresponding respectively to A_g and two B_g Raman active modes. It can be seen that the Raman spectra of Pb:CuO films exhibit shifts and broadening due to the phonon confinement effect [20]. This behavior can be attributed to the decrease in the size of the Pb:CuO crystallites with an increase in the Pb concentration, in agreement with the XRD results.

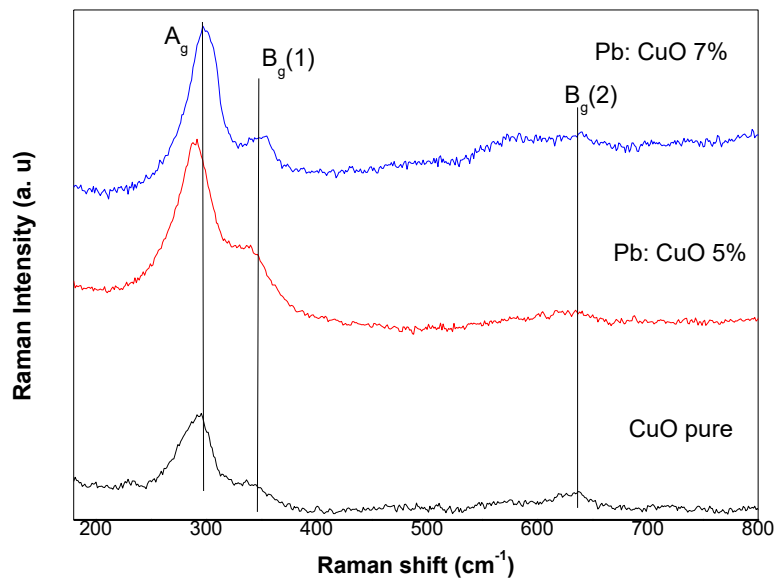


Fig. 3. Raman spectra of undoped CuO and Pb doped CuO

FT-IR analysis

The FTIR spectra for undoped CuO and Pb doped CuO thin films are shown in Figure 4. A broad transmittance band of the metal-oxygen bond was found around 475 cm^{-1} [21], which was assigned to vibration of the Cu-O bands; thus determining the presence of CuO in the system. We also note the presence of a peak around 2363 cm^{-1} due to the $\text{O}=\text{C}=\text{O}$ vibrational band of CO_2 [22].

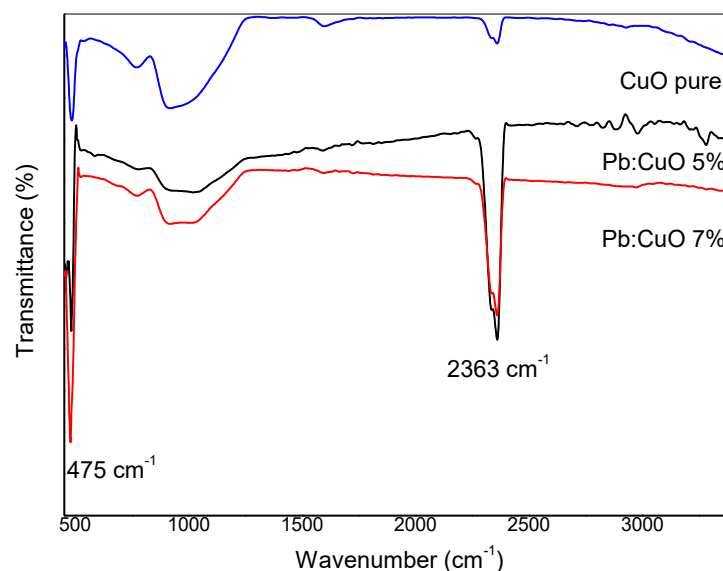


Fig. 4. FTIR spectra of undoped CuO and Pb doped CuO

Optical analysis

The UV-Vis absorption spectra of samples are shown in Figure 5. The absorption intensity of CuO:Pb thin film is greater than that of pure CuO thin film in the visible region. This means that the doped thin films were enhanced, which was due to the increase in defect

sites. Assuming a direct band gap for the determination of the band gap energy E_g , we have plotted $(\alpha h\nu)^2$ versus $(h\nu)$, by employing the Tauc formula [23]:

$$\alpha h\nu = C(h\nu - E_g)^{1/2} \quad (6)$$

where α is the optical absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap and C is the constant for a direct transition.

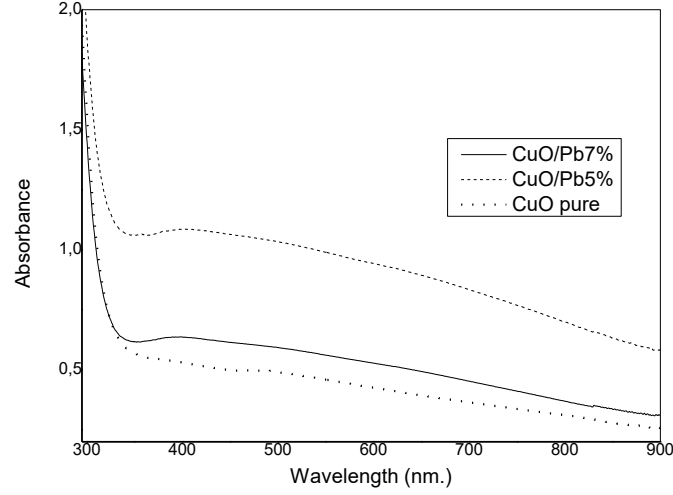


Fig. 5. Optical absorption spectra of undoped CuO and Pb doped CuO thin films

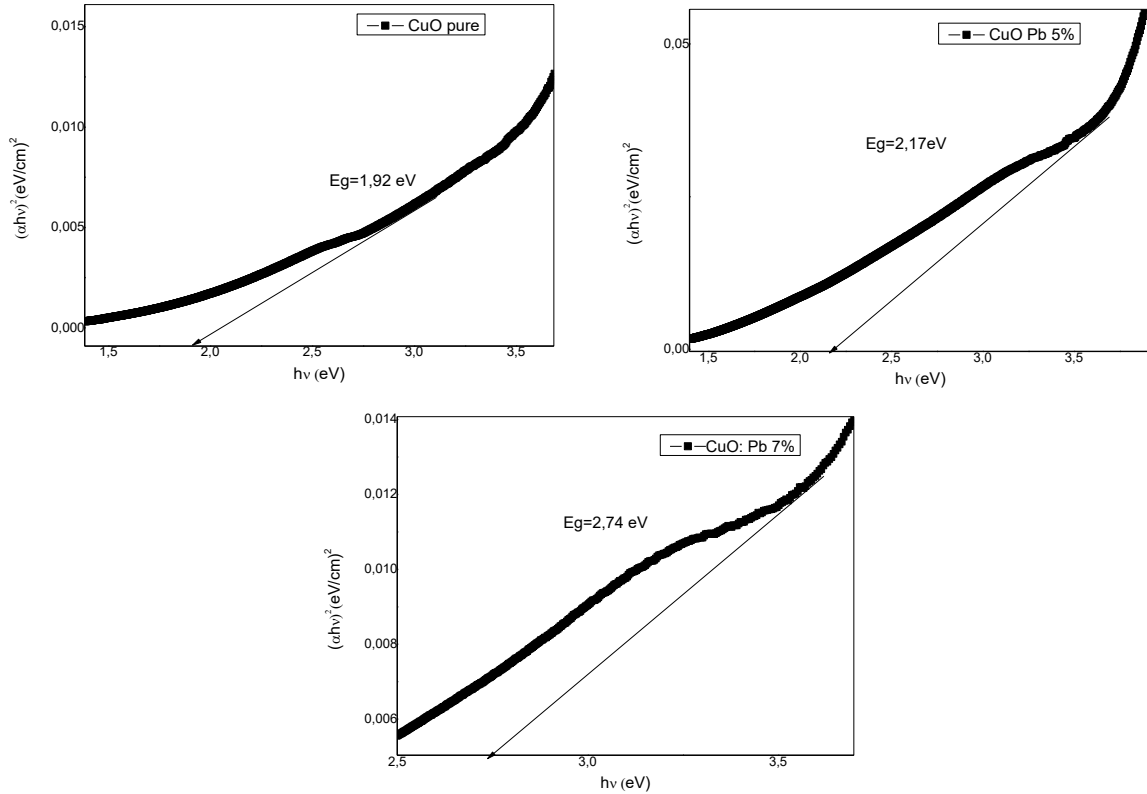


Fig. 6. Band gap energy for undoped CuO and Pb doped CuO thin films

The band gap energies of the films were determined by the extrapolation of the linear part of the curves towards the energy axis $(h\nu)$, as shown in figure 6. The optical band gap

energies of undoped CuO and Pb doped CuO thin films were estimated to 1.92, 2.17, and 2.74 eV (Fig. 5) and found that E_g increases with the Pb concentration. Because the size of the crystallites is reduced according to the results of the XRD, the optical band gap increases with the decrease of particle size.

CONCLUSIONS

CuO and Pb:CuO thin films have been deposited by the sol-gel process using the spin coating technique. Lead at two different concentrations was introduced in thin layers having a thickness corresponding to three layers. The structural characterization by XRD reveals that the prepared films were tenorite phase and have a high level of purity and crystallinity. The crystallite size of the CuO films was affected by Pb concentration and was found to be decreased with the increase of Pb concentration. Raman and FTIR measurements of CuO pure and Pb:CuO films confirmed the structure of CuO. SEM studies revealed a cubic and spherical nano-textured surface in presence of the Pb dopant. A clear correlation between the broadening of the optical band gap with increasing Pb doping concentration was observed.

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