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The Effect of Annealing Time on Lead Oxide Thin Films Coated on Indium Tin Oxide Substrate

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Abstract : Lead thin films were deposited on ITO substrate using the thermal vacuum evaporation method at a substrate temperature of 100°C and then thermally oxidized in air at an annealing temperature of 270˚C with a varying annealing time of 1h and 3 h. The structural, surface morphological, and optical properties of the films are determined using X-ray diffraction (XRD), atomic force microscopy (AFM), and UV-visible spectroscopy. The structural studies confirmed that the lead oxide films are in the amorphous state. From the atomic force microscope (AFM) images, it was found that the roughness of the film surface increased as the film annealing time increased. The optical band gap values of the lead oxide thin films are slightly decreased as the annealing time increased.
Keywords: Lead Oxide, Thermal evaporation, XRD, AFM and UV-Visible.

Introduction

Transition metal oxide materials have been attracting of researchers, only their special properties of chemical and physical properties. Since the high temperature transfer through the windows is subjected by radiation, optical coating can be used to get better thermal as well as visual simplicity. In a warm climate this can be achieved by using solar control coatings, which diminish the transmission of non-visible near infrared radiation from the sun[1]. Many oxide materials are usually wide band gap compounds. The thin films conductivity can change from an insulator to a conductor, depending upon the deposited method, substrate, annealing condition, and so on[2]. Due to their unique optical and electrical properties, metal oxide materials have been used in microelectronic and optoelectronic applications[3]. In the recent years, increased attentions have been focused on the synthesis of nanostructured lead oxide. Lead element has a lot of oxide forms, such asPbO, Pb_2O_3, Pb_3O_4, $PbO_2$and phase of α, β[4]. Due to theirvarious properties, lead oxides have wide applications such as pigments gas sensors, paints, thin film batteries, storage devices and optoelectronic devices. Lead oxide thin films have been prepared by metalorganic chemical vapor deposition[5], photochemical metal organic deposition[6], atomic layerdeposition[7], electro deposition[8,9]and thermal evaporation[10]. In this paper, we are reporting lead oxide thin films coated on ITO substrate using thermal evaporation technique. The crystalline phases in the films were investigated on the characterization of the films using XRD, AFM and optical study.

Experimental Work

The thin films of lead (Pb) was deposited on an ITO substrate by using a vacuum thermal evaporation method. Pb films were obtained by evaporating commercially available high purity Pb powders (99.9% Aldrich) from an electrically heated molybdenum boat at about 4 x 10^{-5}Torr. After deposition, Pb films were heated, in the ambient atmosphere, which was fixed at 270°C, were maintained 1 hour and 3 hour at the maximum temperature and finally were cooled down to room temperature. The samples were then taken out of the muffle furnace and characterized by the XRD, AFM and UV.

XRD analysis was carried out by X'Pert PRO diffractometer, employing CuKα radiation (λ=1.5418 Å). Atomic force microscopy (AFM) images were recorded using a Park Systems XE70 instrument operating in non-contact mode, was used to study the surface topography of the films. Surface roughness were estimated over an area of 10 x10 μm^2. The optical absorption and transmittance measurements, recorded within the wavelength range from 300 to 800nm, were used to calculate the absorption coefficient (α), and the optical band gap, E_g.

Results and Discussion

X-ray Diffraction studies

Figure 1 shows the typical XRD patterns of lead oxide thin films prepared by thermal oxidation of lead films, at temperature of 270˚C 1 hour and 3 hour respectively.

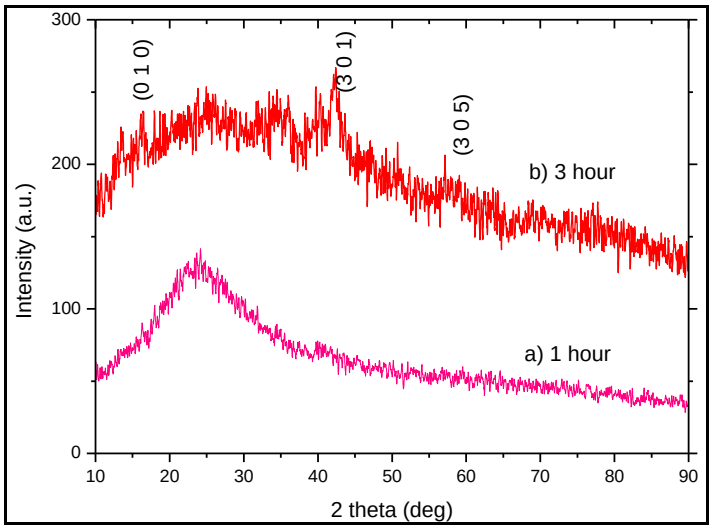

Figure 1 (a) & (b)XRD pattern of lead oxide thin films on an ITO substrate

The XRD patterns characteristic for oxidized films, presented in figure 1(a), it can be observed that lead oxide film exhibit an amorphous state. In order to improve the films crystallinity, the sample was submitted to a further heat treatment which consists of the oxidation temperature of 270˚C and maintained at the respective temperature for 3 hour, whereas figure 1(b) indicates only the start of the crystallization process. In figure 1(a) the 1 hour annealed lead films indicates, there is no diffraction peaks were observed. It was observed that after the 3 hour oxidation process, at annealing temperature of 270˚C, the diffraction peaks of lead metal disappear, indicates that the metal is completely transformed into lead oxide. XRD patterns of oxidized films show small and narrow peaks superimposed on the largebackground of the amorphous component of the ITO substrate. Three diffraction peaks appear in the range of 2θ with values of approximately 15˚, 42˚ and 58˚ which correspond to the miller indices (hkl) produced by the (010), (301) and (305) crystalline planes of α-Pb_2O_3, Pb_2O_3 and Pb_3O_4 respectively.

Atomic Force Microscopy (AFM)

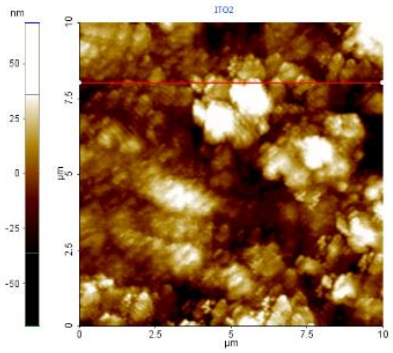

Figure 2 (a) AFM 2D image of lead oxide thin films on ITO substrate for 1 hour annealed film

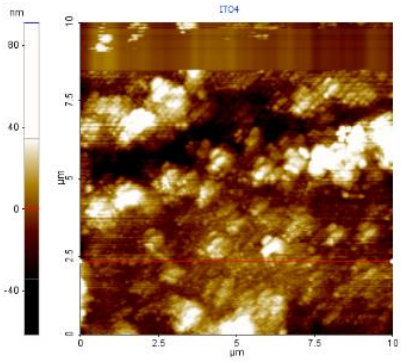

Figure 2 (b) AFM 2D image of lead oxide thin films on ITO substrate for 1 hour annealed film

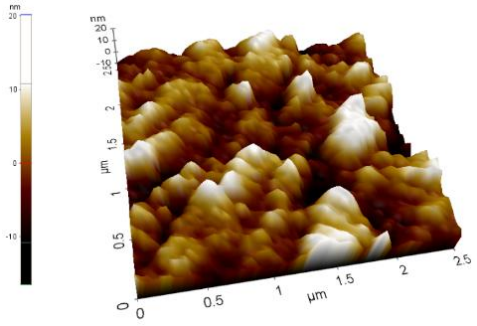

Figure 3(a) AFM 3D image of lead oxide thin films on ITO substrate for 1 hour annealed film

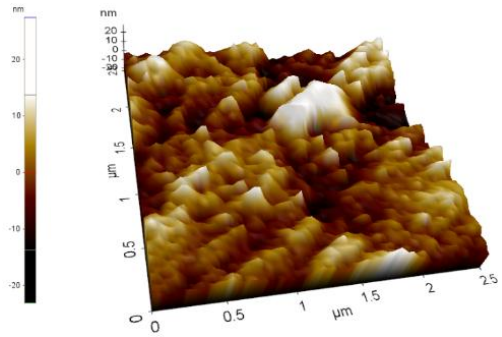

Figure 3(b) AFM 3D image of lead oxide thin films on ITO substrate for 3 hour annealed film

Surface scanning was done in the studied films, using AFM technique.2 dimensional and 3 dimensional AFM images are shown in figure 2 (a), (b) and figure 3 (a), (b).From the two-dimensional AFM images we can observe that the investigated surfacesare covered by crystallite with a well-defined shape and small sizes. The color distribution ishomogeneous on the analyzed surface, shows a uniform composition of the films. We

canobserve that, as the oxidation time was increased, from 1 hour to 3 hour, the average surfaceroughness increases from0.016 nm to 6.992 nm. An increase of the surface roughness maybe a consequence of the structural modification produced by the increase of oxidation time. The film crystallites becomelarger and consequently the surface roughness is larger [11]. The observed values were tabulated in table 1.

Table 1. AFM surface roughness analysis of the lead oxide thin films of 1 h and 3h.

Annealing Time	Average roughness (nm) R_a	RMS roughness (nm) R_q	Max. height (nm) R_{max}	Skewness R_{skw}	Kurtosis R_{kur}
1 h	0.013	0.016	0.037	-0.276	2.243
3 h	6.992	8.423	23.001	-0.349	2.466

Optical Properties

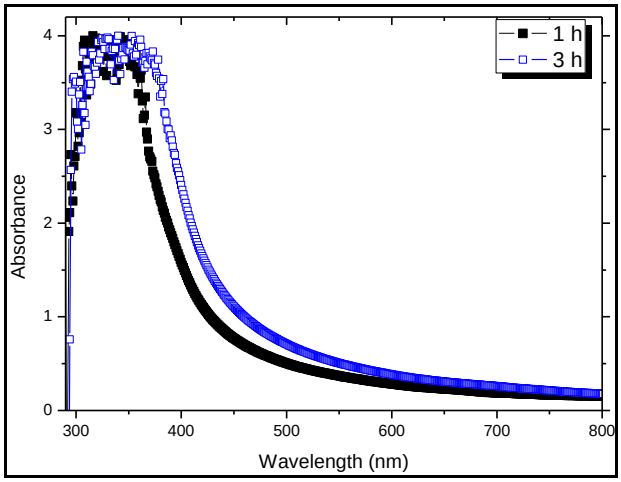

Figure 4 (a)Plot of optical absorption versus wavelength for lead oxide films

Optical transmittance spectra of the PbO films, recorded in the spectral range from 300 nm to 800 nm, are presented in figure 4 (a). The experimental results indicate that the increase of the oxidation time determines an important increase of the film transmittance. The investigated films exhibit relatively high transmittance in visible region of the spectrum and a sharp fundamental absorption edge at about 350 nm. The lower values of optical transmittance obtained for the 1 h and 3 h oxidation of the metallic films depends on various parameters such as oxidation time, oxidation temperature, film thickness, etc.L.M. Droessler et al [10] concluded that the entire transformation of Pb into PbO depend only on annealing time. By increasing the oxidation time, from 1 h to 3 h, the optical transmittance, in the visible domain, increases. We consider that, at a higher oxidation time all metallic atoms are oxidized and the decrease of optical scattering followed by crystallite growth and the reduction of crystallite boundary density will cause an increase of the optical transmittance.

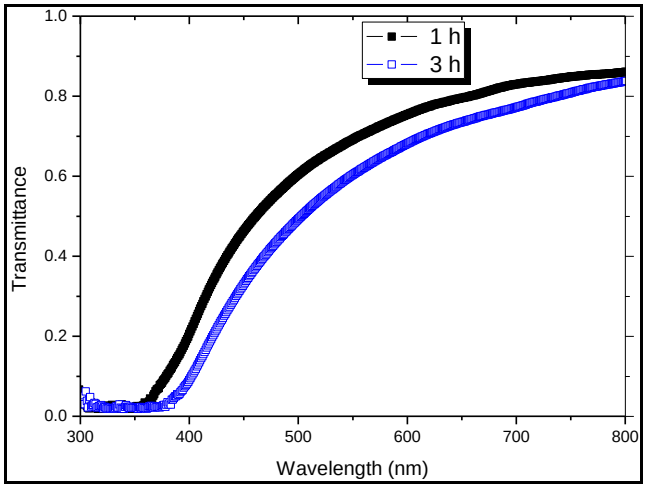

Figure 4 (b)Plot of optical absorption versus wavelength for lead oxide films

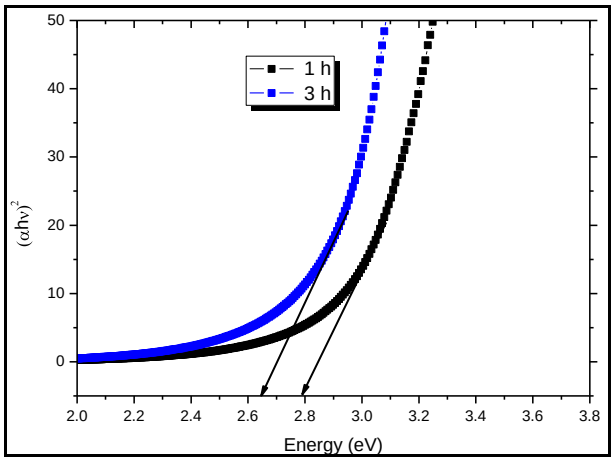

Figure 4 (c)Plot of $(\alpha h\upsilon)^2$ versus Energy for lead oxide films

The optical transmittance spectra, obtained after the samples were annealed, are plotted and presented infigure 4 (b). As it may be observed, by applying a heat treatment for 1 h and 3 h samples Pb metallic were oxidized and the film become more transparent. It is known that a stoichiometric semiconducting compound has a sharp transmission edge in that photon energy which corresponds to the forbidden energy gap of the lead oxide compound. Assuming a direct transition between the edge of the valence and the conduction band, the variation of the absorption coefficient with the photon energy can be calculated by the following relation [12].

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

where α represents the absorption coefficient, hvis incident photon energy, $E_g$denotes the optical band gap, for allowed direct transition and Ais a characteristic parameter, independent of photon energy. Figure 4 (c). Shows that the optical band gap energy is calculated by extrapolation of the linear part of $(\alpha h\nu)^2$ vs $h\nu$. The energy band gap values were found to be in the range of 2.64 eV to 2.78 eV, values which were found to increase with increasing annealing time.

Conclusion

Lead oxide (PbO) films were prepared by thermal oxidation of Pb metallic films, deposited by vacuum thermal evaporation. Structural investigationof XRD measurements, showed that Pb metallic film possess a polycrystalline structure, whereas oxidized Pb films, at different annealing time. AFM analysis byincreasing in annealing time changes in the structure. The investigated samples are characterized by low transmittance and high absorption rangein the visible region. The values of optical band gap were evaluated and were found to be ranged between 2.6 eV and 2.8 eV, these values being in a good agreement with the values reported for lead oxide thin films.

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