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STUDIES ON THE PHYSICAL PROPERTIES OF SPRAY AND SILAR DEPOSITED LEAD OXIDE THIN FILMS

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ABSTRACT

Lead oxide thin films were fabricated on suitably cleaned glass substrates by employing two low cost chemical techniques, viz. Spray pyrolysis and SILAR. The films were characterized by X-ray diffraction, scanning electron microscopy, UV-Vis-NIR spectrometer and two point probe setup. XRD studies revealed that both the spray and SILAR deposited films appear to be polycrystalline in nature having tetragonal phase with a (0 0 2) preferential orientation. SILAR deposited film appears to be amorphous in nature. Better optical transparency and low electrical resistivity is observed for the spray deposited PbO film.

Keywords: X-ray diffraction; crystal structure; optical band gap; thin films; electrical properties

1. INTRODUCTION

Transition metal oxide thin films constitute a very interesting class of materials because of the various properties they exhibited. Mostly studied oxide films usually have wide band gap values. Depending on the preparation conditions, the conductivity of these oxide films varies from insulator to conductor [1]. Due to their enhanced optical and electronic properties, the metal oxide based thin films have been used in a wide variety of microelectronic and optoelectronic applications such as electroluminescent devices [2], magnetic memories [3] and dielectric layers [4], etc. Among the various transition metal oxide thin films, lead oxide is technologically important due to its attractive properties. Due to the different oxidation states adopted by lead (+2 or +4), lead oxide thin film may exist in different forms and it is difficult to deposit in a single phase with definite crystal structure [5]. Lead oxide thin films with different phases possess multiple levels of reflectance which makes them suitable for optical storage devices [6]. Among the different phases possessed by lead oxide, lead monoxide (PbO) is an attractive material with low electrical conductivity, interesting semiconducting and photo conducting properties which make it suitable in laser technology and imaging device applications [7]. It also finds applications as semiconducting gas sensors for CO_2 [8] and also as high refractive index materials [9]. PbO thin films have been used as anodic material for lithium secondary batteries [10].

The preparation of PbO thin film is often complicated by its high volatility at relatively low temperatures. It has been reported earlier that at low temperature, PbO exist in tetragonal phase (α – PbO) and at high temperature it exist in orthorhombic phase (β – PbO). At 490°C under atmospheric pressure, α – PbO undergoes a phase transition to β – PbO [7]. PbO thin films have been deposited by various methods such as metal organic chemical vapor deposition [11], dc magnetron sputtering [12], electro-deposition [13] and spray pyrolysis [14]. Among the chemical methods, spray pyrolysis and SILAR have been proved simple and inexpensive [15]. Although, both of these techniques are very much comparable with each other regarding low cost, large area coating, minimum wastage and simple apparatus requirements, the microstructural properties of the PbO films deposited by these techniques differ remarkably. Considering these factors, in this work PbO thin films were fabricated by these two techniques and the structural, morphological, optical and electrical properties of the films were studied and the results are presented here.

II. EXPERIMENTAL

PbO thin films were deposited on glass substrates (dimensions – 76mm x 25mm x 1.5mm) by employing two different chemical techniques, viz. spray pyrolysis and SILAR. Lead acetate, [$Pb(CH_3COO)_2$] supplied by Sigma with purity of 99% is used as the precursor salt for preparing PbO thin films. To prepare PbO films by spray pyrolysis technique, 0.1M of lead acetate salt is dissolved in deionized water (50ml in volume) and the solution is sprayed on glass substrates (micro glass slides, Labtech make) kept at 400°C. When the solution is sprayed, pyrolytic decomposition takes place resulting in the formation of orange colored PbO films. The optimized preparative parameters used to deposit PbO thin films by SILAR method are presented in Table 1.

Table 1: Optimized preparative parameters of PbO thin films by SILAR method

Deposition parameters	Cation precursor	Anion precursor
Bath composition	$Pb(CH_3COO)_2$	H_2O_2
Complexing agent	NH_4OH (5ml)	-
Concentration (M)	0.1	2% (in total solution volume)
pH	~10	~8
Immersion time	15 seconds	15 seconds

To deposit PbO thin films, one SILAR growth cycle involves the following steps: i) the cleaned glass substrates are first immersed for 15 seconds in beaker containing aqueous solution of lead acetate and liquid ammonia so that lead complex ions got adsorbed on the substrate; ii) the substrates are then immersed into a beaker containing de- ionized water for 10 seconds so that loosely bound lead complex ions gets detached from the substrate surface; iii) the substrates are then immersed in a beaker containing 2% H_2O_2 solution (5ml) dissolved in 50 ml water for 15 seconds where lead complex ions reacts with H_2O_2 to form lead oxide; iv) finally the substrates are immersed in a beaker containing water for 10 seconds to detach the loosely bounded PbO ions. After 25 deposition cycles, a dense PbO layer becomes visible. The deposited films were annealed at 100°C for 30 minutes to remove any hydroxide phase present in the sample. The thickness of the PbO films was measured by a gravimetric weight difference method in terms of the weight of PbO deposited on the glass substrate per unit area (mg/cm^2). To study the structural property of PbO films, X-ray diffraction (XRD) patterns were obtained using diffractometer with a CuKα (λ = 1.5406 Å) target. The surface morphological study was accomplished using scanning electron microscope (SEM model HITACH S-300H) and atomic force microscope respectively. The elemental analysis of the films was performed using energy dispersive X-ray spectroscopy (EDS). The electrical resistivity of the films was measured by dc two point probe set up. The optical absorption spectra of the films were measured by PerkinElmer UV-Vis-NIR double beam spectrophotometer, in the 300-1100 nm wavelength range, with glass substrate as a reference.

III. RESULTS AND DISCUSSION

III.1 Structural Analysis

Fig. 1 shows the XRD patterns of spray and SILAR deposited PbO thin films. The diffraction pattern of sprayed film depict a polycrystalline structure of tetragonal phase (α-PbO) according to JCPDS Card No.85-1739 with a (0 0 2) preferential orientation. The other peaks observed at 2θ = 17.669°, 28.662°, 31.863°, 48.63° and 59.86° are associated with (0 0 1), (1 0 1), (1 1 0), (1 1 2) and (1 0 3) planes respectively.

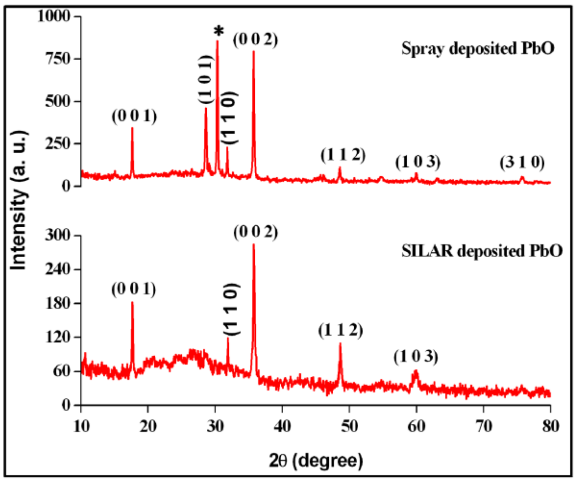

Fig. 1: XRD patterns of spray and SILAR deposited PbO thin films

Traces of orthorhombic phase (β-PbO) were also observed at 2θ=30.863° (represented by asterisk) corresponding to (2 0 0) plane which might be due to the substrate temperature adopted here (400°C) to coat the film. The presence of orthorhombic phase strongly supports the fact that PbO thin films make a transformation from α-PbO to β-PbO at 490°C [16]. The XRD pattern SILAR deposited PbO film shows an amorphous nature with the same (0 0 2) preferential orientation as that of the spray deposited sample. The observed d-spacing values along with the standard values are listed in Table 2.

Table 2: Observed and standard ‘d’ spacing’s values of spray and SILAR deposited PbO films

Standard values*		Observed values				
		Spray pyrolysis		SILAR		
2θ	d-spacing	2θ	d -spacing	2θ	d -spacing	(h k l)
17.643	5.023	17.669	5.023	17.675	5.016	(0 0 1)
28.628	3.1158	28.662	3.112	----	----	(1 0 1)
31.830	2.8090	31.863	2.8063	31.925	2.8021	(1 1 0)
35.722	2.5115	35.761	2.5089	35.53	2.5024	(0 0 2)
48.593	1.8720	48.63	1.8706	48.675	1.8721	(1 1 2)

*JCPDS Card No. 85-1739

III.2 Surface Morphological Studies

Fig. 2 shows the SEM images of PbO thin films fabricated by spray pyrolysis and SILAR techniques. Spray deposited film surface appears to be closely packed with grains of different sizes having well defined boundaries (Fig. 2(a)). No cracks or holes are evident confirming its improved crystallinity. In the SILAR deposited film (Fig. 2(b)), no grains with well defined boundaries are visible. The surface is fully covered with fused grains with overgrown crystallites.

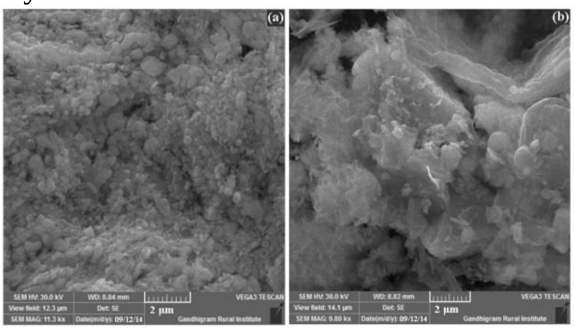

Fig. 2: SEM images of a) Spray deposited and b) SILAR deposited PbO films

No cracks are visible but traces of few holes appear in the film surface. The SEM images confirm that both spray and SILAR deposited PbO films have different morphologies, even though the XRD patterns appear to be similar.

Fig. 3 shows the three-dimensional AFM images of spray deposited and SILAR deposited PbO thin films. For the spray deposited film, it is clear that the film covers the entire area of the surface with well faced spherical grains. Relatively lower surface roughness has been observed for this sample, whereas the SILAR deposited sample shows non-uniform growth due to the availability of many nucleation sites on the substrate due to the low deposition temperature adopted (40°C) to coat this film.

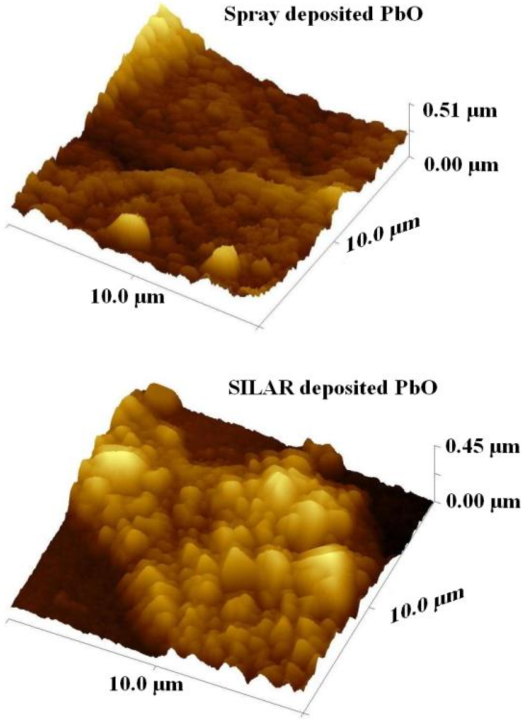

Fig. 3: AFM images of spray and SILAR deposited PbO films

Some overgrown grains were observed which are confirmed from the yellowish regions visible in the sample. Traces of few ungrown regions are also visible which confirms the amorphous nature of this sample which very well supports the fact that the morphologies of both spray deposited and SILAR deposited PbO films vary significantly.

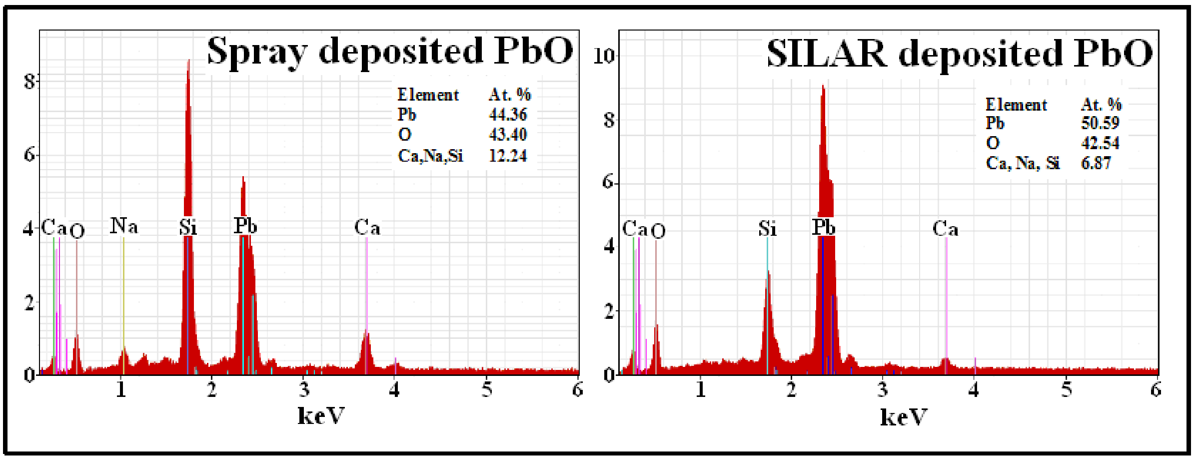

Fig. 4: EDS spectra of spray and SILAR deposited PbO films

III.3 Elemental Analysis

Fig. 4 shows the EDS spectra of the spray and SILAR deposited PbO thin films. The elemental composition (at.%) of the constituents are given in the insets. It is observed that the O/Pb ratio for the spray deposited film is almost equal to 1 confirming its perfect stoichiometric nature and this might be the reason for the minimum resistivity value observed for this film whereas for the SILAR deposited film it takes lesser value (0.88) confirming that oxygen vacancies increases in the sample and this impacts on its resistivity value.

III.4 Optical Properties

Fig. 5 shows the transmittance spectra of PbO films prepared by spray pyrolysis and SILAR methods. Film coated by spray pyrolysis technique has a maximum transmittance of 79%, whereas the SILAR deposited film exhibit a transmittance of 68%.

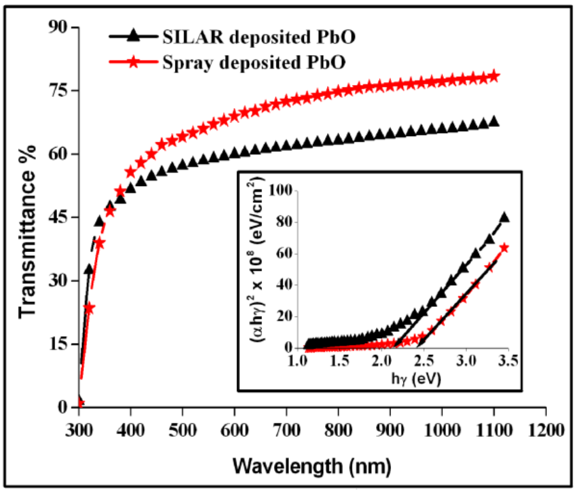

Fig. 5: Transmittance spectra of PbO films. Inset fig. Plots of $(\alpha h\nu)^2$ vs. hν

The low transmittance value observed for the SILAR deposited film might be due to the high thickness value obtained for this sample which results in increased absorption of free carriers [17]. It is also observed that the absorption edge of SILAR deposited PbO shifts to higher wavelength. This suggests that the bandgap of SILAR deposited film should have the minimum value. The value of band gap was calculated from the Tauc's plots using the fundamental absorption, which corresponds to electron excitation from the valence band to conduction band [18, 19]. The absorption coefficient α and the incident photon energy hν are related by the equation (1):

$$(\alpha h\nu)^{1/n} = A(h\nu - Eg) \qquad (1)$$

where A is constant, E_g is the bandgap and the exponent n depends on the type of transition. The exponent n assumes values of 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. The bandgap of the films was calculated from the Tauc's plot, by extrapolating the linear portion of the curves until they intercept the photon energy axis at α = 0 (inset of Fig. 5).The band gap value of spray and SILAR deposited PbO films were found to be equal to 2.36 and 2.16eV respectively. The band gap values obtained in this work are consistent with the values reported by Radhakrishnan et al. [20]. The low value of E_g obtained for SILAR deposited PbO film is due to decrease in free electron concentration in the film and this strongly favors for the high resistivity value obtained for this film (section 3.5). Better crystalline quality due to increased carrier concentration might be the reason for the high value of E_g obtained for the PbO film coated by the spray technique.

III.5 Electrical Studies

The electrical resistivity of the PbO films was measured by two point probe method. The resistivity values of both spray and SILAR deposited PbO films were found to be in the order of 10^2 Ω cm. The resistivity values of spray and SILAR deposited PbO films were found to be equal to 0.368 x 10^2 Ω cm and 0.587 x 10^2 Ω cm respectively. The resistivity values obtained in this work exactly matches with the values reported by Suganya et al. [14]. The high resistivity value observed for the SILAR deposited film might be due to the decrease in the free carrier concentration due to the incomplete removal of H_2O vapor which may resist conduction between PbO grains. This is in accordance with Salunkhe et al. [21] for SILAR deposited CdO thin films. Increased carrier concentration due to improved crystallinity might be the reason for the low resistivity value obtained for the spray deposited PbO film.

IV. CONCLUSION

The structural, morphological, optical and electrical properties of PbO thin films prepared by spray pyrolysis and SILAR techniques has been studied. XRD studies revealed that both the films exhibited tetragonal structure with a (0 0 2) preferential orientation. Optical studies showed that the absorption edge of SILAR deposited PbO shifts to higher wavelength. A low band gap of 2.16 eV is obtained for SILAR deposited PbO film. Electrical studies showed that SILAR deposited PbO film are more resistive in nature than the spray deposited film.

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