

Elemental and Compositional Studies on $Hg_xPb_{1-x}S$ Nanoparticle Films Grown from an Alkaline Chemical Bath

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ABSTRACT

An elemental and compositional study on $Hg_xPb_{1-x}S$ nanoparticle films grown on glass substrates under the optimized conditions ($0 \leq x \leq 0.2$) from an alkaline chemical bath is made in this paper

Keywords: $Hg_xPb_{1-x}S$ nanoparticle films.

INTRODUCTION

Technological advancement of modern society depends on the materials science and engineering community's ability to consider the novel materials with an extraordinary combination of physical, chemical and mechanical properties [1, 2]. Modern technology entails thin films for a variety of applications, which are thin material layers ranging from fraction of a nanometer to few micrometers in thickness. The semiconductor devices and optical coatings are the main applications benefiting from thin film fabrication. Some work is being done with ferromagnetic thin films for use in computer memory. Ceramic thin films are also in wide use. The relatively high hardness and inertness of ceramic materials make this type of thin film coatings of interest for protection of substrate materials against corrosion, oxidation and wear. In particular, the use of such coatings for cutting tools may extend the life of these items by several orders of magnitude. The engineering of thin films is intricated by the fact that their physics is, in some cases, not well understood. In particular, the problem of rewetting may be hard to solve, as there is ongoing debate and research into some processes by which this may occur.

Under such circumstances, a thin film is defined as a low dimensional material created by condensing, one by one, atomic /molecular /ionic species of the matter. The thickness is typically less than few microns. Films are said to be thin films if their layer thickness is $\leq 1\mu\text{m}$ on the substrate surface. The thin films without substrate are called foils. Thin film materials are the key elements of continued technological advances made in the fields of optoelectronics, photonic and magnetic devices. The processing of materials as the thin films allows easy integration into various types of devices. The properties of these materials significantly differ when analyzed. Most of the functional materials are rather employed in thin film form due to their specific electrical, magnetic and optical properties or wear resistances. Thin film technologies make use of the fact that the properties can significantly be controlled by the thickness parameter. Thin films are formed mostly by deposition, either by physical or chemical methods. Both crystalline and amorphous thin films have immense importance in this Hi-Tech. age. Thin film technology is a relatively younger and ever growing field in the physical and chemical sciences which is a confluence of the Materials Science, Surface Science, Applied Physics and Applied Chemistry. It has objectives in the provisions for scientific bases for the methods and materials used in thin film electronics. Additionally, it provides a sufficient data in the area of applications to permit for understanding of those aspects of the subject that might still be termed an 'art'. Thin film of metals was probably first prepared in a systematic manner by Michael Faraday using an electrochemical method. In general, thin films have a variety of applications such as in A.R. coatings, solar energy conversion, transistors, coating technology, interference filters, polarizers, narrow band filters, photoconductors, IR detectors, wave guide coatings, temperature controlled aerospace devices, photothermal solar coatings [3,4] (such as black chrome, nickel, cobalt), etc. Magnetic films in recording devices, superconducting films, thin films in microelectronics, diamond films and high wear coatings are used for engineering applications, corrosion resistive and decorative thin film coatings. The enormous flexibility offered by the thin film growth processes allows the fabrication of desired geometrical, topographical, physically crystallogra-

phic and metallurgical microstructures into two or lesser dimensions and to study the structure sensitive properties [3, 4]. In this paper therefore, the reaction mechanism and growth kinetics of PbS and $\text{Hg}_x\text{Pb}_{1-x}\text{S}$ ($0 \leq x \leq 0.2$) thin films deposited by a well set chemical bath deposition are presented elsewhere.

Deposition of the PbS and $\text{Hg}_x\text{Pb}_{1-x}\text{S}$ thin films

The substrates used for deposition were non conducting glass micro slides and conducting stainless steel strips of the dimensions mentioned earlier. A series of the $\text{Hg}_x\text{Pb}_{1-x}\text{S}$ ($0 \leq x \leq 0.2$) thin films were obtained onto the optically plane and meticulously cleaned glass and mirror polished stainless steel substrates [11-13]. For the deposition, solutions of lead acetate [$\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$], mercuric chloride (HgCl_2) and thiourea [$(\text{H}_2\text{N})_2\text{CS}$], all 1 M, were used as the source materials for Pb^{2+} , Hg^{2+} and S^{2-} ions, respectively [11-13]. PbS and $\text{Hg}_x\text{Pb}_{1-x}\text{S}$ thin films were formed by the reaction between dissolved Pb^{2+} , Hg^{2+} and S^{2-} ions in an alkaline medium ($\text{pH} = 10.5 \pm 0.1$). An appropriate quantity of lead acetate (10 ml, 1M), TEA (1 ml), mercuric chloride (1 M) and thiourea (10 ml, 1 M) solutions were mixed in a 250 ml beaker. To this, distilled water was added to make the total volume of 200 ml and stirred well to form a homogeneous solution. The glass slides were mounted vertically on a specially designed substrate holder and kept rotating by an ac / dc constant gear motor at 70 ± 2 rpm, in the reaction bath. The deposition temperature was maintained at 80 ± 0.5 °C throughout the deposition. The reaction was allowed to take place for 1 hour. The deposition takes place via the condensation of metal and sulfide ions. After deposition, the films were detached from the solution bath and washed gently with a double distilled water to remove loosely bound PbS and $\text{Hg}_x\text{Pb}_{1-x}\text{S}$ powder. Finally, the films were dried in air and preserved in a dark desiccator before characterization.

The Elemental and Compositional Studies

Compositional analysis by an EDS

An energy dispersive X-ray analysis was conducted on both PbS and HgPbS samples to determine the qualitative measure of Hg^{2+} substitution. The analysis showed that Pb^{2+} from the PbS lattice has been replaced by Hg^{2+} ions and that the content of Hg went

on increasing when Hg-content in the chemical bath was increased [5-7]. Correspondingly, Pb-content decreased, whereas S-content remained almost constant throughout the composition range. Table I

shows the contents of Pb, Hg and S in pure PbS and the composite $Hg_xPb_{1-x}S$ thin films. Fig.1 shows the EDS micrographs of various thin films under investigation.

Table I The contents of Pb, S and Hg in PbS and $Hg_xPb_{1-x}S$ ($0 \leq x \leq 0.2$) thin films as revealed by the EDS and XPS

Compositio n x	Atomic %								Ratio, $\frac{Pb}{S}$		Ratio, $\frac{Pb}{Pb+Hg}$	
	EDS			XPS					EDS	XPS	EDS	XPS
	Pb	S	Hg	C 1s	O 1s	Pb 4f	S 2p	Hg d				
0	54.63	45.37	-	72.61	17.42	5.29	4.68	-	1.2	1.13	1	1
0.035	49.41	41.93	8.66	71.19	18.68	4.89	4.39	0.85	1.18	1.11	0.851	0.85
0.2	39.49	41.66	18.85	68.96	21.62	3.42	4.17	1.83	0.95	0.82	0.677	0.65

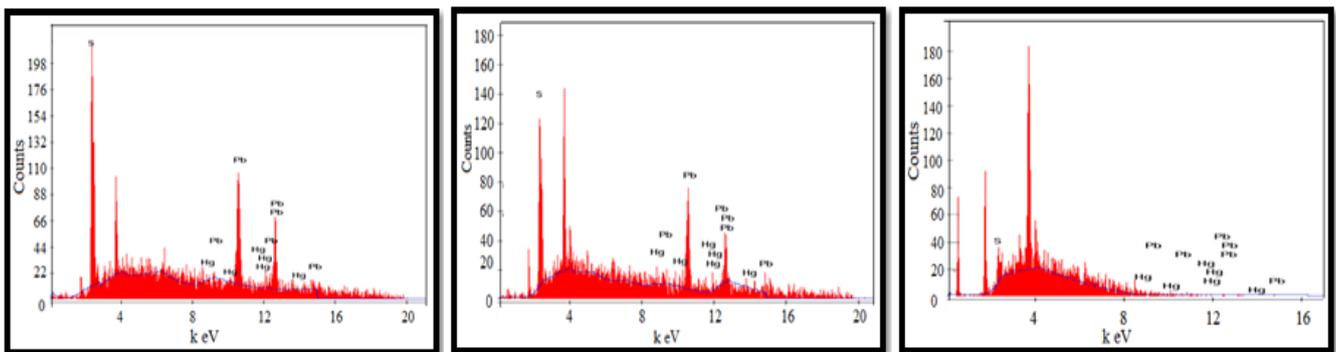


Fig1. ED's micrographs of PbS and HgPbS thin films.

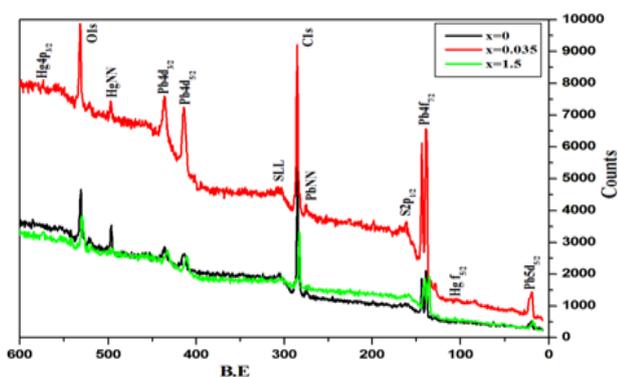


Fig2. XPS survey graphs of typical samples with: $x=0$, $x=0.035$ and $x=0.15$.

Compositional analysis by an XPS

An X-ray photoelectron spectroscopy (XPS) is widely used for the characterization of surfaces of the materials, e.g. nanoscale advanced materials, electrodes of fuel cells, photo catalysts, etc. For both conductive and nonconductive samples, XPS can meet the strong requirement for chemical state analysis. The measurement of the thickness of a surface film is also a common requirement met with XPS [22].

The development and characterization of the materials therefore received considerable attention. One desire for the analysis of these materials is the elemental depth profiles within these thin films. For this analysis, the maximum entropy method (MEM) has been explored to estimate the depth distribution. This is done by angle-resolved XPS (ARXPS) [18-26]. The estimation of the background generated by energy loss of the electrons from the photoelectron peak has also been applied if the thickness of the thin film is sufficiently less than approximately 3 times the inelastic mean free path of the observed photoelectron peak [27]. When the thickness of a thin film on a substrate approaches this thickness, a sputter etching method is generally applied to evaluate the elemental composition profile and ideally the chemical state of these elements. Table I shows the contents of Pb and S in PbS and Pb, Hg and S in composite $Hg_xPb_{1-x}S$ thin films. Fig.2 and fig.3 shows the XPS micrographs for three typical compositions.

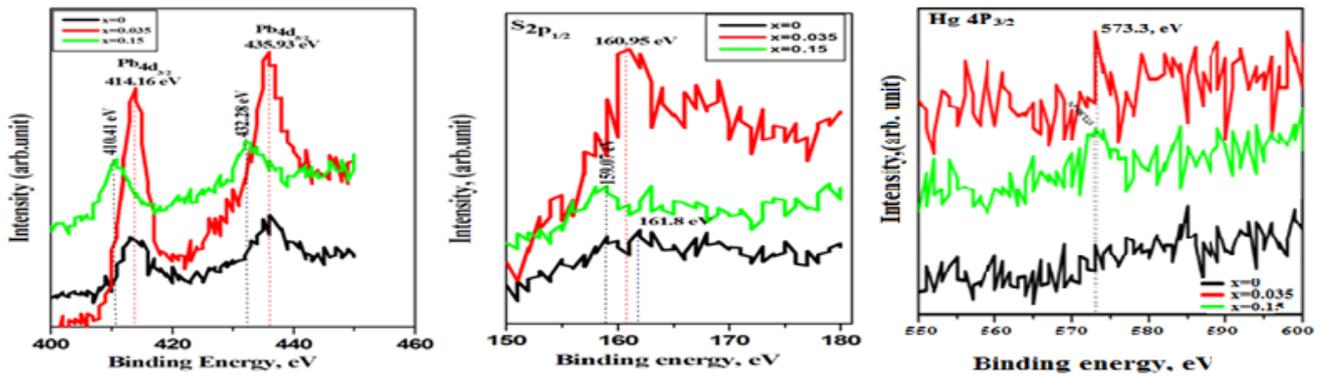


Fig.3 High-resolution XPS spectra for: (a) Pb 4d_{3/2}, (b) S 2p_{1/2} and (c) Hg 4p_{3/2} regions for HgPbS thin films.

Survey scans (Fig.2) were carried out and showed the presence of Pb_{4d}, Pb_{5d}, Pb_{4f}, S_{2p}, and Hg_{4p}, Hg_f core level signals. High-resolution XPS (HRXPS) (Fig.3) spectra of Pb_{4d(3/2,5/2)}, S_{2p(1/2)}, and Hg_{4p(3/2)}, Hg_{f(5/2)} levels of HgPbS nanoparticles are shown in fig.3 and the FWHM for the signals are less than 1 eV for all the signals and the binding energies (BEs) have been referenced to C1s.

The Pb_{4d} spectrum has a double feature due to spin orbit coupling resulting in 4d_{3/2} and 4d_{5/2} signals at 414.16 eV and 435.93 eV, respectively. A peak separation of 21.77 eV is an indicative of Pb (II). The signal observed at 160.95 eV is due to S_{2p(1/2)} binding energy and that observed at 573.3 eV is due to Hg_{4p(3/2)}. XPS investigations on α -HgS and β -HgS have shown that the two forms show similar binding energies [28] and it is not possible to differentiate them based on XPS. The binding energies reported for Hg, Pb and S in these studies are in consonance with those reported earlier within 1 eV [29]. Measurements of the Pb_{4d}, Hg_{4p} and S_{2p} peak areas showed the ratio of Pb to S as 1.11 (for x= 0.035), which is very close to the ratio determined from EDS measurements (1:18). Our results are very similar to the results of Yang et al [28] for CuInSe₂ material as far as percentages of the constituents are considered and referred to C1s and O1s. These observations are in close consonance with that of the expected stoichiometry (1:1). No peaks corresponding to the impurities such as those of oxides or metallic lead (Pb) and mercury (Hg) are observed in the spectrum indicating high purity of the HgPbS product.

CONCLUSION

Among the various methods available to deposit PbS and Hg_xPb_{1-x}S thin films, our indigenously developed chemical bath deposition (CBD) process must be ranked conceptually the simplest, easiest and having meaningless consumption. The various preparative parameters like deposition temperature, pH of the reaction mixture, deposition time and speed of the substrate rotation can easily be manipulated and optimized to obtain excellent quality thin, relatively uniform, smooth, and physically adherent and diffusively reflecting thin films. The binary and multi component homogeneous layers of controlled composition can be made feasible with this technique.

Conflicts of interest: The authors stated that no conflicts of interest.

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