

Influence of a polymeric solution buffer layer on the chemical bath deposition of polycrystalline PbS films

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Polycrystalline thin films of PbS grown on glass substrates previously coated with PbS colloidal particles in a polyvinyl alcohol solution were obtained by chemical bath deposition (CBD). The X-ray diffraction procedures showed evidence of polycrystalline films of cubic PbS with a preferred normal orientation of the planes [100] with the growth direction. The film texture showed a strong influence of the initial conditions of the surface. Moreover, changes in colour, morphology and grain size of the films were observed by optic and atomic force microscopy (AFM). Rutherford backscattering spectrometry (RBS) showed a dependence of the thickness and roughness of the PbS films with the growth initial conditions. A kinetic growth model is proposed to explain the changes in the structure and morphology of the PbS.

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1 Introduction

Polycrystalline PbS thin films are currently attracting general interest, mainly due to their potential as infrared detector materials [1–3]. These films can be obtained by several methods [4, 5], but chemical bath deposition (CBD) is just one of the more utilized due to its low cost and the quality of the obtained films. The manufacture of advanced electronic devices with desired physical properties requires the availability of growth semiconductor films with controllable compositions, sizes, shapes and orientations. Indeed, it is known that photosensitive response of the PbS films depends on its structural characteristics [1, 6]. Oriented crystallization of nanoparticles was observed in the growth of PbS nanocrystals mediated by surfactant polymer templates [7–10].

In this paper, we study the influence of a buffer thin layer of polymeric solution with PbS colloidal particles on the growth of polycrystalline thin films of PbS by chemical bath deposition (CBD). Elemental composition, composition profile distribution and stoichiometry of PbS thin films were determined by Rutherford backscattering spectrometry (RBS). In addition, for a better morphological characterization, the topography and structure of the films were characterized by grazing incidence X-ray diffraction data (GIXRD) and atomic force microscopy (AFM).

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2 Experimental details

The method for growing PbS thin films has been described in detail elsewhere [6]. Before the introduction of the glass substrates into the growth solution, it were: A) mechanically cleaned with detergent; B) (A), and immersed in a solution of polyvinyl alcohol, thiourea, SH_2 and $\text{Pb}(\text{NO}_3)_2$ for 24 h; and C) (B), and dried in air for 10 min. Afterwards, the substrates are introduced immediately in the chemical bath for 50 min. The samples were identified by the corresponding letter to the initial treatment of the substrate surface (A, B and C).

The RBS analysis of the samples was performed with 2.0 MeV 4He^+ ions using a 4 MV Van de Graaff KN-4000 accelerator. A surface barrier detector with 18 keV FWHM was positioned at an angle of 165° . The RBS spectra were analyzed using the RUMP code [11]. Every single step of the growth process was studied (substrate, treated substrate, seeding process and PbS deposited layer), making possible a better simulation of the multilayer RBS spectra of the analyzed samples.

The AFM images were obtained with a Nanoscope III microscope (Digital instruments) operating in tapping mode. The grain size and shape measurements were determined by applying the Watershed technique [12], together with a shape factor algorithm [13]. The shape factor, defined as $\text{SF}=4\pi A/P^2$, P being the perimeter of the grain and A its area, was used to obtain information about the shape of a grain. The rugosity values (R) were also determined.

Grazing incident X-ray diffraction measurements (GIXRD) were performed in the PbS films using the $\text{CuK}\alpha$ radiation of a ω -diffractometer (Siemens model D5000). The detector was equipped with a Soller slit for thin films and a LiF monochromator.

3 Results and discussion

All the PbS films had black color, however they become darker and with a mirror-like surface (from A to C) in dependence of the substrate treatment, which was confirmed by optical and atomic force microscopies.

It was detected that a great amount of precipitated material appears into the bath initially, when mixing the components of the growth solution. Then, the precipitation process diminishes gradually and the growth solution becomes transparent. If a substrate with the treatment A is introduced into the bath after the initial precipitation process (when the growth solution is transparent), the growth of PbS film generally does not take place. The growth of the PbS film on substrates with these treatments was observed when the substrates were introduced in the growth solution during the initial stage of the mix, when the precipitation process had not finished. Therefore, this condition is necessary to obtain a catalytic surface on the substrate. On the other hand, the PbS film growth always takes place on a substrate with the treatment B or C. This is due to the existence PbS germs on the substrate as a result of the seeding process. Therefore, the thin film growth occurs if a catalytic surface is available on the substrate surface, even though the precipitation does not take place into the bath.

Figure 1 shows the RBS spectra of all the analyzed samples. The film thickness values are shown in Table 1. The films have a constant Pb:S 1:1 stoichiometry through the thickness. However, the left tail of the Pb signal peaks reveals differences in the film roughness; longer left tail means higher roughness of the films. In this sense, the sample B has the larger roughness value and the sample C the lowest one. The thickness and the roughness are parameters that also reveal peculiarities of the deposition process. The deposition over substrates with the treatments A does not take place unless a nucleation layer is created and a catalytic surface of the semiconductor is available. In the cases B and C the deposition can occur almost once the substrate is introduced into the growth solution. Thus, the beginning of deposition process in the case A is retarded as compared with cases B and C. Moreover, the growth in the case A is affected by the poor adherence of the PbS clumps on the glass substrate. For these reasons samples B and C are thicker than sample A (Table 1).

In Fig. 2 are shown the X-ray diffraction pattern of the PbS thin films. The XRD analysis showed a galena type cubic structure for all the samples. In addition, the intensity distribution of the X-ray diffrac-

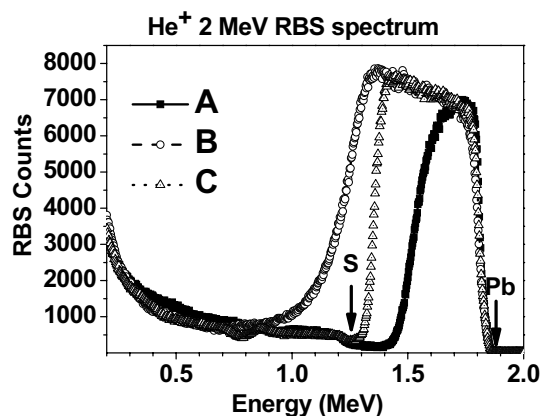


Fig. 1 RBS spectra of the PbS/glass analyzed films. The arrows indicate the starting position of the Pb and S elements.

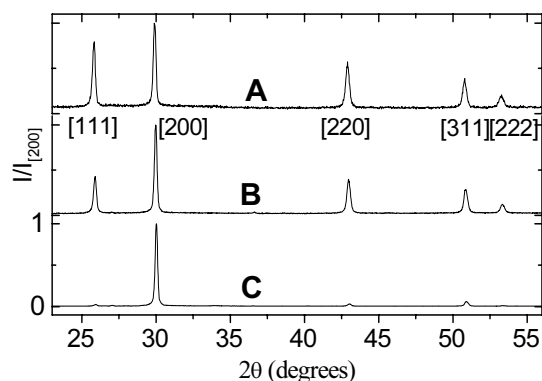


Fig. 2 Normalized X-ray diffraction pattern of PbS thin films with different substrate treatments.

tion peaks deviates drastically from the characteristic distribution of the bulk PbS powders, with the exception of the sample A. It can be noticed that the relative intensity of (200) diffraction peak with respect to the other peaks is much stronger in the other samples (B and C). The analysis of the intensity distribution evidences a preferred orientation with (100) diffraction planes parallel to the substrate surface, in the way as the substrate is coating with colloidal PbS particles in a polyvinyl alcohol solution and then dried. From these results is confirmed that the film texture has a strong influence on the initial conditions of the substrate surface. The more oriented film corresponds to the sample C.

The orientation process could be the result of long range interactions among substrate, polymeric chains, water molecules and PbS germs. Our results were independent of the way as the substrate surface was dried, even when the dried process was carried out at vacuum. Moreover, when introducing a substrate in the growth solution when the surface is not completely dry (condition C), the obtained layer has an inhomogeneous coloration. In the regions where the surface was even wet the layer was dark gray and rough, and in the dry regions was black and with a mirror-like surface. The structural characteristics of these regions (wet and dry) are in correspondence with the ones obtained for the conditions B and C, respectively. Therefore, the orientation process could be related with capillary forces, which are more intense in the dry front.

Table 1 Thickness (as measured by RBS); mean grain size, roughness R ($30 \times 30 \mu\text{m}^2$), and shape factor SF ($5 \times 5 \mu\text{m}^2$) for the analyzed PbS samples.

Sample	RBS Thickness ($10^{15} \text{ atom/cm}^2 \mid \text{nm}^*$)	Mean grain size (nm)	R (nm)	SF
A	$1650 \pm 10 \mid 460 \pm 3$	950 ± 60	100	0.58 ± 0.01
B	$3500 \pm 10 \mid 975 \pm 3$	680 ± 100	225	0.4 ± 0.02
C	$2650 \pm 10 \mid 783 \pm 3$	500 ± 85	34	0.63 ± 0.01

* Thickness values in nm were calculated considering the PbS density values as $3.5885 \times 10^{22} \text{ atom/cc}$.

Figure 3 shows the AFM images of the PbS thin films. Watershed (WS) patterns were generated from this AFM images to identify the grain boundaries. The roughness values R and shape factor SF values are also presented in Table 1. A significant difference in the films topography is obtained in dependence of the condition of the initial growth surface. The SF values are roughly close to $\text{SF} = 0.60$, that corresponds to a triangular shape of the grains. Previously, highly oriented triangular PbS crystals were reported using the Langmuir-Blodgett technique [14]. The grain size differences among the samples with

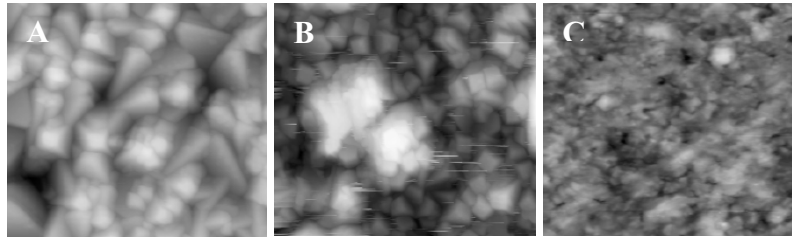


Fig. 3 AFM images of the PbS thin films ($5 \times 5 \mu\text{m}^2$).

respect to the influence of the initial stage of the growth surface can be explained attending to the differences in the growth during the nucleation or induction period. When the substrates are immersed into the growth solution, the first monolayer of PbS is formed from the nucleation centres or PbS germs created during the initial precipitation process (condition A) and during the seeding process (conditions B and C). By controlling the surface concentration of germs, it is possible to control the grain size and the grain size distribution of the final product. Moreover, the amount of effective nucleation centres created during the initial precipitation process is smaller (treatment A) than the amount created in the seeding process (treatments B and C), which is confirmed from the mean grain size results (Table 1).

4 Conclusions

Polycrystalline films of cubic PbS with a preferred (100) lattice plane orientation parallel to the substrate surface were obtained by chemical bath deposition, by coating the surface of glass substrates with a colloid in a polymeric solution. The orientation increases when a thin layer of polyvinyl alcohol with PbS colloidal particles onto the substrate is dried. Changes in morphology, composition, grain size and thickness were characterized by different techniques. The results of this work give some enlightenment about the character of the interactions related to the orientation process of the germs of PbS in the interface and propose a simple way to obtain oriented-semiconductor-films.

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References

- [1] P. Kottiyal, B. Gosh, and R.Y. Deshpande. *J. Phys. D: Appl. Phys.* **13**, 869 (1980).
- [2] Bianchetti, H. Canepa, J. Casanova, R. D'Elia, and G.R. Mahrwon Staszewski, *Rev. Teleg.-Elect.* 194 (1984).
- [3] R.H. Bube, *Photoelectronic Properties of Semiconductors* (Cambridge University Press, 1992), p. 205.
- [4] R. Resch, G. Friedbacher, M. Grasserbauer, T. Kannianien, S. Lindros, M. Leskela, and L. Niinisto, *Appl. Surf. Sci.* **120**, 51 (1997).
- [5] A.A. Preobrajenski and T. Chasse, *Appl. Surf. Sci.* **142**, 394 (1999).
- [6] E. M. Larramendi, O. Calzadilla, A. González-Arias, E. Hernández, and J. Ruiz-García, *Thin Solid Films* **389**, 301 (2001).
- [7] F. Rosei, M. Schunack, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim, and F. Besenbacher, *Science* **296**, 328 (2002).
- [8] S. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, and S. Mashiko, *Nature* **413**, 619 (2001).
- [9] T. A. Jung, R. R. Schlittler, J. K. Gimzewski, H. Tang, and C. Joachim, *Science* **271**, 181(1996).
- [10] T. W. Fishlock, A. Oral, R. G. Egdell, and J. B. Pethica, *Nature* **404**, 743 (2000).
- [11] L.R. Doolittle, *Nucl. Instrum. Methods B* **9**, 344 (1985).
- [12] J. Serra, *Image Analysis and Mathematical Morphology* (Academic Press, London, 1988), p. 260.
- [13] M. Cremona, M. H. P. Mauricio, L. C. Saarda do Carmo, R. Prioli, V.B. Nunes, S.I. Zanette, A.O. Caride, and M.P. Albuquerque, *J. Microscopy* **197**, 260 (2000).
- [14] X.K. Zhao, J. Yang, L.D. McCormick, and J.H. Fendler, *J. Phys. Chem.* **96**, 9933 (1992).