

## INFLUENCE OF LASER FLUX DENSITY ON THE SURFACE MORPHOLOGY OF LEAD SULPHIDE THIN FILMS

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Structural quality of lead sulphide thin films synthesized on glass substrate by ultraviolet pulsed laser deposition with different flux density has been studied. Confirmation of phase of this compound was estimated using XRD data. Surface morphology of the samples was examined using AFM. Optical properties were studied at room temperature by reflectance measurements. Studies revealed that there is an improvement in the structural quality with increasing the laser flux density in some range. However, too high laser flux density could lead to the degradation in structural quality of thin film. Reflection data shows a reflectance of the film depends upon the flux density of the laser also. SEM investigation of the samples reveals that the surface morphology of the films and confirm the AFM results.

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### 1. Introduction

The use of thin film polycrystalline semiconductors has attracted much interest in recent years, and has found many applications in various electronic devices. The main reason in this interest is the low costs production. As result, this class of semiconductor materials is now occupying an outstanding situation in the basic research and solid state technology. In this category, the IV–VI compounds often named as lead salts have been considered as the most attractive semiconductors, because of their various applications in the infrared technology. These materials are produced in the crystalline and polycrystalline forms and used as detectors, emitters, as well as solar control coatings [1–5]. In addition, the rock salt structure lead chalcogenides, which are known as narrow gap semiconductors and their alloys, have been applied in the long wavelength imaging [6], and thermo-photovoltaic energy converter [7]. From lead salt family material, the PbS is known as a famous compound and is used as IR detector. This material is fabricated mostly in the form of sensitized polycrystalline film.

Nevertheless, it shows a lower crystallinity, with respect to other semiconducting compounds. Therefore, they are highly defective and their structural properties are mainly linked to the growth processes used for the layer deposition [8,9]. Among the new and up to date techniques used for thin film deposition, pulsed laser ablation (PLA) is one of the most versatile methods to obtain layers of several materials that can be processed into a pellet target. One of the important features of this method is based on the possibility of maintaining the stoichiometry of the ablated target in the deposited layer [10–12]. The target ablated by laser can create a highly energetic growth precursor, leading to non equilibrium growth conditions. Therefore high quality

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films can be obtained at a fairly low substrate temperature. Furthermore, PLD is more flexible than other conventional techniques, and it is feasible to control the thickness of films [13, 14]. With this aim, in the current work, we study the influence of the laser flux density on the crystalline quality, the surface morphology, PbS thin films on glass substrate grown by pulsed laser deposition.

## 2. Experimental

The UV-PLD is performed with a KrF laser operating at 248nm with a repetition rate of 10 Hz. PbS films were deposited on corning glass substrates by ablating stoichiometric home-made targets. During the film deposition the substrate temperature and ambient pressure were kept at 400°C and  $10^{-5}$  torr respectively. In order to investigate the effect of laser flux density on the surface morphology and structural properties of PbS thin film, a series of samples were deposited using the laser flux density of 2.5 J/cm<sup>2</sup>, 3.5 J/cm<sup>2</sup> and 4.16 J/cm<sup>2</sup>. X-ray analysis was performed by using a Bruker D8 Advance diffractometer using CuK<sub>α</sub> ( $\lambda = 1.54 \text{ \AA}$ ) radiation. Surface morphology of the deposited films was studied using atomic force microscopy (NT-MDT Ntegra). Room temperature reflectance spectra were measured in the spectral range from 1500 to 2500 nm using a UV-Vis-NIR spectrophotometer (Varian Cary 5000). Microstructural investigations were carried out by scanning electron microscopy by using the FESEM- FEI Quanta 200.

## 3. Results and discussion

XRD patterns of the samples are shown in Fig.1. Three diffraction peaks correspond to (111), (200) and (220) planes of the hexagonal crystalline lead sulphide with reflections positioned at  $2\theta = 26.06^\circ$ ,  $30.12^\circ$  and  $43.39^\circ$  respectively. As shown in Fig 1, the diffraction peaks of the PbS films formed at the laser incident flux density of 2.5 J/cm<sup>2</sup> are broad and weak. With increase in the laser incident energy from 2.5 J/cm<sup>2</sup> to 3.5 J/cm<sup>2</sup> PbS diffraction peaks become more intense and sharper. It is an indication of the improved crystalline quality of the samples. As the laser flux density is increased further to 4.16 J/cm<sup>2</sup>, the intensity of diffraction peaks became weaker slightly, indicates that the crystalline quality of the samples degrades. In laser ablating and sputtering processes, a large amount of ions in the plasma are present. The emitted species appears to be highly peaked normal to the target surface. Kinetic energy of plasma species increases with increase in the laser flux density. When the plasma species reached upon the substrate surface, they congregated and grew as dense aggregates of independent nanoparticles with different sizes to form thin films. Improvement in the crystallinity of the films deposited at moderate laser flux density was due to sufficient molecular mobility that in turn allows orientation of the molecules into a crystalline conformation [15]. However, too high laser incident flux density raises kinetic energy of electrons and thus, may lead to too high plasma density. As the laser incident energy was increased to 4.16 J/cm<sup>2</sup>, the direct bombardment of the ions led to induce a large structural disorder during film growth.

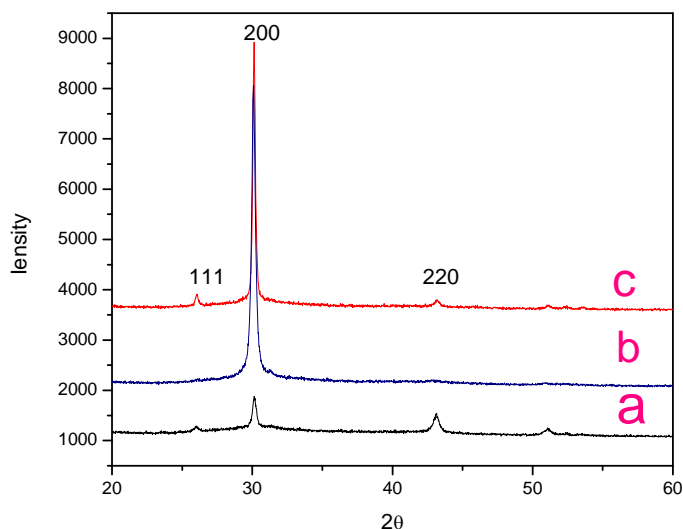


Fig. 1. X-ray diffraction pattern of lead sulphide thin films formed at different flux density (a)  $2.5 \text{ J/cm}^2$  (b)  $3.5 \text{ J/cm}^2$  and (c)  $4.16 \text{ J/cm}^2$

AFM images for samples deposited at the laser flux density of  $2.5$ ,  $3.5$  and  $4.16 \text{ J/cm}^2$  are shown in Fig.2. The AFM micrographs confirm that the films have a smooth surface with good adherence to the substrate and the spherical agglomerates have a narrow size distribution. With increase in laser flux density from  $2.5$  to  $3.5 \text{ J/cm}^2$  there is an increase in particle size, and it is relatively uniform as shown in Fig. 2(b). Further increase in laser flux density to  $4.16 \text{ J/cm}^2$  results in relatively large size particles leading to increased surface roughness of the film as depicted in Fig.2(c). The root-mean square roughness of the samples were measured over  $2.0 \times 2.0 \text{ }\mu\text{m}^2$  scanning range, and found  $15.3$ ,  $10.8$  and  $14.1 \text{ nm}$  for the samples with laser flux density of  $2.5$ ,  $3.5$  and,  $4.16 \text{ J/cm}^2$  respectively. During the film growth, species (ions and neutrals) are propagating with various velocities reaching the surface of the film. The higher energy component of plume was related to ions, while neutral particles can obtain their velocities by collisions with fast ions. When the plasma formed under these conditions of the laser incident energy of  $4.16 \text{ J/cm}^2$ , led to the ions with too high kinetic energy. The atoms on the growing films could be bombarded and sputtered by incident ions with too high kinetic energy. While, a few large size neutral particles or debris could be emitted from the target under very high laser incident energy ablation, results in too coarsening and the large non uniformity of particle size. A destructive effect due to high energy could lead to deterioration of the growing films.

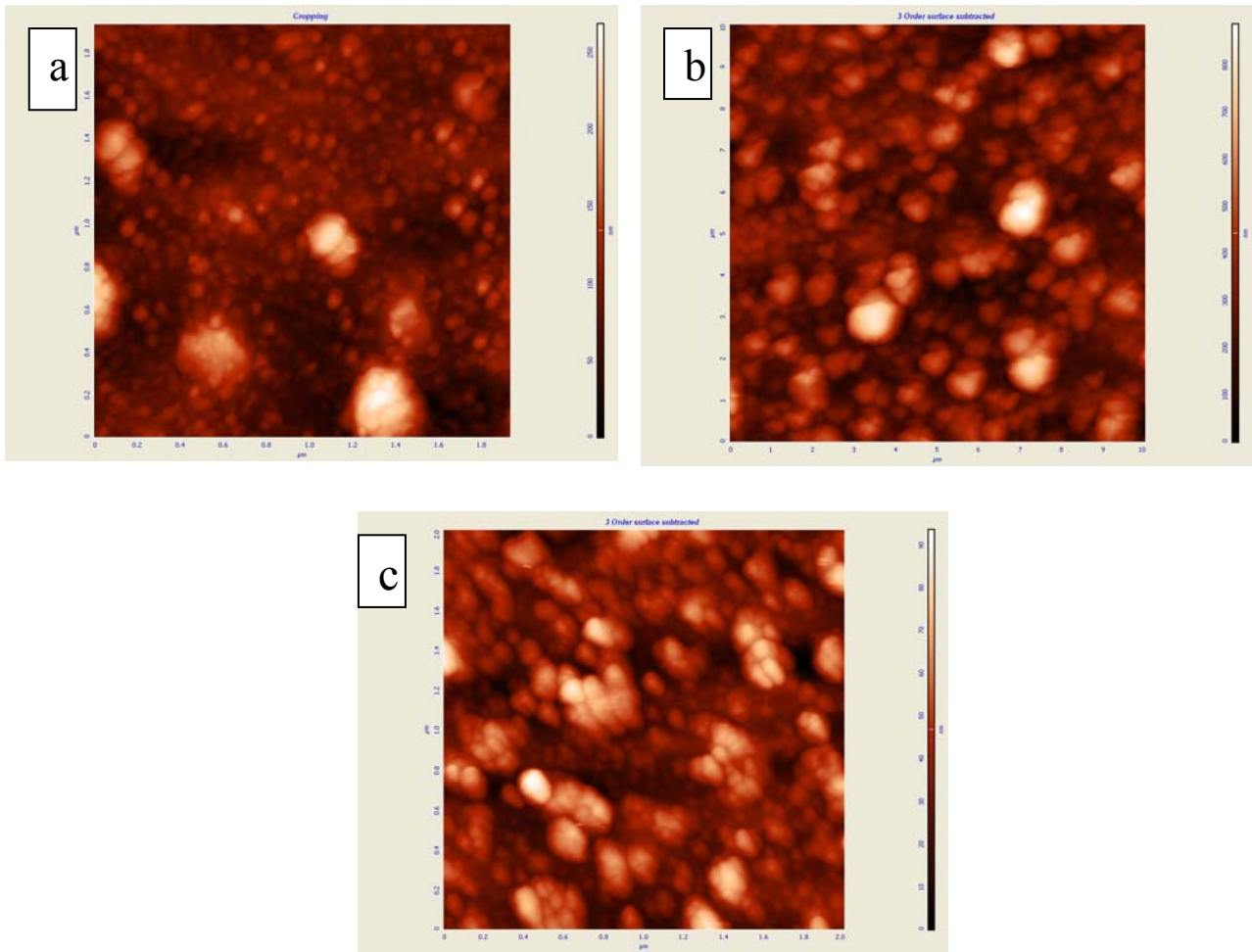


Fig. 2. Surface topography of lead sulphide thin films formed at different flux density (a)  $2.5 \text{ J/cm}^2$  (b)  $3.5 \text{ J/cm}^2$  and (c)  $4.16 \text{ J/cm}^2$

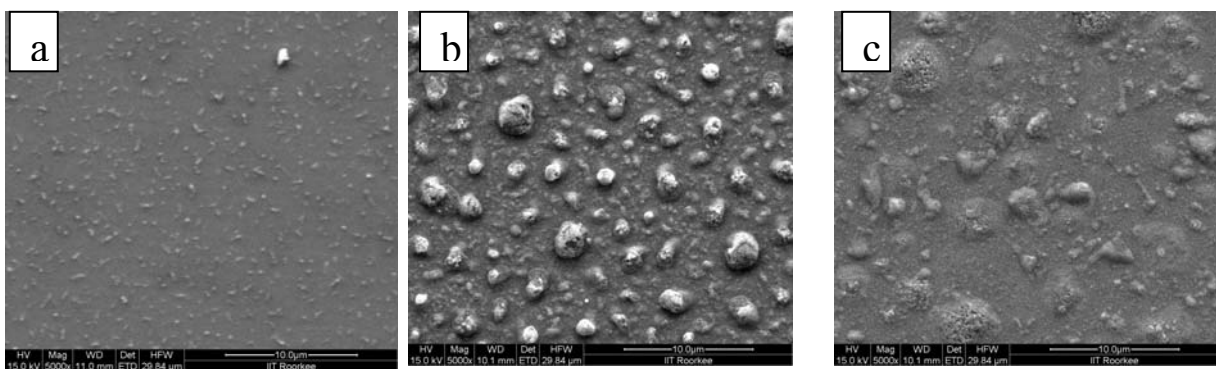


Fig. 3. Scanning Electron Micrograph of Lead Sulphide Thin Films with the different Flux density (a)  $2.5 \text{ J/cm}^2$  (b)  $3.5 \text{ J/cm}^2$  and (c)  $4.16 \text{ J/cm}^2$

Fig. 3 shows the scanning electron micrographs (SEM) micrographs evidently show the microstructural homogeneities and remarkably different morphologies for PbS films prepared with different laser flux density of  $2.5$ ,  $3.5$  and  $4.16 \text{ J/cm}^2$  at  $400^\circ\text{C}$ . All samples show SEM images justify the AFM data. We do not observe any stepwise change in the contrast across the

diameter of the crystals; this suggests a random distribution, instead of any heterostructured crystal embedded in the film or a phase separation within the crystal.

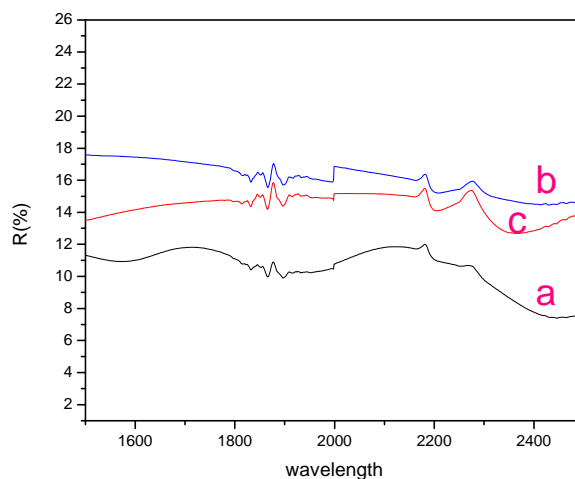


Fig. 4. Refraction Spectra of lead sulphide thin films formed at different flux density (a)  $2.5 \text{ J/cm}^2$  (b)  $3.5 \text{ J/cm}^2$  and (c)  $4.16 \text{ J/cm}^2$

Reflectance measurements were done at room temperature with different flux density between the 1500nm to 2500nm wavelength range. Fig.4 shows the percentage of the reflection of the sample **a** is low corresponding to the others. While reflectance increase with flux density of the laser up to  $3.5 \text{ J/cm}^2$ . But at the high flux density the reflectance goes down due the increase in the roughness of the film. At flux density of approximately  $3.5 \text{ J/cm}^2$  the number of fast particles (atoms and ions) decreases and that of slow particles (cluster and droplets) increases. As a result, at flux density of approximately  $4.16 \text{ J/cm}^2$ , the films are preferentially formed by clusters and droplets, which cause grain boundaries during the film deposition [16]. These grain boundaries give rise internal scattering of light on the surface. At the same time with increasing laser flux density from  $3.5$  to  $4.16 \text{ J/cm}^2$  reflectance intensity decreases that can be attributed to the increased surface roughness with increase in laser flux density.

#### 4. Conclusions

The above results prove that the crystallinity, the surface quality and the optical properties of PbS thin film is dependent on the laser flux density and the optimal incident energy is around  $3.33 \text{ J/cm}^2$ . Surface morphology of the PbS thin films is strongly dependent on the laser incident flux density and is confirmed via R value curve in addition to AFM micrographs. A slight decrease in reflectance is observed with increase in laser flux density.

#### References

- [1] T.H. Johanson, SPIE **443**, 60 (1981).
- [2] M. Agne, A. Lambrecht, U. Schiessi, M. Tacke, Infrared Sci. Technol. **35**, 47 (1994).
- [3] Z. Bielecki, et al., Proceedings of the 12th European Conference on Solidstate Transducers and the Ninth UK Conference on Sensors and their Applications, **2**, 941 (1998).
- [4] A. Lee, SPIE **3857**, 92 (1999).
- [5] B. Thargaraju, P. Kaliannan, Semicond. Sci. Technol. **15**, 849 (2000) .

- [6] H. Zogg, et al., *Opt. Eng.* **33**(5), 1440 (1994).
- [7] T.K. Chaudhuri, *Int. J. Ener. Res.* **16**(6), 481 (1992).
- [8] M. Gunasekaran, and M. Ichimura, *Jap. J. Appl. Phys.*, 44, 7345 (2005).
- [9] P. K. Schenck, M. D. Vaudin, D. W. Bonnell, J. W. Hasti, A. J. Paul, *Appl. Surf. Sci.*, **655** 127 (1998).
- [10] B. Ullrich, H. Sakai, and Y. Segawa, *Thin Solid Films*, **385**, 220 (2001).
- [11] H. S. Kwok, J. P. Zhang, S. Witanachchi, P. Mattocks, L. Shi, Q. Y. Ying, X. W. Wang, and V. T. Shaw, *Appl. Phys. Lett.*, **52**, 1095 (1988).
- [12] K. T. Hillie, C. Curren, H. C. Swart, *Appl. Surf. Sci.*, 177 (2001) 73.
- [13] A. Gupta, D. B. Chrisey, G. K. Hubler (Eds.) *Pulsed Laser Deposition of Thin Films*, Wiley, New York, 1994, p.265.
- [14] J. T. Chung, and J. Madden, *J. Vac. Sci. Technol. B*, **5**, 705 (1987).
- [15] X. L. Tong, D. S. Jiang, Q. Y. Yan, W. Bhu, Z. M. Liu, M. Z. Luo, *Vacuum*, **82**, 1411 (2008).
- [16] H. Zhao, E. P. Douglas, B. S. Harrison, and K. S. Schanze, *Langmuir*, **17**,8428 (2001).

