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## Effect of selenium layer thickness on structural and optical properties of nanocrystalline PbSe multilayer thin films

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### ABSTRACT

Lead selenide multilayer thin films were prepared by thermal evaporation technique by successive coatings of Lead and Selenium layers. The layer thickness of Se varies from 10 to 40 nm whereas 10 nm layer thickness of Pb maintained at the cases. The polycrystalline nature with cubic structure of all as deposited films observed from X-Ray diffractogram. The lattice constant of  $1.53 \text{ \AA}$  observed in all the films. The absorption shift toward shorter wavelength shows the presence of nanoparticle trapped at the interfaces of Lead and Selenium. The rise in transmittance spectra around 1585 nm indicates the nanocrystalline effect of the prepared films. To confirm the quantum confinement effect of as deposited films the Brus and quantum mechanical modal calculation were done from energy shift and are well agreed with each other and the calculated particle size varies from 1.2 to 2 nm

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### KEYWORDS

PbSe;  
Multilayer;  
Pb/Se layer thickness;  
XRD;  
UV-Vis-NIR.

### INTRODUCTION

Metal chalcogenides like Sulfides, Tellurides and Selenides are of great importance for researchers because they are potential candidates for optoelectronic applications<sup>[1,2]</sup>. Lead Selenide (PbSe) thin films are one of the most promising materials due to its narrow band gap (0.27 eV at room temperature) and very large Bohr radii of 46 nm<sup>[5]</sup>. Semiconductors like PbSe quantum dot produce as many as seven Excitons from one high energy photon of sunlight (7.8 times the band gap energy). In electronic applications they have proven to operate like single electron transistor (SET) and show the Coulomb blockade effect<sup>[9]</sup>. The multilayer thin films are smaller, faster and more efficient in

electronic and optoelectronic devices. They produce the change the potential energy of electron and holes at the interfaces. Defect and the impurities will provide the new state of the electrons and holes, life time and transition energies. Spray pyrolysis, sputtering, electro deposition, vacuum evaporation, chemical vapour deposition and chemical bath deposition are widely used techniques for deposition of thin films. Particularly vacuum evaporation is used to prepare the multilayer thin films and hetero structures. Also it is possible to control each and every layer thickness during multilayer preparation. In this paper, we report thermally evaporated PbSe multilayer thin films and effect of Pb/Se layer thickness on structural and optical properties.

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### EXPERIMENTAL

Lead Selenide multilayer thin films were prepared by successive coatings of Pb and Se by thermal evaporation technique at the vacuum of  $2 \times 10^{-5}$  torr. The source materials of Lead and Selenium were placed in two individual molybdenum boats (200 amps). The ultrasonically cleaned glass substrate was placed in the substrate holder directly above the source material nearly 17 cm. Now the source material of Lead was evaporated first with the thickness of 10 nm and then the Selenium was evaporated with the thickness of 10 nm. The process was repeated for five layers with the total thickness of 50 nm. The thickness of each layer was monitored by quartz thickness monitor and the constant rate of evaporation ranging  $1-3 \text{ \AA}/\text{sec}$  is maintained throughout the experiment. Similarly the multilayer films prepared with different layer thickness such as 20 nm, 30 nm and 40 nm of Selenium and the Pb

layer thickness maintained as 10 nm in all the films. Finally the PbSe multilayer thin films with 50 nm, 70 nm, 90 nm and 110 nm were analysed using X-Ray Diffractometer ((Shimadzu XRD-6000) for structural studies and UV-spectrophotometer (Jasco-570 UV/VIS/ NIR) for optical studies.

### RESULT AND DISCUSSION

#### X-ray diffraction analysis

The X-Ray diffractogram of as deposited PbSe multilayer thin films with different Pb/Se layer thickness are shown in figure 1. A strong peak with  $2\theta$  value about  $29^\circ$  correspond to the (2 0 0) plane of PbSe multilayer is present in all four samples. This peak in these XRD could be indexed to cubic structure of PbSe and the  $2\theta$  value is consistent with the value in standard JCPDS card. The films prepared

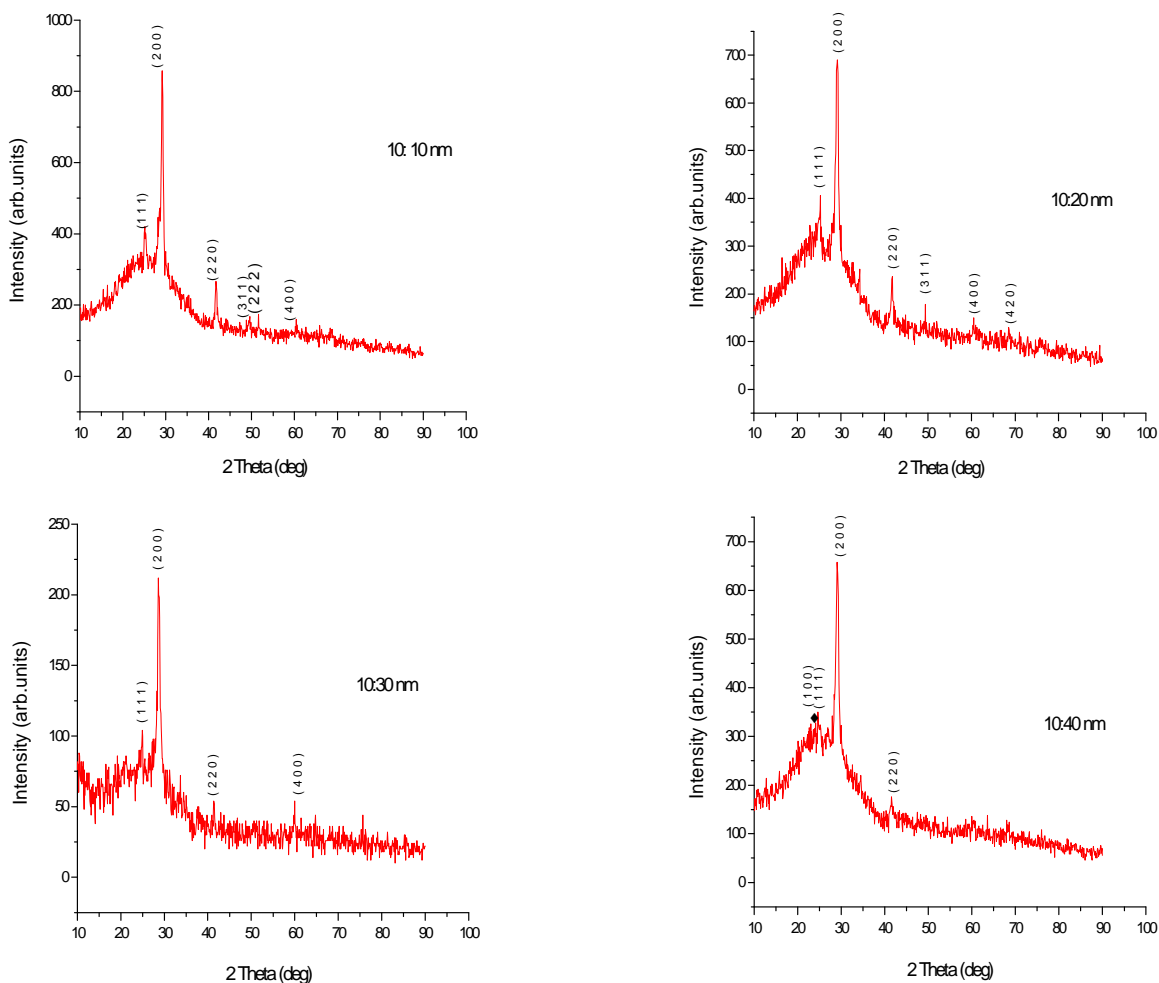


Figure 1 : XRD patterns of PbSe multilayer thin films with different Pb/Se layer thickness.

with the layer thickness of 10:20 nm and 10:40 nm (each layer of Pb and Se) have the strong peak with intensity around 650 (arb.units) and the layer thickness of 10:10 nm and 10:30 have the intensity of 220 and 880 respectively. The plane (1 0 0) corresponds to Selenium observed at the films prepared with 40 nm of each layer thickness of Selenium.

The particle size of as deposited films calculated using Debye –Sherrer’s equation which is given by,

$$D = \frac{K \lambda}{\beta \cos \theta} \quad (1)$$

Where K is the constant taken to be 0.94,  $\lambda$  is the wavelength of X-Ray used,  $\beta$  is the full width half maximum of the peak (FWHM) and the  $\theta$  is the glancing angle. The lattice parameter (a) are calculated in this case by means of the plane-spacing equation for cubic crystal, which is given by,

$$a = d / \sqrt{(h^2 + k^2 + l^2)} \quad (2)$$

TABLE 1 : Structural parameters of PbSe multilayer thin films

Layer thickness	d (Å <sup>3</sup> )	2 $\theta$ (°)	FWHM (β)	D (Å <sup>2</sup> )	a (Å <sup>3</sup> )	$\rho$ (10 <sup>15</sup> ) lines/m <sup>2</sup>	$\epsilon$ (10 <sup>-3</sup> )
10:10 nm	3.062	29.14	0.6682	122	1.53	23	2.82
10:20 nm	3.06813	29.08	1.0105	81	1.52	52	4.26
10:30 nm	3.0457	29.3	0.6000	136	1.53	19	2.53
10:40 nm	3.07193	29.04	1.1847	69	1.53	81	5.00

The grain size of 8 nm and 6 nm was observed at the films prepared at 20 and 40 nm layer thickness of Selenium with 10 nm Pb layer whereas the films prepared with 10 nm and 30 nm of Selenium layer thickness have the grain size of 12 and 13 nm respectively. The lattice constant of 1.5 Å° observed in all the films. The dislocation density and micro strain were calculated and tabulated in 1. The corrected values of lattice constants are estimated from the Nelson–Riley plots (Figure 2). The Nelson–Riley curve is plotted between the calculated ‘a’ for different planes and the error function

$$f(\theta) = 1/2 (\cos 2\theta / \sin \theta + \cos 2\theta / \theta) \quad (3)$$

It is observed from the Nelson-Riley plots that the accurate value of lattice constant using the equation 2 is 1.7 Å° whereas the experimental value in this case is 1.5 Å° are shown in figure 2a. Figure 2b shows the plots between the observed lattice constant with various Selenium layer thickness.

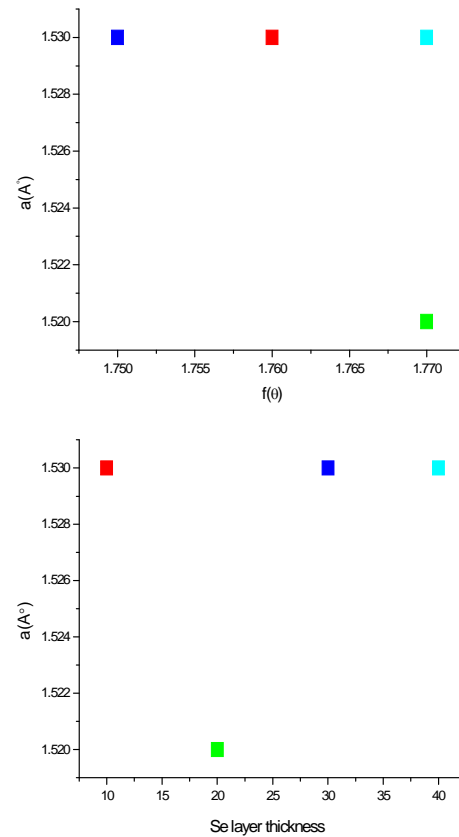


Figure 2 : (a) Nelson–Riley plots for accurate measurement of lattice constants of PbSe films and (b) Variation of lattice constant with Se layer thickness

### UV-Vis-NIR studies on PbSe multilayer thin films

The optical studies on as deposited Lead Selenide multilayer thin films with various Selenium layer thicknesses were analysed under UV-Vis to NIR (800-2500 nm) region are shown in figure 3-5.

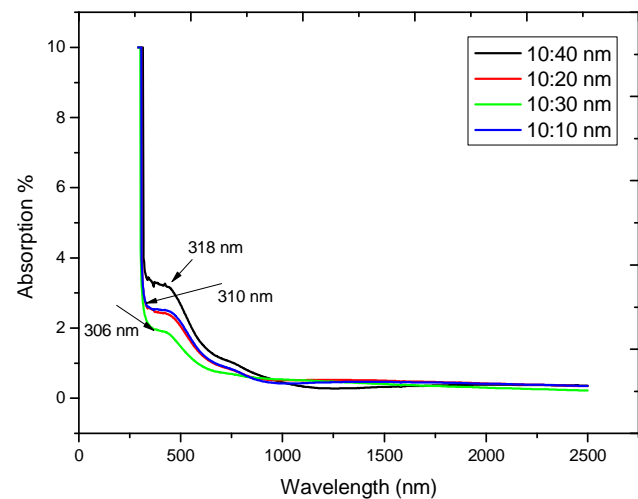
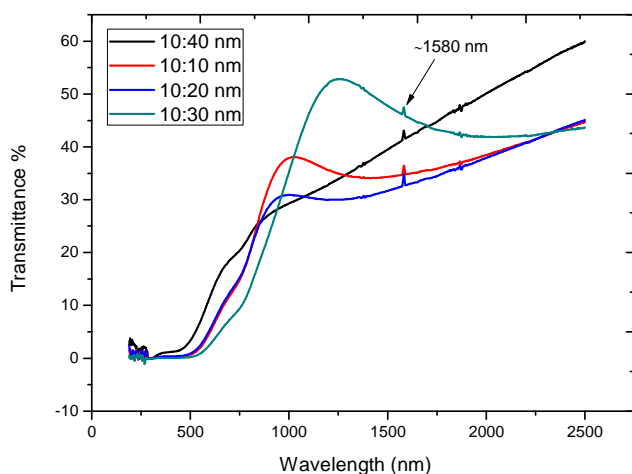
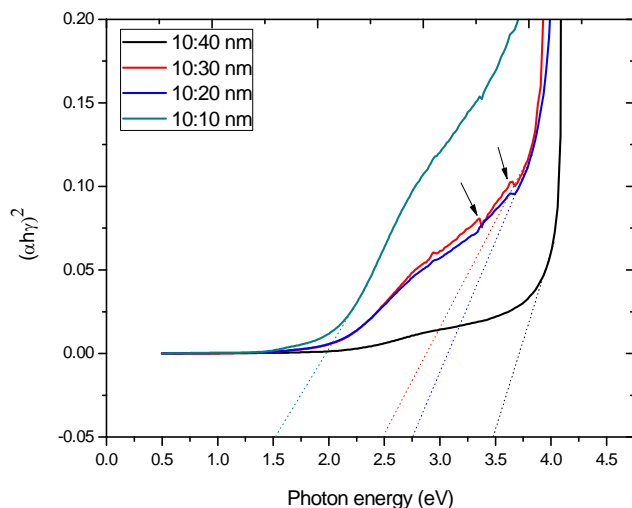


Figure 3 : Absorption spectra of PbSe multilayer thin films

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**Figure 4 :** Transmittance spectra of PbSe films with various Se layer thickness



**Figure 5 :** Optical band gap of PbSe multilayer thin films

The absorption edge starts with 306 nm at the films prepared with 30 nm layer thickness of Selenium and 318 nm of absorption edge observed at 40 nm layer thickness of Selenium. The as deposited films of PbSe multilayer thin films have the absorption edge of 310 nm observed at the films prepared with 10 nm and 20 nm layer thickness of Selenium. It is observed that all the prepared films towards shorter wavelength clearly indicates the presence of nanoparticles trapped at the interfaces of Pb and Se layers (Figure 3). The transmittance spectra of the films are shown in figure 4. The highest transmittance spectra of 50 % observed at 30 nm layer thickness of Selenium. The rise in transmittance spectra around 1580 nm shows the nanocrystalline effect of as deposited films may be due to stress between the layers. The band gap value could be ob-

tained from the optical absorption spectra by using Tauc's relation<sup>[12]</sup>,

$$\alpha = \frac{A}{h\nu} (h\nu - E_g)^n \quad (4)$$

Where  $\alpha$  is the absorption coefficient,  $(h\nu)$  is the photon energy and  $A$  is a constant. The direct band gap semiconductor can be obtained from the relation,

$$ah\nu = A(h\nu - E_g)^{1/2} \quad (5)$$

Figure 5 shows the variation of  $(ah\nu)^2$  versus  $(h\nu)$  for the PbSe multilayer thin film with various Selenium layer thickness. The straight nature of the films over the wide range of photon energy indicates the direct type of transition. The optical gap has then been determined by extrapolation of the linear region on the energy axis (Figure 5). The observed band gap value of the films is more than the bulk band gap (0.27 eV) value of Lead selenide which will lead to quantum confinement effect of the multilayer films. The band gap value of 1.5, 2.5, 2.75 and 3.5 eV was observed at 10, 30, 20 and 40 nm layer thickness respectively on the formation of nanocrystalline Lead selenide multilayer thin films. To confirm the quantum confinement effect of the films the Brus and quantum mechanical model was used and the particle size calculated from the energy shift from the bulk band gap.

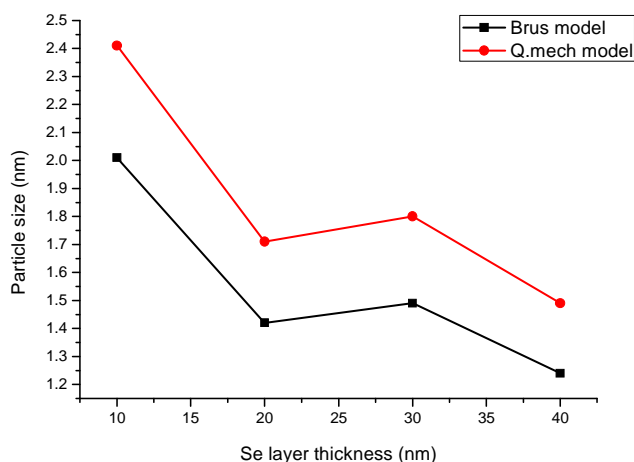
It has been generally proven that the quantum confinement effect should be observable if the radius of nano crystallites becomes less than the Bohr excitonic radius for corresponding material. The expression for weak ( $E_w$ ) and strong ( $E_s$ ) confinement energies can be written as

$$E_s = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.8e^2}{\epsilon R} \quad (6)$$

where,  $E_g$  is the bulk band gap (PbSe=0.27 eV),  $\mu$  reduced mass of Exciton ( $\mu = 1/m_e^* + 1/m_h^*$ ) the second term represents the kinetic energy of the confined Exciton and the third term indicates the Coulomb interaction of the electron with the hole. Here coulomb interaction is negligible. Using above equation the radius of the particle has been calculated which is much smaller than Bohr radius (46 nm). From the blue shift on the multilayer films the particle size were calculated by using this modal and tabulated in TABLE 1.

**TABLE 2 : Particle size variation from brus and quantum mechanical model**

Layer thickness	Band gap observed (eV)	Shift in band gap (eV)	Particle size (nm)	
			Brus model	Q.mech model
10:10	1.50	1.23	2.01	2.42
10:20	2.75	2.48	1.42	1.71
10:30	2.50	2.23	1.49	1.80
10:40	3.50	3.23	1.24	1.49

**Figure 6 : Variation of particle size from brus and quantum mechanical model**

The condition for strong quantum confinement based on the work of Yu et al<sup>[14]</sup>, is  $Q_{dot} \ll Q_b$  where  $Q_{dot}$  is radius of quantum dot and  $Q_b$  is Exciton Bohr radius (PbSe = 46nm) by using the following relation<sup>[14]</sup>,

$$E_{ob} = E_g + \pi^2(Q_b/Q_{dot})^2 R_y^* - 1.786(Q_b/Q_{dot}) R_y^* - 0.248 R_y^* \quad (7)$$

Where  $E_{ob}$  = Energy calculated from UV/VIS spectrum,  $E_g$  = bang gap (PbSe= 0.27 eV) for bulk material  $Q_b$ = Exciton Bohr radius,  $Q_{dot}$ = radius of crystallite,  $R_y^*$  = Rydberg constant (PbSe= 0.35 meV), the size of the crystallites were calculated and well agreed between the crystallite size calculated from Brus model and Quantum mechanical model has been shown in TABLE 2.

Figure 6 shows the variation of particle size with respect to Brus model and quantum mechanical model for satisfying the quantum confinement effect of the Lead Selenide multilayer thin films. It is observed that there is no much difference between those two theoretical model and the calculated particle size varies from 1.2 nm to 2.4 nm. This clearly indicates the confinement effect on interfaces of the multilayer PbSe thin films.

## CONCLUSION

Lead Selenide multilayer thin films were prepared with various Selenium layer thicknesses by thermal evaporation technique by successive coatings of Pb and Se layers. The cubic structure with polycrystalline nature of as deposited films observed from X-Ray diffractogram. The absorption edge starts with shorter wavelength is evident for the presence of nanoparticle trapped at the interfaces of the layers. The transmittance spectrum with sudden rise at around 1580 nm happens due to nanocrystalline effect of the films. The large shift in band gap energy is observed due to quantum confinement effect of the films. The calculated particle size from Brus and quantum mechanical model is also the signature of the quantum size effect.

## REFERENCES

- [1] F.W.Wise; ACC Chem.Res., **33**, 773 (2000).
- [2] A.Munoz, J.Melendez, M.C.Torquemada et al.; Thin Solid Films, **317**, 425-428 (1998).
- [3] V.Dmitri, Talapin, Christoher B.Murray; Science, **310**, 86 (2005).
- [4] Seiki Kitada, Einosuke Ki Kuchi et al.; Solid State Communication, **149** 1853-1855 (2009).
- [5] Sustro Kumar et al.; Current Appl.Phys., **5156**, (2005).
- [6] Myung-Hyun Lee, Woon Jin Chung; Nanotechnology, **16**, 1148-1152 (2005).
- [7] Jieun Chang, Chao Liu, Jong Heo; J.of Non-Crystalline Solids, **355**, (2009).
- [8] Z.Hens, D.Vanmacekelbegh; Phy.Rev.Letters, **92**, (2004).
- [9] Joshua J.Chol, Yee-Fun Lim; Nano Letters, **9**, 3749-3755 (2009).
- [10] N.C.Greenham, Xiaogang Peng; Physical Review, **54**, (1996).
- [11] V.Arivazhagan, S.Rajesh; Chalcogenide Letters, **7(7)**, (2010).
- [12] D.R.Sahu; Microchem.J., **38**, 1252 (2007).
- [13] R.D.Schaller, V.I.Klimov; Physical Review Letters, May (2004).
- [14] W.Yu, L.Qu, W.Guo, X.Peng; Chem.Mater., **15(14)**, 2854-2860 (2003).
- [15] K.Roy Choudhury, Y.Sahoo, T.Y.Ohulchansky; Applied Physics Letters, (2005).

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- [16] Dehu Cui, Jian Xu, Ting Zhu, Gary; Applied Physics Letters, (2006).
- [17] N.C.Greenham, Xiaogang Peng; Physical Review, **54**, (1996).
- [18] Matthew C.Beard, Kelly P.Knutsen et al.; Nano Letters, **7&8**, (2007).
- [19] V.Arivazhagan, S.Rajesh; Chalcogenide Letters, **7(9)**, (2010).
- [20] Marjin A. Van et al.; Nano Letters, January (2009).
- [21] Chris G.Van De Walle, J.Neugebauer; Letters to Nature, **423**.
- [22] V.Arivazhagan, S.Rajesh; Chalcogenide Letters, **7(7)**, 465-470 (2010).
- [23] A.Sawaby, Z.S.EIMandouh, S.A.Naseer; J.of Applied Science Reserch, (2008).
- [24] Zhen Li, Chao Wu, Yanyan Liu; Indian Academy of Science, **31**, (2008).
- [25] Uday Mushin Nayef; Eng. & Technology, **25**, (2007).
- [26] John Sinclair, Solid State II; Instructor: Dr.Dagotto, April 9, (2009).