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Design of materials for IR detectors using high Z elements for high energy radiation environment

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ABSTRACT

There is a strong need for rad hard and high operating temperature IR detectors for space environment. Heavy metal Selenides (high Z and large density) have been investigated for more than half century for high operating temperature mid wave infrared (MWIR) applications. Most of the efforts have been devoted to make detector arrays on high-resistivity Si substrates for operating wavelengths in the 1.5 to 5.0 µm region using physical vapor transport grown poly crystalline materials. For most of the biological spectral and imaging applications, short wave infrared (SWIR) detectors have shown better performance. Recent growth materials have shown variation in morphology with slight change in growth conditions and hence variation in performance parameters such as bandgap, mobility and resistivity from sample to sample. We have performed growth and optical characterization of binary materials CdSe-PbSe to determine the suitability for IR detector. We have determined bandgap using several theoretical models for different morphologies observed during growth on silicon wafers.

Keywords: Detector, Lead selenide, Growth, Detector, Infrared, Vapor, Transport, Morphology
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1. INTRODUCTION

Mercury cadmium telluride (MCT) has been studied and found to be an excellent material system for the infrared (IR) detectors since very long time due to tunability and good detectivity performance. In order to achieve good performance material requires cryogenic cooling. This causes great complexity specially for space applications due to weight and arrangements for cryocoolers. Also, there is a strong need for rad hard and high operating temperature IR detectors for space environment. Heavy metal Selenides (high Z and large density) such as lead selenide (PbSe) and some other compounds have been investigated for more than half century for high operating temperature for mid wave infrared (MWIR) applications. We have studied [1-4] PbSe materials system since past decade and developed parameters for its performance. This material system is unique and other researchers have used [5-9] variety of methods including solution growth, physical vapor transport, chemical vapor transport and molecular beam evaporation for the growth of film for detectors. The morphology and resistivity of material depend very much on processing, post annealing and dopant such as iodine in the detector. There have been continuous efforts to improve the performance by doping to increase mobility and operating temperature. Some low Z materials such as CdSe have been used to fabricate lead selenide ($Pb_{1-x}Cd_xSe$) layer-based detectors on the silicon substrate. There are some reports that the limiting factor for this material system and imager is noise. Both spectral and spatial resolutions are limited by signal to noise (S/N) ratio caused by the low energy excitation and dispersed emission. In some cases, materials inhomogeneity (CdSe mixing) in matrix can be responsible in the system causing high noise. In order to understand this type of problem, there is a strong need to understand morphology, cutoff wavelength and resistivity. Phase diagrams of the lead and cadmium salts have been evaluated [10, 11] and eutectic systems have been observed. For the PbSe-CdSe system, there is no congruent compound observed at any composition. A simple eutectic system at 46% mole fraction of CdSe melts at 995°C. This indicates that growth methods based on melt techniques will not be suitable for the film or crystal growth. Also, a temperature above eutectic will produce liquid trapping in the film. In this paper we describe the effect of CdSe doping on the morphology of the lead selenide grown by physical vapor transport method.

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2. EXPERIMENTAL METOD

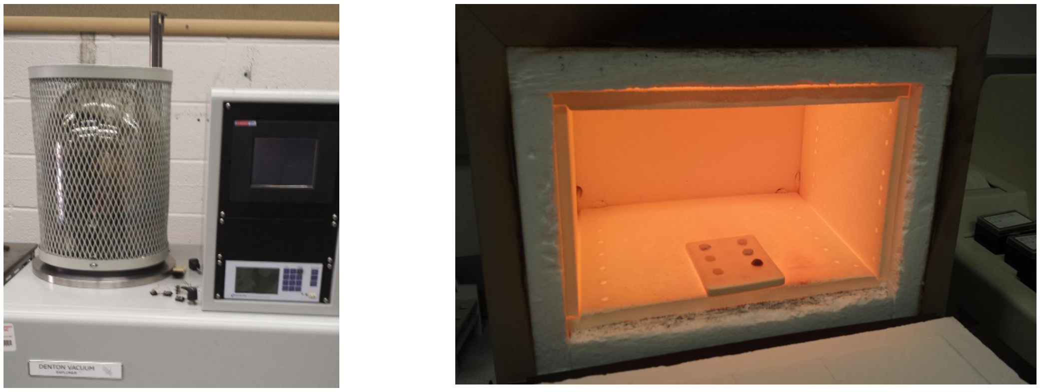
2.1 Material Preparation, purification and reaction: As supplied PbSe and CdSe materials had listed purity of 99.995%. These materials were mixed and annealed in a cleaned quartz tube in vacuum. We always observed dark small carbon rich residue left behind in the bottom of crucible after evaporation. In order to ensure to avoid the moisture we heated samples at 120^{o}C before starting the purification and growth. The evaporation temperature was above 300^{0}C in vacuum.

2.2 Growth and characterization: We have used both physical vapor transport (PVT) growth method for the growth of nanoparticles. Details of these methods are described by authors elsewhere [1-4]. Before starting the film growth, the vacuum system was sufficiently pumped and purged to eliminate oxygen contamination. For the growth of lead selenide-cadmium selenide nanoparticles physical vapor transport growth was used at a source temperature range of 300^{o}C to 400^{o}C. Silicon wafers (111) were used as substrates for PbSe-CdSe system. For the growth on glass substrates, we etched the glass with very dilute (1%) hydrofluoric acid-water solution.

We characterized these films for their morphology, resistivity and bandgap changes. Thickness measurements indicated that film is very thin. The growth temperature was intensively kept lower than melting point of CdSe and PbSe. Because of this reason, the film was less than 20nm. On annealing even at low temperature, the film showed buckling and appearance was like precipitates. This indicated large stress in the film due to very large difference between the lattice parameters. The morphology of nano structure was studied using a Hitachi FE-SEM equipped with a PGT EDS.

3. RESULTS AND DISCUSSION

PbSe-CdSe powders were placed in molybdenum (Mo) boat and thermally evaporated (sublimated) using different powers. In some cases, we used tungsten (W) boats also. The temperature of the substrate was kept around 300^{o}C. The transport path was 12 cm and it kept constant for each run. The percentages we used range from 13 to 16% and the current is equal to value % + 1 in amps (i.e. 14 to 17A). The details of furnace (**Figure 1**), wafer holders and heating arrangements are previously described in references 2. As grown films on the glass and silicon wafers are shown in **Figure 2.** We observed that film nucleation on the etched glass substrate was faster and thicker film could be grown in identical growth conditions in shorter growth .time



(a) (b)

Figure 1 DENTON (a) growth system and growth (b) chamber used in this study for PbCdSe system

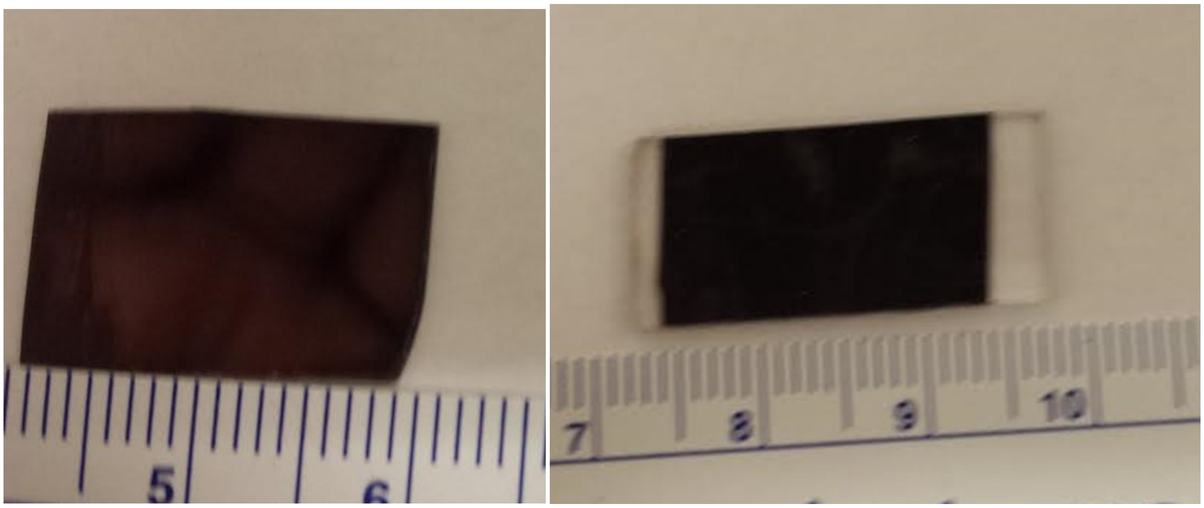


Figure 2. Typical thin and thick samples of PbCdSe films grown on glass substrates

As mentioned earlier CdSe was used as dopant and low concentration was used on PbSe matrix. Detailed studies on PbSe [1] has demonstrated that high purity PbSe could be observed as nano particles, nanoubes, small and large paraboloids. **Figure 3** shows that as the film thickness increases and a temperature in the range of 400^0C for the growth is used, 40-60 nm long and 10 nm in diameter round terminated shaped paraboloids are grown on the top of thick nanocubes. But this morphology was completely changed due to addition of CdSe.

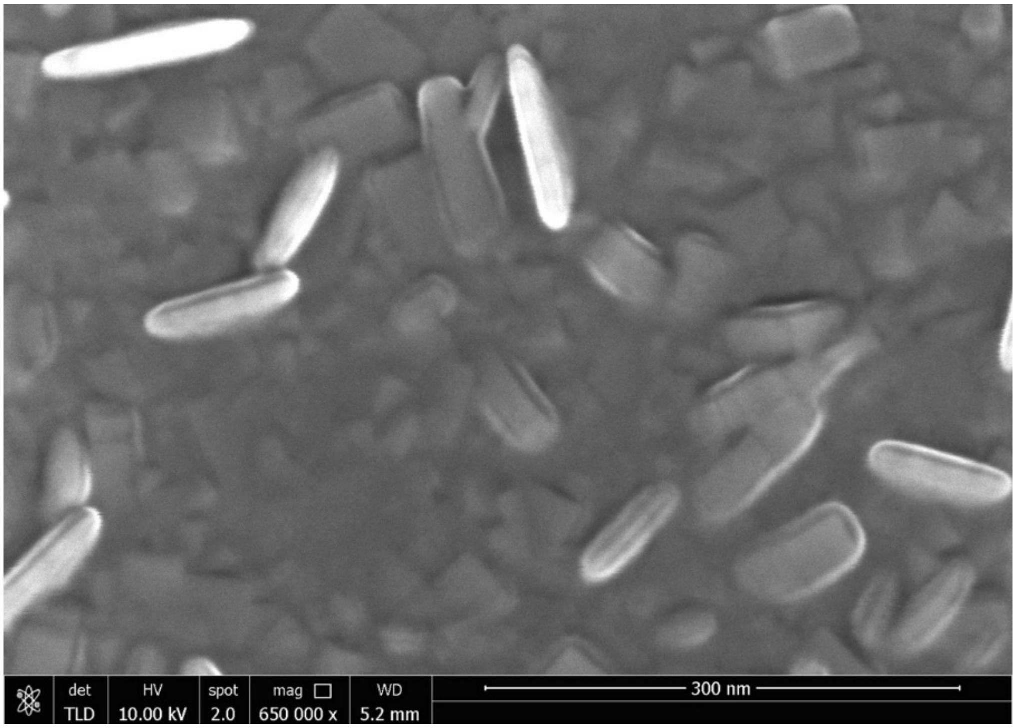
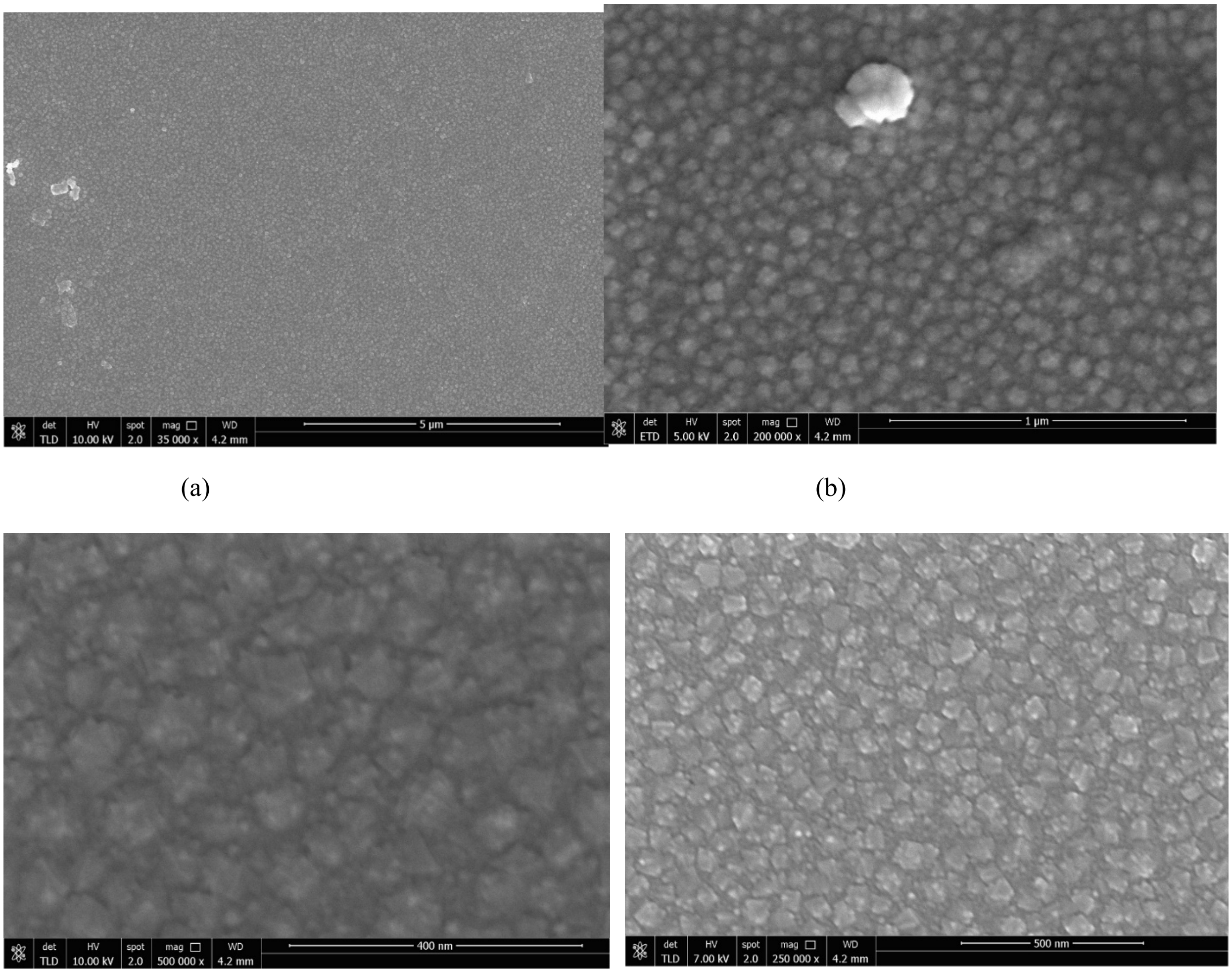


Figure 3. Typical morphology of PbSe grown by using high purity source materials

Figure 4 shows the morphology of CdSe-doped PbSe samples with increasing magnification. Doping changed the morphology significantly. There was no similarity between both samples. As shown in **Figure 4** we observed continuous growth of octahedrons with broken interface.



(a) (b)

(c) (d)

Figure 4. Typical morphology of doped PbSe with increasing magnification

The compositions of CdSe in the materials were evaluated at several spots of the film (**Figure 5**). The composition was very small in both places. Results are shown in **Figure 6.** Although composition was low, it was large enough to change the morphology and band gap of the grown materials. Silicon peak was observed due to the substrate used for the growth of film. The measured resistivity of the as grown film was in the range of 82-96 KOhm/cm range. This value was in the range of as grown (without annealed) lead selenide film. Preliminary results showed that annealing did not increased resistivity of CdSe -doped PbSe as high as observed [1] for the pure PbSe.

We observed white color on the top of annealed film. Which indicates oxidation of cadmium to form Cadmium oxide even at low temperature. This can be explained on the basis of phase equilibrium data [10,11] reported for PbSe-CdSe and PbS-CdS materials system. In both cases solubility is extremely and both systems form eutectics. This indicates that cadmium rich phase can oxidized easily during evaporation.

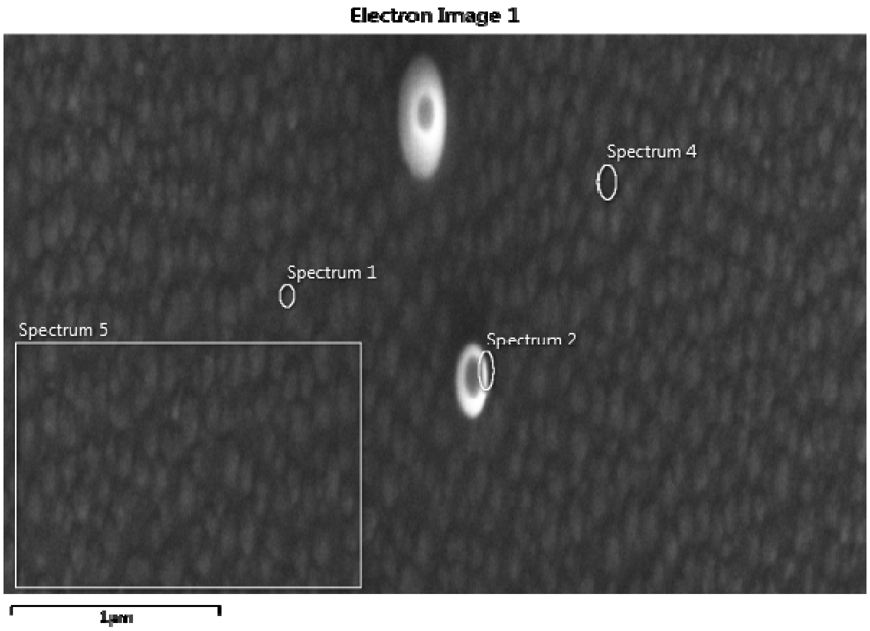


Figure 5. Materials spots selected to evaluate for the CdSe composition

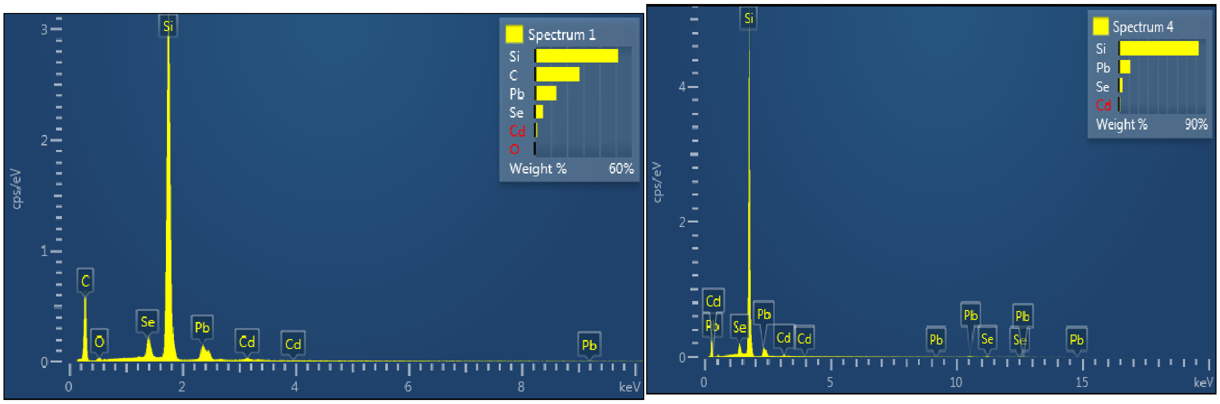


Figure 6. Composition of each components for the selected spots 1 and 4 shown in Figure 5.

For the semiconductor materials the band gap is good measure of the threshold for absorption of photons. Also, the refractive index is a good measure of its transparency and cutoff wavelength. A correlation between these two fundamental properties has significant bearing on the band structure of semiconductors. Several reviews [12-13] have summarized the results of different theories correlating the refractive index and energy gap of semiconductors which are two fundamental parameters that are directly responsible for their optical and electronic properties. For the design of electronic and optical devices these two material properties are extremely important. Knowledge of the temperature coefficient of the band gap and refractive index in semiconductors is also very important to evaluate performance of devices. Transmission studies indicated that there was small difference in bandgap of CdSe doped film. The transmission curves for the films of different morphology of the CdSe doped material indicated cutoff at 2.29, 2.34 and 2.36 µm. **Table 1** summarizes the refractive indices of PbSe-CdSe films of different morphologies using some of these theories.

Table 1. Refractive index using different equations for the PbSe-CdSe material based on the measure cutoff wavelength for different films.

Parameter	Equations used for estimation	$\lambda_a = 2.29\ \mu m$	$\lambda_b = 2.34\ \mu m$	$\lambda_c = 2.36\ \mu m$
Bandgap Energy	$E_g = \frac{hc}{\lambda}$	0.541	0.530	0.525
Refractive Index	$n = 4.16 - 0.85 \cdot E_g$	3.70	3.71	3.71
Refractive Index	$n = \sqrt[4]{95 \cdot E_g}$	3.70	3.71	3.71
Refractive Index	$n = 3.367 \cdot {E_g}^{-0.332}$	3.54	3.55	3.55
Refractive Index	$n = \ln\left(\frac{36.3}{E_g}\right)$	4.13	4.16	4.17
Refractive Index	$n = \sqrt[4]{\frac{154}{E_g - 0.366}}$	4.21	4.23	4.24
Refractive Index	$n = \sqrt{12.3 - 5.35 \cdot lnE_g}$	3.59	3.61	3.62

4. CONCLUSION

Lead selenide selenides (high Z and large density) has been investigated for more than half century for high operating temperature mid wave infrared (MWIR) applications. We have evaluated effect of CdSe doping on the morphology, cutoff wavelength of the PbSe-CdSe system. Films were grown by PVT method on glass and silicon substrates. Even at very concentration, the resulting morphology was very different than pure PbSe. This reflects that the variation in morphology with slight change in stoichiometry (due to CdSe), growth conditions alters the performance parameters such as bandgap, refractive index and resistivity of the sample. Based on the cutoff wavelength of the films grown on the silicon wafers, we have determined bandgap and refractive index using several theoretical models. We are continuing growth of PbS-CdS system also for comparison with PbSe based material.

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