Hyperstructure and Meta Morphology Formation in Heavy Metal Chalcogenides

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ABSTRACT

Researchers have designed and developed many artificial patterns and shapes of materials in different sizes for RF and EO applications and designated as metamaterials. We have grown cubic, hexagonal, octagonal and pyramidal structures of commercially important infrared materials such as PbSe and its alloys which change to nanocubes at high temperature. We report the growth, nanomorphology and electrical characteristics of hyperstructured PbSe on Si substrates. Hyperbranched PbSe networks are synthesized by low temperature physical vaour transport method. The formation of branches and facets were produced in diffusion growth region. This was supported by facets formations. When PbSe and PbS-CdS were grown at 400 C without catalyst shapes stabilized into cubic morphology and nanocubes were observed significantly. X-ray showed strong growth in (001) and (111) orientations for facets. A similar study was performed for doped lead sulfide. Pure PbS showed oriented hexagonal rods which had strong directionality. PbS doped with CdS produced small rods (nanowires) randomly oriented. All these structures ultimately changed into cubes similar to that of PbS system   The resistivity was very much dependent on the processing conditions. Annealing in atmosphere increased the values orders of magnitude higher. We observed significant changes in morphology after oxidation process. The level of the oxidation processes and filling of selenium vacancies with oxygen may be the reason for resistivity to increase from the range of 60KΩ to 5-10 MΩ. Also the stability of oxidized lead selenide can be explained on the basis of selenium vacancies filled by oxygen.

Introduction

In the past two decades, very large numbers of papers have been published on the theoretical and experimental studies of structures called meta-materials. The careful observations indicate that these structures existed since millions of years in nature in stones such as topaz and designers used in decorating glass, ceramics and wood windows and doors of palaces and churches. Also, by designing and cutting. quartz crystals handy crafted assemblies show reflections from the many surfaces and scatter even visible light in every direction, resulting in white sand that is no longer possible to see through. Based on this type of concept it has been suggested that by controlling the size and shape and arranging in an orderly fashion it is possible to use them to design different properties which can be very beneficial for devices. Lead chalcogenides are unique materials and excellent materials for high operating temperature (HOT) mid infrared wavelength (MWIR) and long infrared wavelength (LWIR) detectors. Since the early experiment of Miller, Metz and Mazelsky (1) using encapsulated pulling method to grow crystals variety of techniques have been used to produce materials with uniform and consistent properties. Solution growth, vapor growth [2], liquid phase epitaxy and travelling solvent [3] methods have produced good quality materials. Until few years back all these efforts were focused on IR detectors. However, some morphologies including nanostructures of lead selenidehas great promise for the thermoelectric cooling and power generating devices [4-6]. Nanoparticles can potentially improve the thermoelectric properties over bulk by increasing the Seebeck coefficient due to the altered electronic density of doped states or making use of a compositionally modulated material that would block phonons while transmitting electrons. Also, Quantum confinement of charge carriers in lead chalcogenides has potential to be much stronger than in most II-VI and III-V

semiconductors. The energy level spacing can be even larger than the band gap of bulk material.
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Experimental methods

Several sets of growth conditions were used for developing the selenidenanodots on Si wafers.

Cleaning of Si wafer

Before the growth, Si and sapphire wafers were cleaned to remove residual impurities of the surface. Si and sapphire wafers were cleaned and cycle purged in a load lock to remove moisture. The wafers were then placed on a SiC susceptor and lamp heated to 900°C in hydrogen. The wafers were then cooled to the process temperature.

Growth of Nanoparticles and Nanocubes

High-purity PbSe, PbS, CdS and Se (99.999%) were used in this study. Since the objectives of this method were to develop low cost growth on large area substrates, silicon wafers and sapphire were selected for the substrate and used a modified commercial evaporator for the transport process. Several substrate temperatures [2] were used, ranging from 250C to 400C, for the growths. The substrate was etched prior to film growth to remove any residual impurities or native oxides.
The details of growth by physical vapor transport method experiments have been described by Singh et al [2-3]. We used a similar concept. In the present experiment we used DENTON commercial evaporator for the film growth. The detailed process parameters used are described in reference 2. Also, we used selenium rich solution to grow selenides.

Characterization

We characterized the chalcogenide nanoparticles and nanocubes for its crystallinity, morphology. X-ray diffraction was used to determine the orientation and X-ray rocking curve. Scanning electron microscopy (SEM) was used to determine the morphology and orientation of the film. Compositional analysis was performed to determine the presence of residual impurities. We used four point probes to evaluate the resistivity. Bandgap was determined using k and n and averaging for large area of the material.

Results and discussion

Wagner et al [2] demonstrated that lead selenide has great tendency to transform from nonfaceted morphology to crystallographically oriented facetted nano crystals. With continuous growth these crystals grow in micrometer size also.

Lead Selenide

In the case of lead selenide we observed different sized particles by adjusting the substrate temperature, growth time and evaporation rate. The typical microstructures for high purity lead selenide after few minutes of deposition are shown in Figure 1. But this morphology also transformed into nanocubes when nutrient was supported in the growth chamber and growth temperature was closed to 400C. Several hyperstructured structures were observed before reaching to nanocubes. All these structures were observed without any catalyst used for nucleation on the substrate. Figure 2 shows different meta

structures which ultimately reached to facetted cube morphologies. It was cleared that best crystal quality could be achieved near the growth temperature of 350C. The full width of half maxima for the X-Ray rocking curve was <0.35 degree.
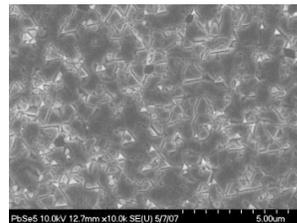

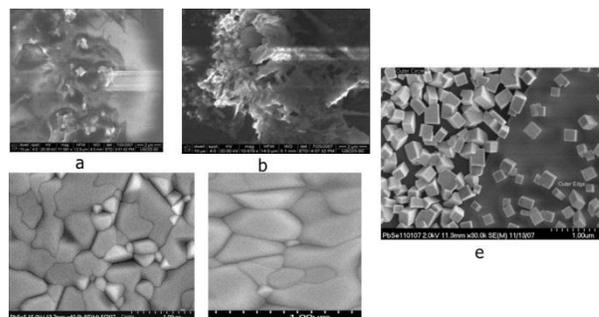Figure 1.Typical micro morphology of PbSe.

Figure 2.Different structures of lead selenide which ultimately transformed to facetted cubic morphology when growth temperature was in the range of 300-350.
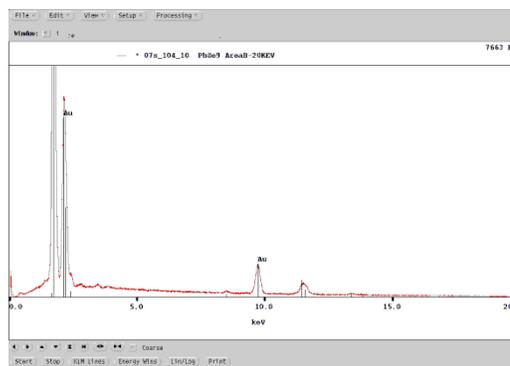

Figure 3.Compositional analysis of PbSe sample grown on Si wafers. Sample did not show any residual impurity.

Very often impurities act as the nucleation sites in vapor transport growth. But we did not observe any significant residual impurities in the grown material. Figure 3 shows the results of impurity analysis in the grown lead selenide sample. When we used gold as the catalyst, we always observed nanocubes nucleated from the gold nucleus. Figure 4 shows clearly these phenomena. It appears that higher growth rates are responsible for the cubic morphology. Although a mechanism was proposed [7,8] where it transformation of several morphologies were proposed to cubic as the function of time. But our observation of growth at 400C without catalyst, and growth at lower temperature at using gold catalyst even for short growth time produced faceted cubes. This demonstrates that kinetics at higher temperature is responsible for the cube development. We interrupted a growth run of 400C after 30 second and observed a

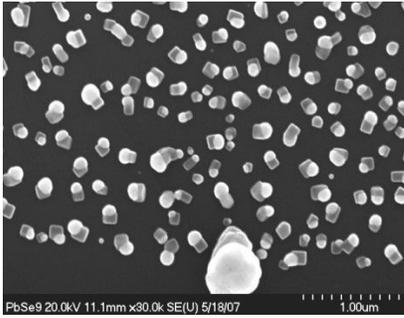morphology shown in Figure 6 where sparatic cubic nucleation was observed.

Figure 4.Growth on Silicon wafer with gold catalyst always showed nanocubes.

The translational ordering from the hexagonal close packed assembly changed to directional ordering forming facetted cubes. This may show partial alignment of the crystallographic axes of the individual nanoparticles.
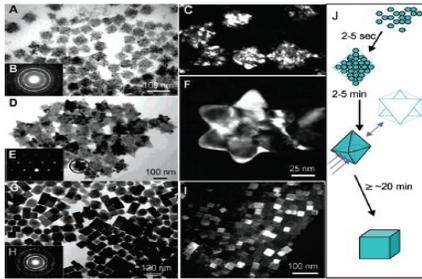

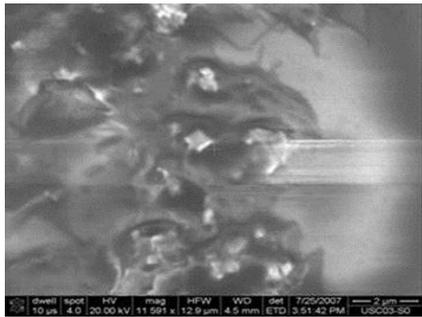Figure 5.Transformation of structures into cubic morphology [Ref.7].

Figure 6.The morphology of PbSe in an interrupted growth run. The facetted rectangular morphologies of nucleus were obtained at high temperature (400C) even without catalyst.

The films obtained from controlled PVT growth method were not electrically conducting. We tried annealing samples in vacuum, and oxygen. . The resistivity of the virgin sample was around 60 kΩ near room temperature and it could vary slightly when placed in atmosphere. It indicates that it was unstable due to presence of oxygen content. The resistivity went up to *5-10* MΩ after annealing in different conditions. The sample was stable in air for hundreds of hours with that resistivity. The morphology of the annealed sample (Figure 7) showed surface oxidation. Large mm size hyperstructures in the form of layers and merged with each other were observed. Some of the hypothesis has

demonstrated formation of oxyselenides.This is supported by observations of Jones [8]. As low as annealing temperature of 280C their measurements indicated the oxidation of lead selenide, in the form of a powdered single crystal. Their results indicated that two processes were occurring during oxidation. In the range of temperature considered the predominating process appears to be the diffusion of oxygen ions to vacant selenium sites in the lattice; this was found to have an activation energy of 17 kcal mol^{-1}. The second process revealed itself only at the highest temperature employed, and they believed that at high oxidation rate all or nearly all the selenium vacancies were occupied by oxygen ions. The postulation of two oxidation processes may be the reason for resistivity to increase from the range of 60KΩ to*5-10* MΩ. Also the stability of oxidized lead selenide can be explained on the basis of selenium vacancies filled by oxygen. There is some indication [9, 10] that hyper structures of selenides can produce TMΩ resistivity. This may inspire investigation of nanodendrites and branched morphologies. Wagner et al [2] have already reported the variation in bandgap of different PbSe grains. They have reported that nanocubes have bandgap in the range of 0.75eV compared to the reported values of 0.3eV for the polycrystalline PbSe
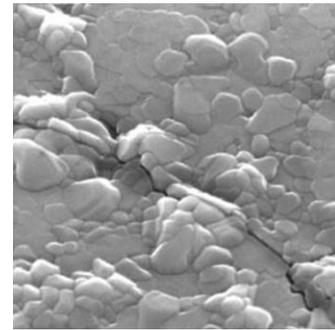

Figure 7.Large mm size oxidized lead selenidehyperstructured grains in the form of layers and merged with each other were observed.

Pure and doped Lead Sulfide

Similar to that of lead selenide we have performed studies on pure lead sulfide and lead sulfide-cadmium sulfide systems. We used the growth temperature of 400C for these two systems. We observed that the quality of lead sulfide was much superior that of lead selenide film on silicon wafer. Figure 8shows the morphology of lead sulfide film. Uniform hexagonal morphology was observed all over the substrate.
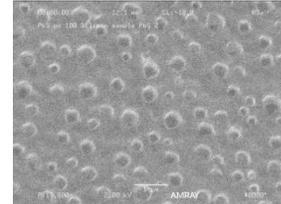

Figure 8 shows the morphology of lead sulfide film.

X-ray characterization indicated that film grew in the [111] orientation. Figure 9 shows observed peaks along with Si peak. The growth followed and was epitaxial on the [111] orientation of silicon wafer. Unlike PbSe case the X-ray diffraction

pattern did not show any other orientation such as [001]. The film quality was extremely good and free from other micromorphologies seen in PbSe. The X-ray rocking curve (Figure 10) did not show any other peak and full width of half maxima (FWHM) was less than 0.4 degree, an excellent value for the chalcogenide film grown on silicon wafer. In spite of large difference in the lattice parameter of the Si substrate, PbS film grew in the same [111] orientation. This value was for the mm size wafer showing large area uniformity and free from mosaic structures and low angle boundaries.
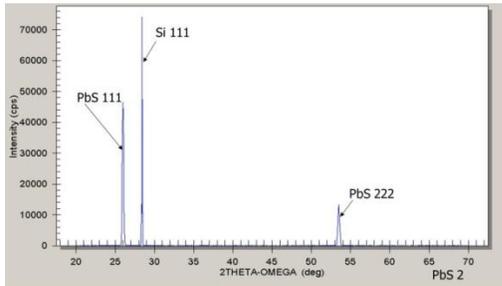

Figure:9 X-ray diffraction of lead sulfide shows only [111] orientation in the film observed peaks along with Si peak.
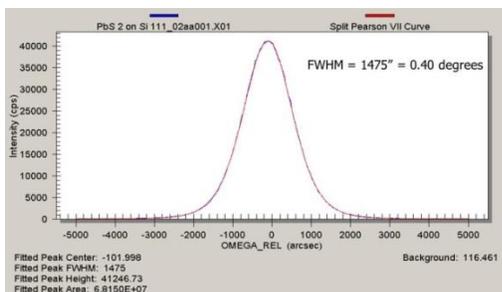

Figure 10. XRD Rocking curve shows good crystallinity

Figure 11 and 12 shows the SEM images of as-grown PbS-CdS at 20 and 10 KeV on a [001][[Si substrate surface with intrinsic oxide and indicate the formation process of the hyper intangled networks. At the initial stage of growth some these fat elongated particles have reached lengths of 100 nmwhile others have just nucleated. . Each nanostructure shows at least one generation of parabolic tips and some have a couple of layers of stacking resulting in a hierarchical structure. The number of random layers of stacking increases as the time of growth is significantly increased. There are several key characteristics that can be determined from SEM morphologies. The diameters of most particles are approximately100nm and do not change significantly over the course of the growth process. Second, the maximum length of each particle is in the range of 100-300nm and does not increase significantly with the growth process. Third, the particles are randomly oriented crystallographic ally in each layer. Figure 13 shows X-ray diffraction patterns where [111] and [001] peaks and their derivatives are observed.

The composition of the grown material was studied using EDX. The EDX data is shown in Figure 14. The data clearly indicated presence of Cd and Pb binary sulfide.
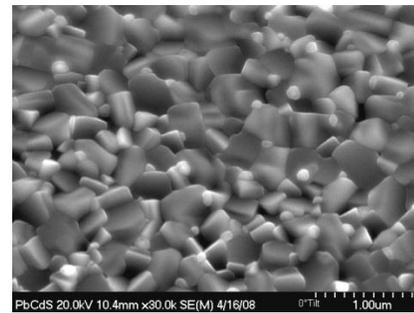

Figure 11. PbS-CdS fat elongated particles grew in the range of 300C substrate temperature.
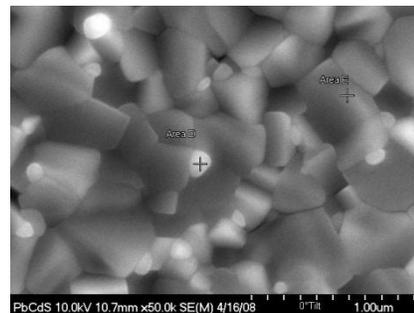

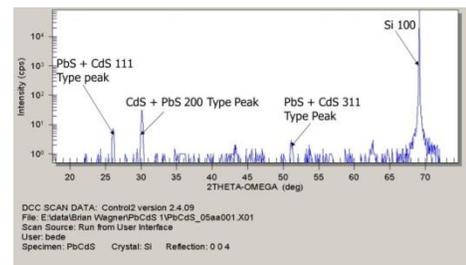Figure 12.PbS-CdS fat elongated particles grown the range of 300C substrate temperature observed at 10KeV.

Figure 13. X-ray diffraction patterns showing [111] and [001] peaks and multiple orientations
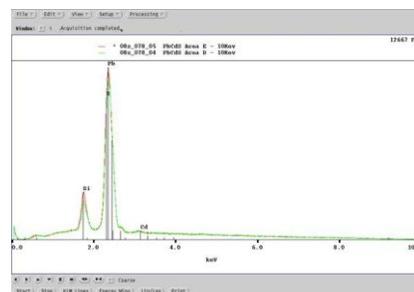

Figure 14.The EDX data for the PbS-CdS grown material on Si [111] wafer.

Similar to the case of lead selenide when the growth temperature was raised to 400C, the morphology of PbS-CdS particles dramatically cahnged to facetted morphology. We observed [Figured 15] nanocubes ranging from 50 nm to 100 nm sizes. In this region of growth temperature growth rate was

much higher than that of lead selenide. In addition to nanocubes, we observed area where large intangled foam was consisted of nanocubes. Uniformity of nanocubes was better in the center of the wafer indicating uniform temperature and growth rate.
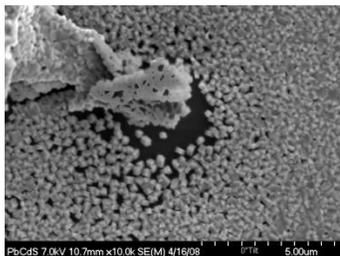

Figure 15. Nanocubes were observed in PbS-CdS case when the growth temperature was raised to 400C.

For the growth of sulfides in low temperature region showed tapered shapes. This type of behavior is reported for nanowires where catalysts are used. Generally metal catalyst is observed at the tips of the nanoparticles or nanowires. However, the majority of the PbS-CdS nanoparticles usually show a tapered shape at the tip (Figure 11 and 12) without the presence of metal catalyst. The absence of catalyst nanoparticles ripen slowly and due to the shrinkage of volume shape changes. The high vapor pressure helps in ripening and coarsening.

The develop of morphology of nanocubes in both lead selenide and sulfide can be explained on the basis of a series of experiment under different growth conditions. Cheng et al [8] demonstrated that only the presence of polyacrylamide can explain the transition to cubic. But our experiments were performed using high purity source materials by PVT growth method without any organics.

As shown in Figure2PbSenano particles with truncated octahedron structures were obtained. These exhibit irregular nano- particles of truncated octahedron structures with an average diameter of 100 ⊠m. The fact that distorted truncated octahedral PbSe or PbS is obtained in high purity source materials indicate that the anisotropy and growth conditions play role in the formation of nanocubes in selenides. Traces of residual impurities may play important role at high temperatures. Since nanocubes were observed at high temperatures, it may be possible that traces of impurities may to different crystal faces directs the growth of nanoparticles into various shapes by controlling the growth rates along different crystal axes. It is shown by Singh et al [11] in PVT growth of mercurous halides that growth rate in [001] was at least twice to that of [111] orientation. The morphology and the shape is determined by the ratio of the growth rate in [001] directions to that of [111] directions. Similarly the evolution of chalcogenide nanocrystals from octahedron to cube in high-temperature growth conditions may be due to anisotropy in growth velocity. The evolution mechanism of morphology is due to the higher growth rate in one orientation compared to the other orientation. This was true in case of lead sulfide case also.

Conclusion

We have performed experiments on the growth of PbSe, PbS and PbS-CdS systems and demonstrated that lead chalcogenides grown by physical vapor transport demonstrated several nano morphologies. Nanocube formation does not require any additional organic materials as impurity. The anisotropy and growth conditions play role in the formation of nanocubes in selenides. At higher growth temperatures (>400C) nano particles with truncated octahedron structures and other distorted shapes grow as nanocubes since anisotropy dominates and growth rates in [111] and [001] orientations are very different. During the oxidation of chalcogenides especially in the case of selenides oxygen fills the selenium vacancy and increases the electrical resistivity. The bandgap and resistivity of thin film of nanocubes on silicon substrates is larger than thin polycrystalline chalcogenide film. Future researches will focus to evaluate if branched particles and nanodendrites in chalcogenides can increase the resistivity further more. There are some indication that resistivity in the range of TΩ-cm can be achieved if branched structures can be developed. This will enhance the sensitivity of high operating temperature IR detectors.

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