Compositional effects on properties of $PbS_{1-x}Se_x$ thin films

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Solid solutions of Lead Chalcogenides are of considerable scientific interest owing to their manifold technological applications [1-5]. Solid solutions of $PbS_{1-x}Se_x$ system were prepared by taking the ingradients i.e. lead, sulphur and selenium in their elemental form. Thin films of the alloy were deposited by flash evaporation of the fused material on the glass substrate at room temperature. Their electrical properties viz. resistivity, Hall co-efficient, carrier concentration and mobility of the carriers were determined using vander pauw's technique. The optical and structural properties were also studied. The absorption edge shifts towards longer wavelength side. Consequently the energy band gap becomes narrower. The electrical resistivity is also found to decrease which proves their utility at longer wavelengths. XRD patterns reveal the crystalline nature of the film which is also confirmed by SEM photographs at room temperature.

1. Introduction

Thin films occupy a prominent place in basic research and solid state technology as they can be used to prepare polycrystalline semiconductors not only in chemically and structurally pure form but with a controlled impurity [1-3]. The polycrystalline material based devices are of great technological interest due to their cost effective production.

Lead salts and their alloys have a number of interesting physical properties as well as numerous potential applications [4-6]. Lead chalcogenides (PbS, PbSe and PbTe) exhibit some unusual and unique properties such as high dielectric constant, narrow energy gap and high mobility. The temperature co-efficient dEg/dT of the minimum energy gap Eg is positive for these materials while it is negative for other semiconducting materials. The most remarkable feature of this group of compound semiconductors is the relative stability of the lattice over a wide range of stoichiometry. **IV-VI** compounds have found a new sphere of applications due to the development of laser technology. Laser diodes based on lead chalcogenides and their alloys act as an important source of tunable radiations in mid infra-red wavelength region [7-8]. They are widely utilized in advance measuring systems to detect hydrocarbon pollutants in atmosphere, high resolution spectroscopy, trace gas analysis and optical fiber communication systems over long distances [9-12].

The study of solid solutions has a distinguished significance because of the possibility of tailoring the material characteristics as per requirement of the device. The continuous variation of electrical and optical properties of ternary alloy semiconductors with relative concentration of constituents is of utmost utility in development of solid state technology. In view of their technological importance in remote sensing [13], thermography chemical sensing [14] and long wavelength imaging [15], the narrow gap semiconductors have been a subject of extensive interest. Depending on the concentration of third element, photovoltaic infrared sensors based on IV-VI compounds such as $Hg_{1-x}Cd_x$ Te [16-19] offer high sensitivity and are easier to fabricate.

In the present work, the solid solutions belonging to PbS_{1-x} Se_x system have been investigated. They are regarded as promising material in injection lasers [20-21] due to their narrow energy gap similar to PbS [22] and PbSe [23]. In order to have better understanding of performance of these solid solutions for any particular application, it becomes quite necessary to work on the fundamental properties (i.e. electrical, optical and structural) of these materials. The electrical properties of the material play an important role in determining whether the material is suitable to our requirements or not. The most important electrical properties i.e. the resistivity, Hall co-efficient, carrier concentration and mobility of the carriers have been investigated here. Furthermore the optical properties throw light on the central feature of the system i.e. their narrow band gap. The absorption and reflection spectra of these samples were studied. The X-ray diffraction (XRD) patterns and scanning electron microscopic photographs (SEM) were taken to investigate the nature and grain size of the material.

2. Experimental details

The semiconducting alloy films of PbS_{1-x} Se were grown by flash evaporation. The reason of using flash evaporation for the alloy films were that the constituent

material of the films were taken in elemental form i.e. lead, sulphur and selenium. Among these, sulphur evaporates at lower temperature due to its lowest melting point. So, just to maintain the stoichiometry, flash evaporation method was used.

In the flash evaporation technique, calculated amounts of lead (99.95% Philadelphia, USA), sulphur (99.999% Fluka,Switzerland) and selenium (99.999% Philadelphia, USA) were taken together and fused in an evacuated quartz ampoule placed in a furnace at sufficiently high temperature of 700^0C and then cooled slowly resulting in small crystallites then the material was then grinded to powder using agate mortar and pestle. Inside the vaccum chamber this material was made to fall on a heated filament. As soon as the material reaches the heated filament, evaporates immediately. This process is called flash evaporation. The evaporated material reaches the substrate and gets deposited there. During the flash evaporation process, the pressure was maintained at 10^{-5} torr and the substrate (glass slide) was kept at room temperature. The distance between the substrate and the source was kept constant i.e. 15 cm. Here the evaporation rate was maintained at $10A^0$ /sec.

After the preparation of the samples their electrical, optical and structural properties were investigated. The electrical   properties studied in the   present work are resistivity, Hall coefficient, carrier concentration and mobility of the carriers. The resistivity of the material was calculated by the sheet resistance which was determined by vander pauw's technique. Hall co-efficient was also determined by the same technique. Optical properties were studied using UV-3400 Hitachi spectrophotometer. The absorption and reflection spectra of the samples were taken. The band gap was calculated from the absorption spectra while the thickness was calculated using the reflection spectra [24]. The X-ray diffraction patterns of the samples give valuable information about structural aspect of the samples. The SEM photographs of the samples evidence the grain size and surface morphology.

3. Results and discussion

Fig.1 shows the resistivity variation of the samples with increasing selenium content. The resistivity decreases continuously with increasing sulphur content except for the selenium concentration x = 0.8.
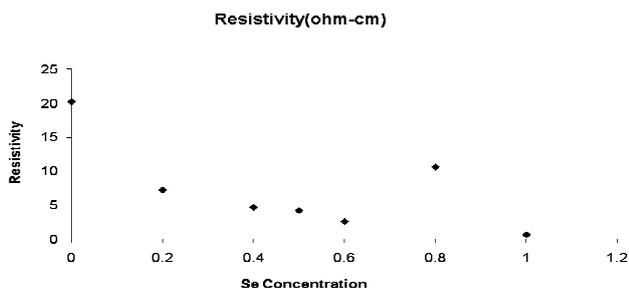
Fig. 1. Resistivity variation.

The resistivity of the alloy films lies in between the resistivity of PbS and that of PbSe. The resistivity of PbSe is the lowest one. The successive decrease in resistivity on partial substitution of sulphur by selenium is accounted for the increased grain size. The increase in grain size can be seen in the SEM photograph shown [fig. 2 (a), (b), (c) and (d)]. The dependence of the resistivity of a film on the mean grain size at room temperature is also reported by Bratashevskil et.al. [22]. When sulphur is completely replaced by selenium then the lowest resistivity material PbSe is formed as the carrier density of PbSe is higher than that of PbS. The only rise in resistivity is at the point, where Se is in excess. It is due to the inhomogeneity introduced in the solid solution. Excess of selenium is also observed in XRD patterns in the form of small peaks originating from Se crystals [fig 3(a),(b),(c),(d) and (e)]. It seems reasonable to accept some sort of segregation of selenium atoms at this point, which causes a rise in resistivity. The rise in resistivity at higher Se contents may also be attributed to the surface scattering effects due to imperfect matching of the various areas of the growing films.
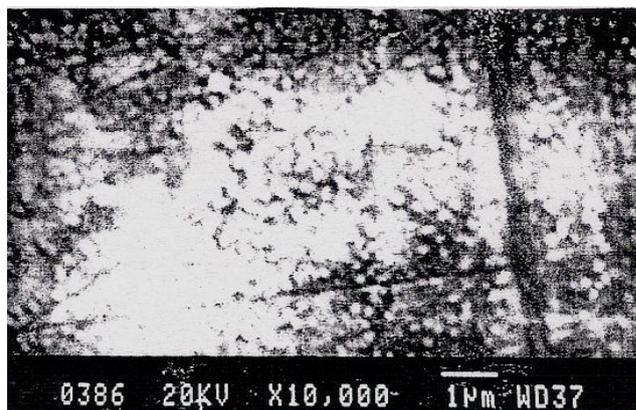
Fig. 2(a). SEM photograph of PbS Film (x=0).
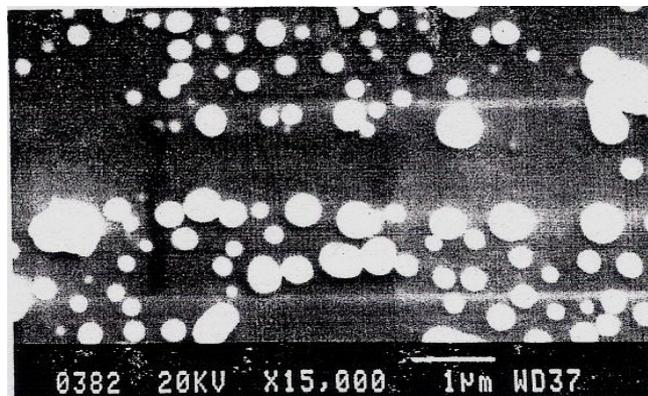
Fig. 2(b). SEM photograph of PbS.8Se.2 Film (x=0.2).
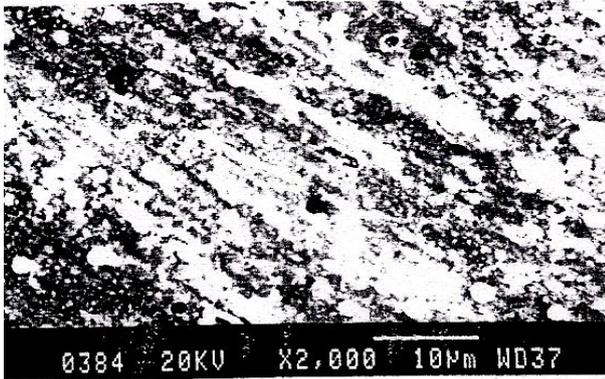
Fig. 2(c). SEM photograph of PbS.2Se.8 Film (x=0.8).
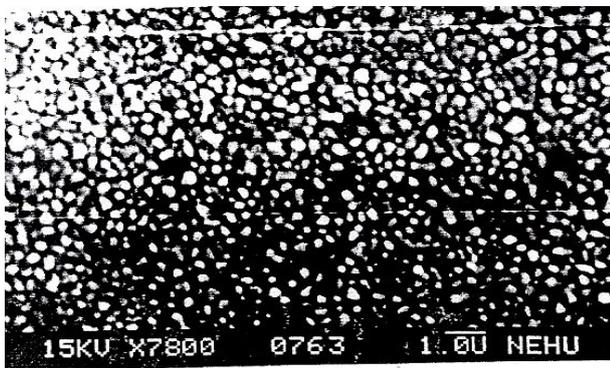
Fig. 2(d). SEM photograph of PbSe Film (x=1.0).

Fig. 3[(a), (b), (c), (d) & (e)] XRD Patterns.

The carrier concentration of these samples is plotted in fig. 4 with increasing Se content. It attains reasonably high value when Se is added substitutionally with sulphur. At higher Se concentrations the carrier density decreases and becomes highest when all the sulphur is replaced by selenium. The primary increase in carrier concentration of these samples, during partial replacement of sulphur, is produced because of the higher carrier concentration of PbSe than of PbS, while the succeeding decrease is proposed to be due to the grain boundary effects which are supposed to dominate in the intermediate range of substitution. Since there is a large concentration of defects at grain boundaries such as trapping states stacking faults and surface states resulting from the incomplete atomic bonding. These states trap the free charge carriers thus reducing the carrier density. At higher Se contents when PbSe is formed these traps vanish since PbSe has fewer defects than ternary alloy PbS$_{1-x}$Se$_x$ but still there are sufficient free carriers to enhance the carrier concentration due to higher carrier density of PbSe.
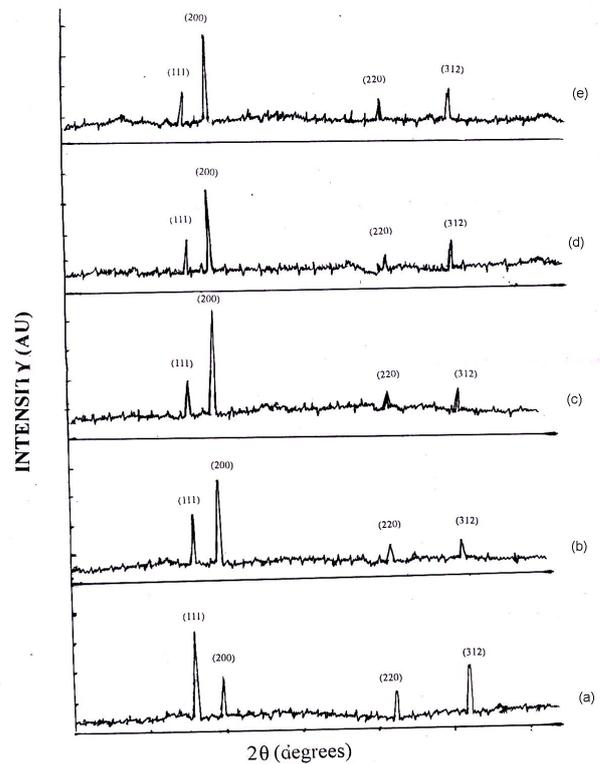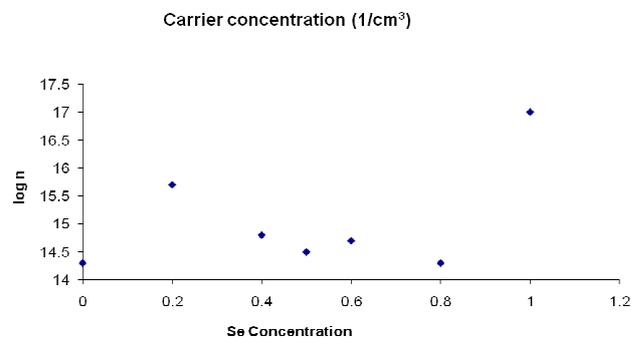
Fig. 4. Carrier concentration.

Fig. 5 shows the graph of mobility with increasing selenium content. For x<0.5 mobility decreases with increasing selenium concentration. After that it increases, stays constant and is followed by a gradual fall on replacing the sulphur completely by selenium.

Mobility(cm²/sec)
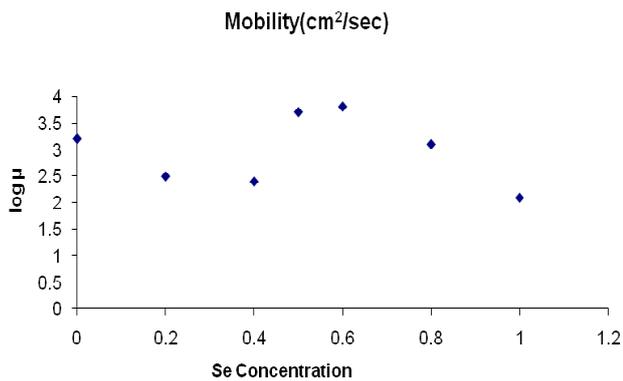
Fig. 5. Mobility.
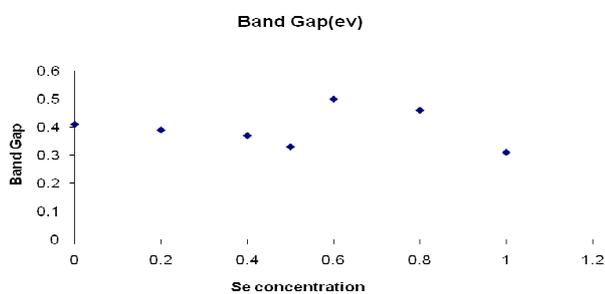
Band Gap(ev)

Fig. 6. Band gap.

The initial decrease in mobility can be attributed to the surface scattering effects as the surfaces have a relatively greater influence on charge transport in the films due to large ratio of surface area to volume. On increasing the Se concentration further, the mobility increases due to enhanced mean free path resulting from the decrease in carrier density. On still higher concentration of Se, the gradual fall in mobility might be attributed to the increase in carrier-carrier scattering, which plays an important role at room temperature.

Tailoring of band gap through variation in composition is the very important aspect of the preparation. The energy band gap against Se content in these films is plotted in fig.6.The energy gap of alloys films becomes narrower gradually on replacing the sulphur by selenium. The forbidden band width of lead sulphide is 0.40 eV while that of PbSe is 0.29 eV. The band gaps of the ternary compounds are supposed to be in between the two. The results which are going off are proposed to be due to the segregation of Se atoms at these concentrations. The same phenomenon is also observed in resistivity plot, which strengthen the above explanation. Furthermore, the band gap at these points becomes lower on annealing the films which indicates that the inhomogeneity due to segregation of Se disappears.

The presence of sharp structural peaks in XRD patterns evindeces the polycrystalline nature of the samples. For PbS, $PbS_{.8}Se_{.2}$ the preferred orientation is along (111) direction while for $PbS_{.4}Se_{.6}$, $PbS_{.5}Se_{.5}$,

$PbS_{.2}Se_{.8}$ and PbSe alloy it is found to be along (200) direction. This indicates that variation in stoichiometry of anion atoms (S and Se) of the series $PbS_{1-x}Se_x$ changes only the direction of preferred orientation but does not cause any structural phase transition.

4. Conclusion

From the present studies, we observe that the solid solutions of lead sulphide selenide are formed over a wide composition range. $PbS_{1-x}Se_x$ alloy films are useful in detection of infra-red radiations at longer wavelength side, because the energy band gap of these filts lie in the range 0.40 eV to 0.30 eV. The significant aspect of these studies is not only the capability of tailoring the band gap with variation of composition but the resistivity, carrier concentration and mobility of the carriers also gets modified accordingly. In the light of their manifold lucrative distinctions, polycrystalline ternary composition materials find application in tunable detectors and in other optoelectronic devices.

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