

Controlled Deviation from Stoichiometry in PbSe

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Deviation from stoichiometry in PbSe is controlled by the heat-treatment under a specified selenium pressure, and P - T - x diagram for PbSe is given. Uniform specimen with low carrier concentration (p -type: $2.9 \times 10^{16} \text{ cm}^{-3}$, n -type: $4.9 \times 10^{16} \text{ cm}^{-3}$) is obtained by the cooling along the p - n transition boundary. Hall mobility does depend not only on the selenium pressure but also on the treatment temperature from which the specimen is water quenched. The highest hole mobility obtained is $4.3 \times 10^4 \text{ cm}^2/\text{V} \cdot \text{sec}$ at 77°K , and this is higher than any value previously reported. The decreasing tendency of hole mobility toward the lower carrier concentration might be due to the scattering by the minor lattice defect, that is, anion vacancies. The lower the quenching temperature, the more regular arrangement of etch pits is observed. This effect might be responsible for the decrease of mobility.

1. Introduction

Lead selenide is a compound semiconductor which is stable over a narrow composition range, it may take up beyond the stoichiometric composition either excess lead resulting in n -type specimen or excess selenium giving p -type material. The vapor pressure of selenium is fairly high at the temperatures required during the process of preparation and adequate precautions must be taken to maintain the compound in stoichiometric or in some specific composition. The purposes of this work are to control the deviation from stoichiometry in this compound by the heat treatment under a specified selenium pressure and to investigate the effects of this treatment upon the electric properties. There are many investigations¹⁾⁻¹³⁾ on the properties of lead sulphide group of semiconductors, especially on PbS very elaborate results were reported by J. Bloem *et al.*²⁾ But on PbSe there are few studies which pay attentions for the deviation from stoichiometry. Recent approach by R. F. Brebrick *et al.*¹⁴⁾ gives some information on its stability limits. One of the characteristic properties of this compound is its high carrier mobility and this high mobility can be used as a measure of the high purity of the prepared specimen. In this work, Hall effect and electric conductivity are measured over a temperature range from 77°K to room temperature on single crystal specimens which are treated under specified selenium pressures. Serious effects of the heat treatment upon the electric properties are observed, and it is

shown that carrier concentration and carrier mobility can be controlled by the heat treatment under the regulated selenium pressure.

2. Experimental

Single crystal bowl of PbSe of about 20 gr in weight is grown by the Bridgman technique from the nearly stoichiometric melt which is sealed in a quartz tube. Thin specimen approximately 1.5-2.0 mm in thickness is cleaved from this bowl, vacuum- or argon-sealed into a quartz tube and heat-treated under selenium pressure. The partial pressure of selenium is controlled by regulating the temperature of selenium which is sealed in the same quartz tube at the separate position. Temperatures are controlled with the accuracy of $\pm 3^\circ\text{C}$, but the corresponding variation in the partial pressure of selenium reaches as high as $\pm 20\%$ at the lower selenium pressure. After attaining equilibrium, it is water-quenched as it is sealed in the quartz tube. In order to obtain a uniform specimen with low carrier concentration, it is found to be efficacious to cool the specimen along the p - n transition i -boundary (line FG in Fig. 1) and then to treat it at a lower temperature, otherwise it results into a non-uniform specimen or it may take much longer time to attain equilibrium. On this specimen Hall effect and conductivity are measured by the conventional d - c method. Platinum wires of $0.075 \text{ mm}\phi$ are used as contact leads and welded to the specimen by the condenser discharge in argon atmosphere. Carrier concentration is determined from Hall

coefficient at the exhaustion range. Carrier concentration is extending over a wide range from 10^{16} to 10^{19} cm^{-3} , and it is rather inadequate to draw a clear border line between Maxwell-Boltzmann and Fermi-Dirac statistics. In this report carrier concentration is estimated tentatively assuming only classical statistics and single type of carrier.

3. Results and Consideration

From a series of these measurements, equi-carrier-concentration curves are obtained and shown in P - T (pressure-temperature) diagram of Fig. 1. Relation between carrier concentration

and composition is referred by R.F. Brebrick *et al.*¹⁵⁾ for PbS of this group of semiconductors. If it can be assumed that the principal types of lattice defects of PbSe, are quite similar to PbS, then carrier concentration can be easily converted into composition. Equi-carrier-concentration curves can be safely regarded as equi-composition curves and Fig. 1 also can be regarded as P - T - x diagram. In stead of usual atomic percent, carrier concentration is used as a parameter which expresses the specimen composition, because this expression is very convenient in considering the semiconducting properties of this compound.

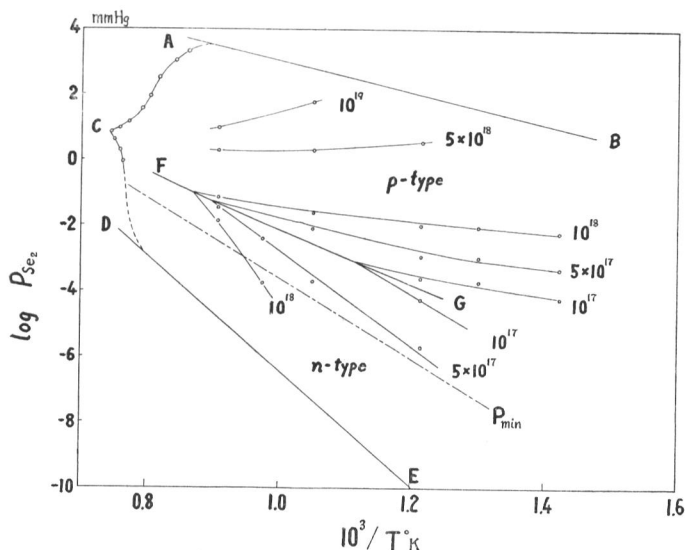


Fig. 1. Equi-carrier-concentration curves and stable range of PbSe as a function of selenium pressure and temperature.

Stability limits of PbSe on P - T diagram is reported in detail in other paper¹⁶⁾. This diagram shows that

1) The aspect of the P - T - x diagram for PbSe is quite similar to that for PbS²⁾, except that the composition with the highest melting point is in the p -type region.

2) The best control of the freezing process itself would not give a specimen with a carrier concentration less than 10^{18} cm^{-3} , and this is the reason why natural or vapor growth crystals often manifest lower carrier concentration than that of the crystals grown from the melt.

3) Cooling along the equi-concentration curve is a fundamental procedure to get a uniform specimen with an expected carrier concentration. Cooling along i -boundary is

efficacious for the purpose to obtain a uniform specimen with a low carrier concentration.

Serious effects of the heat treatment on the electric properties of PbSe are observed. Fig. 2 shows the carrier concentration dependence

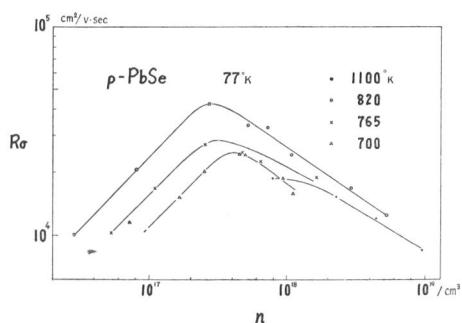


Fig. 2. Carrier concentration dependence of Hall hole mobility at 77°K in p -type PbSe.

of the Hall hole mobility at 77°K. Hole mobility does depend not only on the selenium pressure but also on the heat-treatment temperature, from which the specimen is water quenched. The highest hole mobility obtained in this laboratory is $4.3 \times 10^4 \text{ cm}^2/\text{V} \cdot \text{sec}$ at 77°K, which is higher than any value previously reported. The lowest carrier concentration in *p*-type PbSe $2.9 \times 10^{16} \text{ cm}^{-3}$ is obtained by the above mentioned principle, that is, cooling along *i*-boundary. This value is also lower than any value previously reported for *p*-type PbSe including natural or vapor growth crystals. From these facts it is known that the specimen prepared in this laboratory is of sufficient high purity and that the contamination effects which might be caused by the heat treatment are not serious. As shown in Fig. 2, the highest mobility is obtained for medium carrier concentration and medium heat treatment temperature. The principal lattice defects in this group of semiconductors are thought to be the vacant sites on the cation and anion sub-lattices. The decreasing tendency of carrier mobility toward the lower carrier concentration is already observed for this group of semiconductors, but it is noteworthy that this tendency is very clearly manifested in this work. The disturbance on anion lattice is expected to decrease the hole mobility and to have not so much effects on the electron mobility¹⁷⁾. Similarly the disturbance on cation lattice will greatly decrease the electron mobility but have only small effect on the hole mobility. For *p*-type specimen the principal lattice defect is believed to be cation vacancies. It is known that in the thermal equilibrium the product of the concentration of cation vacancies and that of anion vacancies should be constant at a given temperature. Therefore in the range of low carrier concentration, the effect from minor lattice defect can not always be neglected. Roughly estimating that the concentration of anion vacancies is inversely proportional to hole concentration and assuming the simple impurity scattering by anion vacancies, it follows that hole mobility should be proportional to $2/3$ power of hole concentration. Agreement with the experimental results is rather too excellent for the carrier concentration lower than $2 \times 10^{17} \text{ cm}^{-3}$. Not the vacant site itself, but the electronic disturbance on the anion lattice

might be responsible for the decrease of hole mobility. For the higher carrier concentration the slope in Fig. 2 is more gentle than that expected for the simple impurity scattering, this part may be explained by the similar analysis¹⁸⁾ proposed for some III-V compounds. Fig. 3 shows the temperature dependence of

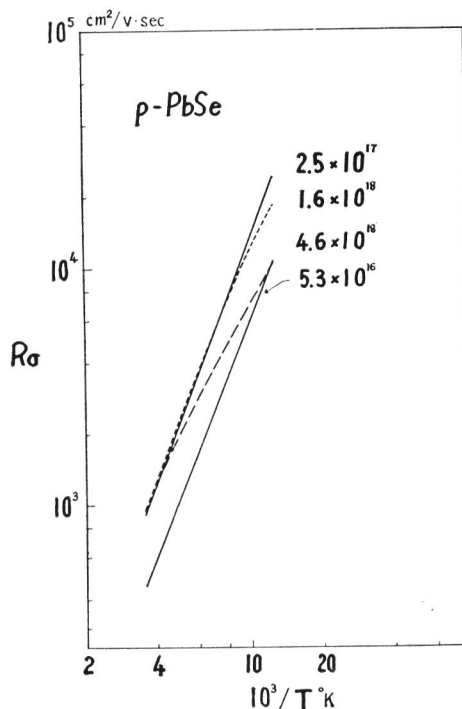


Fig. 3. Temperature dependence of hole mobility.

hole mobility. With the decrease of carrier concentration to $2.5 \times 10^{17} \text{ cm}^{-3}$, upper three curves tend to a line obeying $T^{-5/2}$ law. But for the lower carrier concentration hole mobility decreases still holding the $T^{-5/2}$ relation.

Fig. 4 shows the carrier concentration dependence of electron mobility for *n*-type

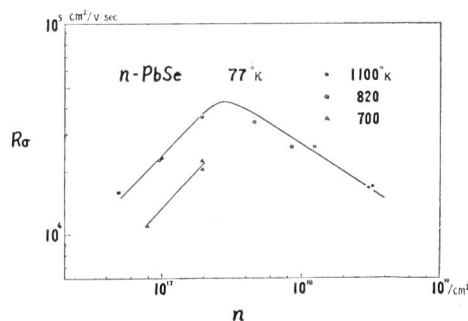


Fig. 4. Carrier concentration dependence of Hall electron mobility at 77°K in *n*-type PbSe.

PbSe. The situations are just the same for *p*-type PbSe. The highest electron mobility at 77°K is expected to be $4.5 \times 10^4 \text{ cm}^2/\text{V} \cdot \text{sec}$ at the carrier concentration of about $3 \times 10^{17} \text{ cm}^{-3}$. It will be worthwhile to note that there is no detectable difference between the values of hole mobility and electron mobility.

Another important effect shown in Figs. 2 and 4 is the decrease of carrier mobility at the lower heat treatment temperature than 820°K. Two approaches are made to explain this effect. The first is the annealing experiment and the second is etch pits observation. The results are not ample enough yet, but some informations are obtained. In annealing experiment we have tried to keep the carrier concentration at a fixed value, but it is very difficult and it is known that hole concentration increases on short time annealing (*ca.* 15 min) at a little higher temperature with no regard to selenium pressure. This effect is similar to the thermal conversion in germanium. More

important information obtained is that the carrier concentration dependence of mobility of the annealed specimen is just the same as before the annealing. This means that the decrease of mobility is not recovered by annealing and the decrease of mobility at the lower quenching temperature has nothing to do with the electronic structure and it may be caused by some irreversible approach to equilibrium, such as association or clustering of lattice defects.

Etch pits are revealed using the etchant recently developed¹⁹⁾. The observed arrangement of etch pits and also of sub-boundaries is the more regular, the lower the quenching temperature as shown in Fig. 5. There is a close relation between the decrease of carrier mobility and the regular arrangement of etch pits. But carrier concentration dependence or carrier type dependence of the distribution of etch pits is not clarified yet and more works will be necessary to obtain their correlations.

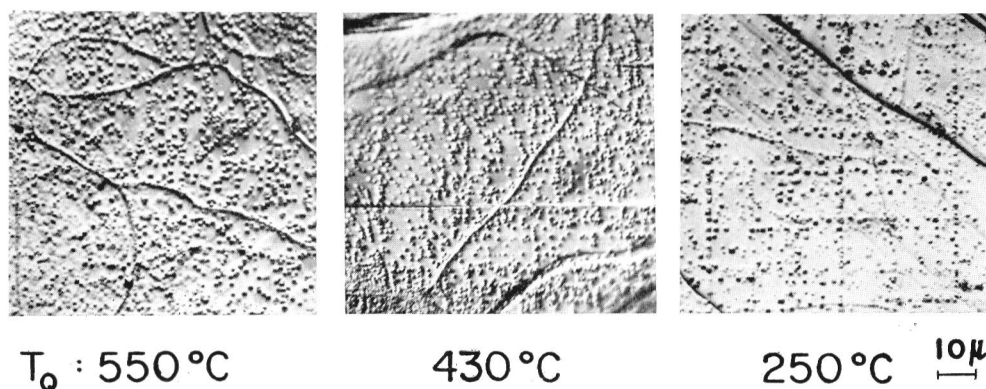


Fig. 5. Dependence of etch pits distribution on the quenching temperature.

4. Concluding Remark

The importance of pressure treatment could not be emphasized too much and the studies on electric properties of the specimens with controlled deviation from stoichiometry would be able to afford much informations on the behavior of lattice defects.

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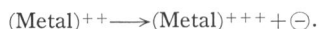
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Vacancy Interaction Energies in Transition Metal Oxides

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Vacancy interaction energies E_{11} and E_{22} (for vacancies with same sign) and E_{12} (with opposite sign) in transition metal oxides of the NaCl-type structure were determined by studying the variations of the partial free energy of oxygen with composition. In MnO, $E_{22}=1.34$ eV; in FeO, $E_{22}=0.120$ eV; in CoO, $E_{22}=2.08$ eV; in TiO, $E_{11}=E_{22}=0.100$ eV, $E_{12}=-0.140$ eV; in VO, $E_{11}=E_{22}=0.202$ eV, $E_{12}=-0.286$ eV; in NbO, $E_{11}=E_{22}=0.780$ eV, $E_{12}=-1.10$ eV. An attempt was also made to calculate the vacancy interaction energies using the Debye-Hückel theory of strong electrolytes to account for the long-range coulombic interaction. This method gave good results for NaCl and KCl, but failed for the transition metal oxides. A qualitative relationship was derived showing that the logarithm of the vacancy interaction energies should depend on E° the potential for the following reaction:



Introduction

Some of the transition metals of Groups IV, V, VII, and VIII form stable monoxides of the NaCl-type structure. Closer examination shows that the structures contain a relatively large concentration of vacancies. The aim of the present work is to obtain some information about these vacancies.

Theory

The theory of compounds with small deviations from stoichiometric composition has been given by Wagner¹⁾ and by Fowler and Guggenheim.²⁾ The theory was expanded by Anderson³⁾ to include larger deviations. However, he considered only the binary compounds AB where the defect is present solely in atom A, either as a vacancy or as an interstitial. In the compounds under present investigation, the defects occur only as vacancies, but both components can show

these vacancies.

The theory for FeO, TiO and NbO was given earlier⁴⁾. MnO, CoO and NiO obey the same relations as FeO. The theory of the VO phase is similar to TiO.

Experimental Results

MnO Phase

Davies and Richardson⁵⁾ studied the oxygen activity at 1773, 1848, and 1923°K, using mixtures of H₂, CO₂, and N₂; their data are shown in Fig. 1. The slope of the solid line gives the vacancy interaction energy: $E_{22}=1.34 \pm 0.05$ eV. Davies and Richardson also calculated a "theoretical" curve, using Wagner's¹⁾ method, which does not consider interaction between vacancies. According to them, when $n_o/n_{Mn} > 1.005$, i.e., the vacancy concentration is larger than 0.0048 per Mn atom, their "theoretical" curve does not fit the data. In Fig. 1, the dotted line ends and