Chapter I

INTRODUCTION

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Over the last two decades, thin film physics has become an independent subject in science. The area of research in this field is rapidly expanding owing to a wide use of thin films in technology and fundamental studies in physics, chemistry and electronics.

Much attention is paid to the studies of films of the solids : Metals, semiconductors and dielectrics. The term "film" usually means a three dimensional structure with one dimension (thickness) much smaller than the other two. Films in the thickness interval of 0.01 to 1 μm are generally called thin films(1) and those with 1 to 100 μm are commonly referred to as thick films.

However, a physically significant measure of the "thickness" is the length of operation of various characteristic parameters, eg. Debye screening length, dislocation spacings, mean free path of charge carriers, etc. The thinner the film, the more its properties are determined by its surface. Therefore, with a variation of thickness within the limits comparable with typical parameters, the film properties change and the observation of size effects indicates the influence of thickness on the properties.

The subject of semiconductors is considered to be of great interest and a particularly active field in solid state physics. Numerous research papers have been published on attempts to understand different properties of these materials such as the electrical, optical, magnetic, thermo-electric, photoconductivity and photovoltaic effects. A better understanding of this wide range of properties as well as the junction and contact properties has helped a lot in the fabrication and development of semiconductor devices. In the last two decades nearly 40,000 papers on semiconductor devices have been published(2).

Next to the elemental semiconductors like Ge, Si, etc., the III-V compound semiconductors have been quite thoroughly studied and developed for many useful applications. Over last ten years or so, other binary, ternary and quaternary compound semiconductors have also drawn considerable attention. Among the various binary compounds of type II-VI, IV-VI and IV-V, the IV-VI semiconducting compounds have many interesting properties and have been comparatively less studied. Apart from the intrinsic interest from the solid state theory point of view, this family of semiconductors finds useful applications in infrared detectors, laser diodes, photovoltaic cells and thermoelectric devices. In particular, SnTe shows super conducting behaviour at low temperatures and affords the interesting possibility of studying superconducting transition as a function of carrier concentration.

In general, the compounds of IV-VI groups have interesting properties characterized by low effective mass, high mobility and non-parabolic dependence of the energy on momentum(3). The binary IV-VI compounds with Ge, Sn or Pb as cations and S, Se or Te as anions form a very interesting class of semiconductors. This can be divided into three groups according to crystal structures. The lead chalcogenides (PbS, PbSe and PbTe) crystallize in a cubic (NaCl) structure. GeTe and SnTe have a rhombohedral structure at low temperatures converting to cubic at 0°C for SnSe and at 400°C for GeTe. GeS, GeSe, SnS and SnSe have an orthorhombic crystal structure(4). These are the least studied compounds of these groups.

Selenium reacts with the elements of group IV with the formation of several chemical compounds. All the elements of this group are characterized by a selenide of MeSe type. In addition, germanium and tin form compounds of the type $MeSe_2$; tin also forms Sn_2Se_3. On the passage from germanium to tin and lead selenides, the lattice changes from the rhombohedral for germanium selenide to cubic for lead selenide. All the selenides of this sub-group are semiconductors of either the hole or the electron type(5). SnSe is a fairly typical member of this interesting class of isomorphoic materials. It occurs at 50 atomic % of each of the elements as shown in the equilibrium phase diagram in Figure - 1. It is seen that there are two equilibrium phases : SnSe at 39.95 wt % Se and $SnSe_2$ at 57.09 wt

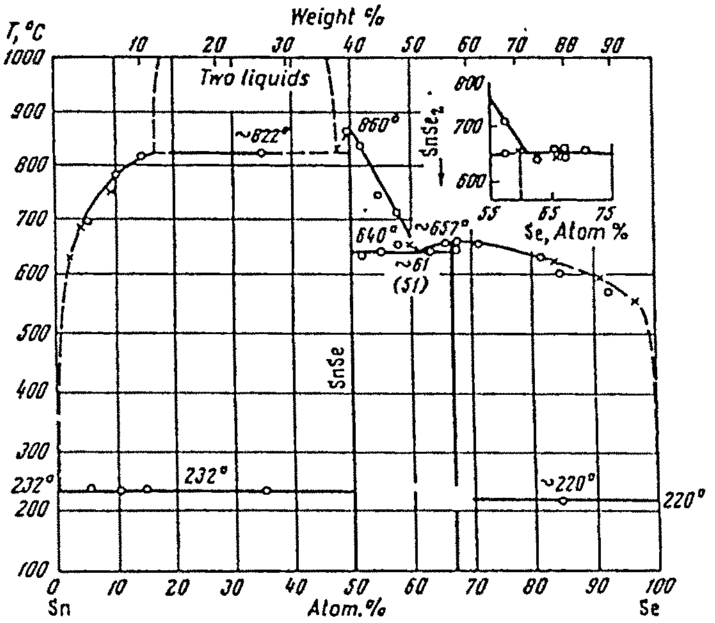


FIGURE - 1 : Phase diagram of Sn - Se

Ref. 9

% of Se. General information about tin mono- and diselenides available from literature is given below together with similar information on SnSe-$SnSe_2$ eutectic.

Tin Selenide :

SnSe has an orthorhombic unit cell belonging to the space group Pbnm. It consists of tightly bonded layers of Sn and Se atoms stacked along the C-axis as shown in Figure - 2. Each atom has three strongly bonded neighbours, within its own layer and three more distant weakly bonded neighbours, one of which lies in an adjacent layer. The bonding between layers is weak, being of Van der waal's type, and therefore the SnSe crystal can be easily cleaved along (001) plane. From this fact, one might expect SnSe to exhibit the typical anisotropy of a layer structure(6,7).

Heat of formation of SnSe is 8 K cal/mol. Its electro negativity difference is 0.7 eV corresponding to a 13 % ionic bond. The basic bond strengths are covalent, predetermining the semiconductor properties of this compound(5).

The lattice parameters of this compound are a=4.33 Å b=3.98 Å and c=11.189 Å (8). The structure has also been described as NaCl (B1) type (9). Its melting point is 860°C. It is a p type semiconductor with specific resistivity in the bulk form about 0.4 ohm-cm. The room temperature mobility (hole) is about 154 cm^2/Vs and the carrier concentration is of the

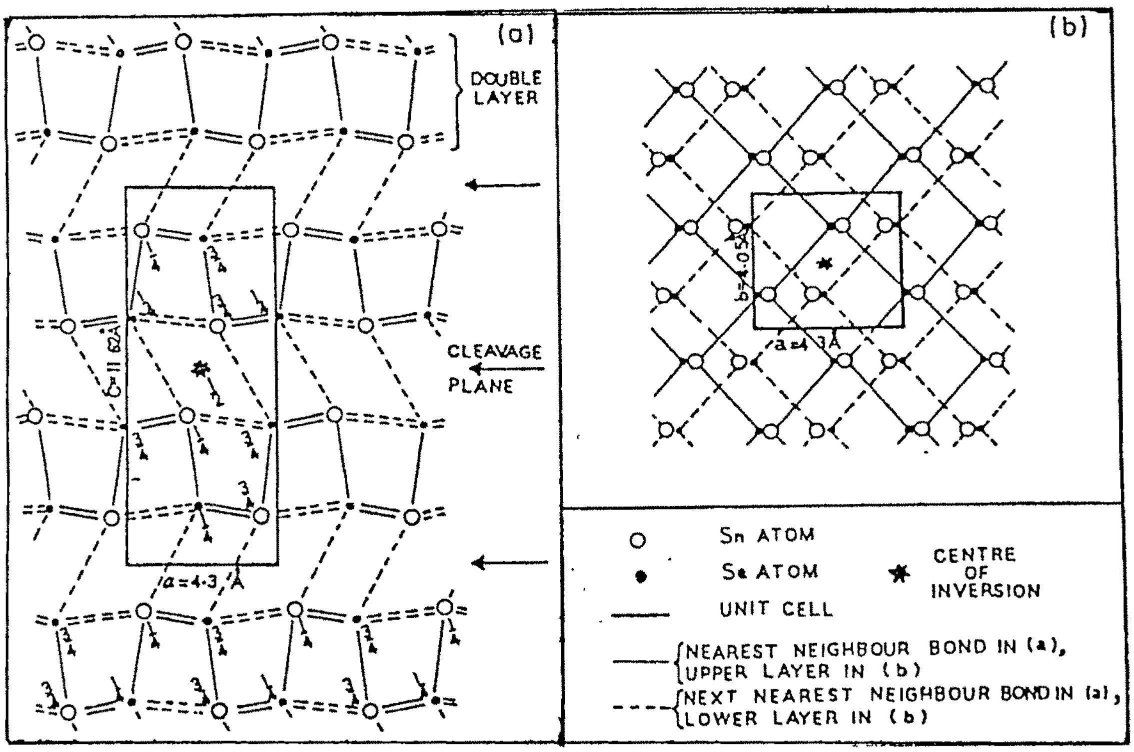


FIGURE - 2 : Structure of SnSe crystal.
(a) Projection on (010) plane.
(b) Projection on (001) plane.

order of 10^{18} cm^{-3}. It has an indirect band gap of about 0.9 eV(10,11) with a high absorption coefficient (greater than 10^4 cm^{-1})(12,13).

Tin diselenide :

The semiconducting compound tin diselenide is a group IV dichalcogenide which crystallizes into the CdI_2 type layered structure (14,15,16,17) with space group $C_{\bar{3}}$ m. This structure consists of sheets of hexagonally close-packed identical atoms, placed perpendicular to the C-axis in the sequence Se-Sn-Se, Se-Sn-Se, etc. along the C direction. One layer is thus composed of one Sn atom sheet sandwiched between two sheets of Se atoms. Each Sn atom within a layer is surrounded by six nearest neighbour Se atoms in an octahedral co-ordination as shown in Figure - 3. Atoms within each layer are strongly bonded together predominantly by covalent forces, while the cohesion between the layers is essentially due to weak, non-localized, Van der Waal's type interactions (18,19).

The lattic parameters of $SnSe_2$ are a=3.811 Å, c=6.137 Å and a/c=1.610(20). Its melting point is about 625 ± 5°C(21). Its electrical resistivity is about 0.3 ohm-cm, and mobility (electron) about 27 cm^2/Vs. It has a direct band gap of about 1.62 eV and also has a possible indirect band gap of 1.01 eV. Like SnSe, it has also a very high absorption co-efficient, viz., more than 10^4 cm^{-1}(20,22).

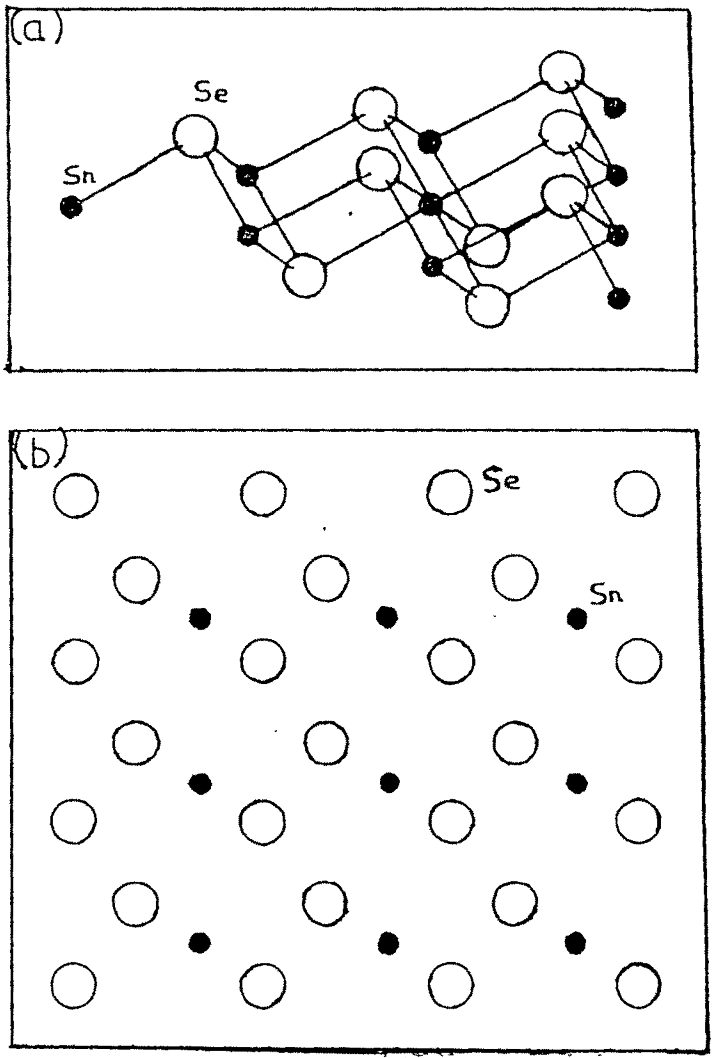


FIGURE - 3 : Structure of $SnSe_2$ Crystal.

(a) Interlayer Co-ordination of the $SnSe_2$ structure.
(b) Projection on the (110) plane.

The Sn-Se system also exhibits a eutectic between the compounds SnSe and $SnSe_2$ at 640°C and at 61 atomic % Se(23). W. Albers has reported the SnSe-$SnSe_2$ eutectic crystals (24) obtained by unidirectional solidification. The lamellae grow perpendicular to the solidification front. The inter-lamellar spacing is regular and inversely proportional to the square root of the growth rate if the eutectic phase exhibits non-faceted growth. It exhibited a high density multilayered p-n heterojunctions. The lamellae of one phase consist of a p type semiconductor while the other phase, an n type semiconductor. The mutual crystallographic orientations of the two phases are shown in Figure - 4. In principle such a structure can be obtained if both the phases are semiconducting and if an added dopant acts as a donor in one phase and as an acceptor in the other. There has been no reference found in literature about any further study on this system.

Films of Tin Selenides :

Thin films of tin selenide have great potentiality because of their application as memory switching devices(25,26). The study of photoconductivity in polycrystalline semiconductor films has a long history which includes an important controversy over the fundamental mechanism of photoconduction. Investigations of non-equilibrium and metastable states in Sn-Se alloys prepared by simultaneous evaporation of the two

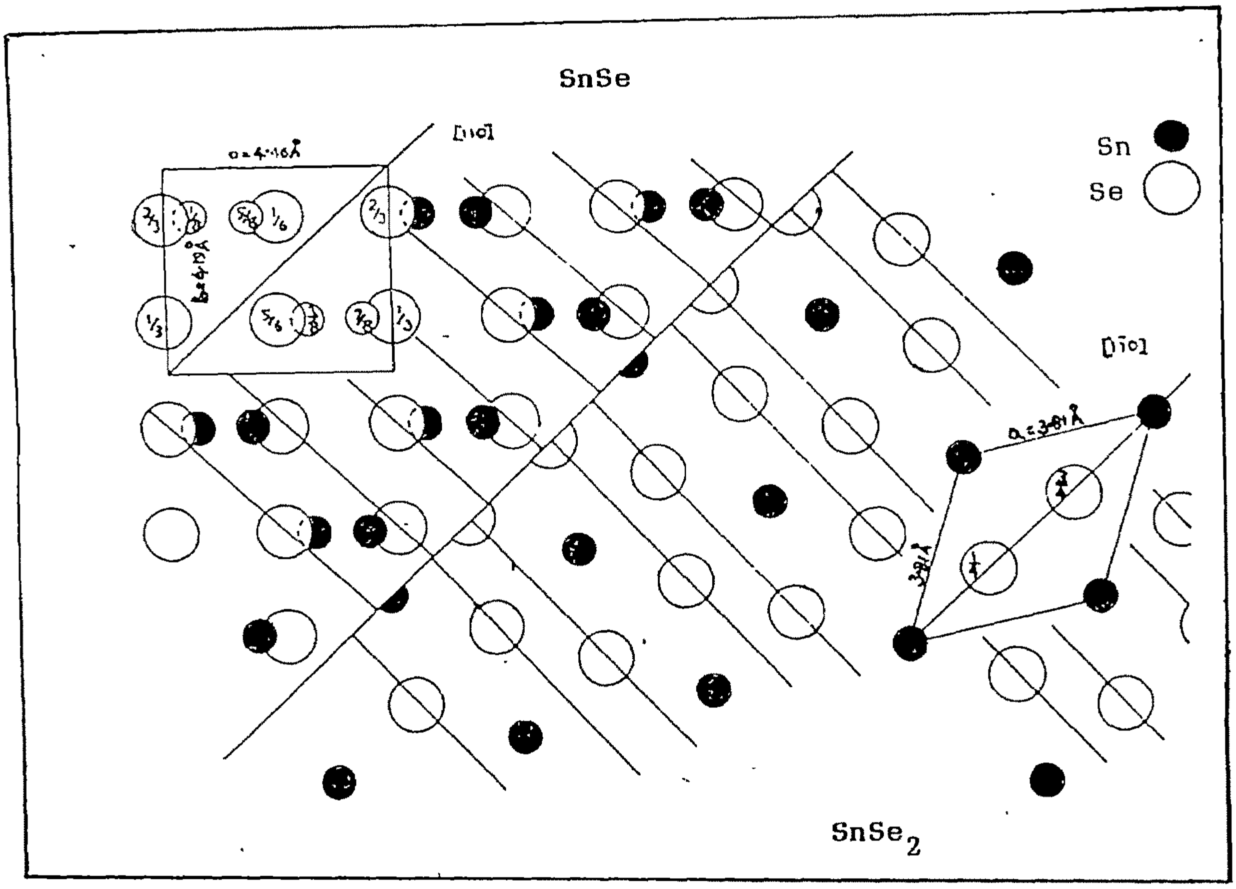
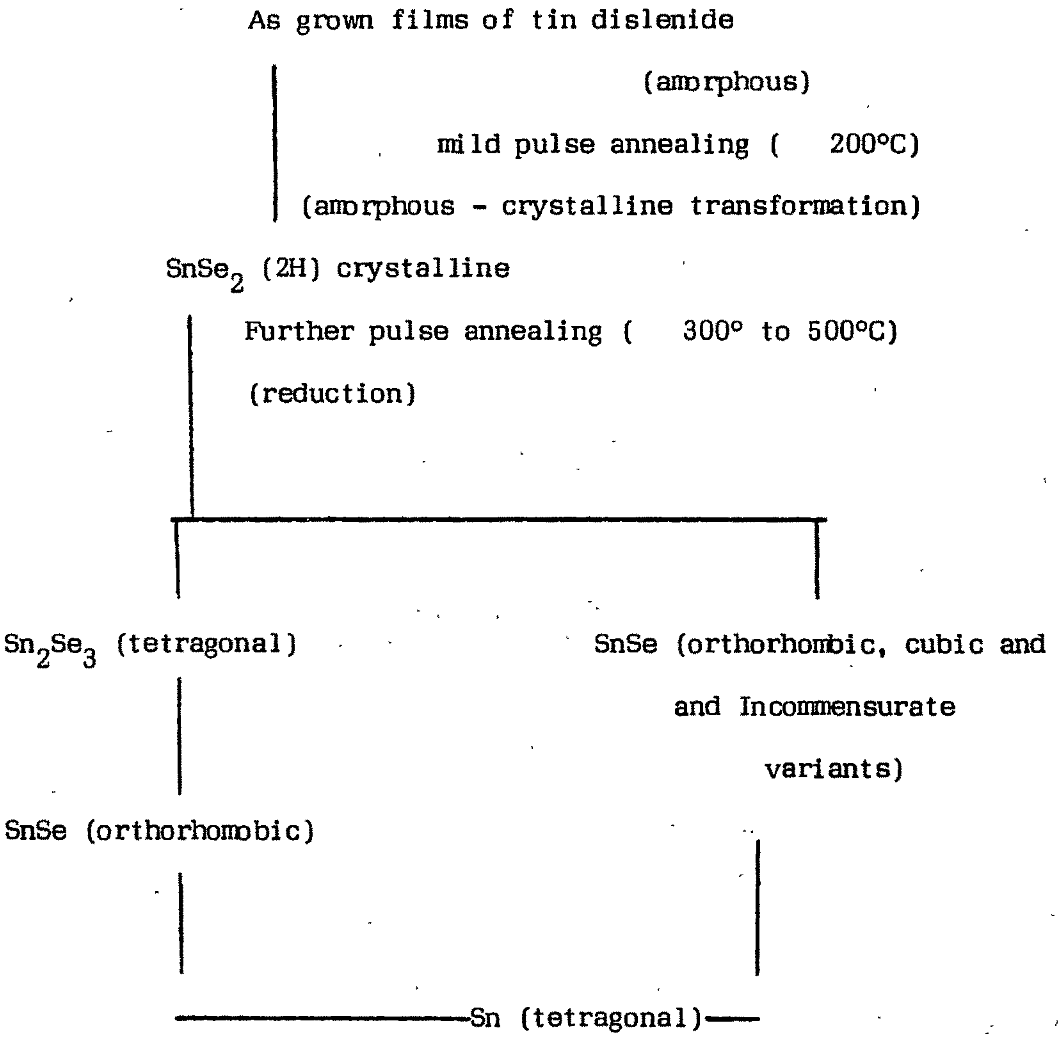


FIGURE - 4 : Crystallographic relationship between the SnSe and the SnSe$_2$ lamellae in the SnSe-SnSe$_2$ eutectic ; projection on the (001) plane.

elements from separate sources and the undergoing solid state reaction have shown the films to be of SnSe. The solid state reacted film of SnSe has the resistivity, the Hall mobility and carrier concentration about ·8 ohm-cm, 59 cm^2/Vs and 10^{17} cm^{-3}, respectively, with a direct band gap of 1.195 ± 0.005 eV.(27)

Directly evaporated SnSe film from the compound is a p type semiconductor. At room temperature, its resistivity, Hall mobility and carrier concentration are about 24 ohm-cm, 10.8 cm^2/Vs and 10^{18} cm^{-3}, resply.(13). It has a direct energy gap of about 1 eV(28). SnSe is sublimed in vacuum at 800°C and is dissociated during the sublimation. As a result of disproportionation, selenium, with a vapour pressure somewhat higher than that of tin and tin selenide, is sublimed together with SnSe. Films prepared in such a manner therefore contains a large quantity of amorphous selenium. Alloys of the system Sn-Se containing 20-40 weight % Se gives a mixture of tin monoselenide with some amorphous selenium in the sublimed films.

$SnSe_2$ thin film exhibits almost exclusively the 2H CdI_2 type structure(5). Tin diselenide thin films prepared by vacuum evaporation undergoes phase transformations and decompositions on pulse annealing treatment. The initial through subsequent to final products that result are summed up in their chronological order as follows(29).



$SnSe_2$ film is an n type semiconductor, with electrical resistivity of about 0.34 ohm-cm and has a direct band gap of about 1.43 eV and the indirect band gap of about 1.24 eV(30).

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