# PART - I

# CHAPTER – 1

# INTRODUCTION

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Apart from the intensive research still going on on the primitive elemental semiconductors Ge and Si, at present much more attention is being paid to compound semiconductors, viz., binary, ternary and quaternary ones.. Among the binary compounds, the group II-IV, IV-VI, III-V and $V_2$-$VI_3$, semiconducting compounds have been receiving considerable attention due to their important photoconducting, photovoltaic, electrooptic and their general electronic properties. Their pseudobinary and ternary compounds have also found their due significance. For the study of basic semiconducting properties, it is of primary importance that these properties be measured on bulk single crystals. The single crystals themselves are also most frequently required directly or indirectly for device fabrication. The performance of the devices principly depends on the bulk crystalline characteristics. Of crucial importance among the characteristics are purity, perfection and homogeneity. Because of this, the field of crystal growth carries no less significance than the crystals themselves. In most of the applications the semiconductors are used in the form of single crystal or thin film or both at a time.

Over the last three 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 semiconducting and other thin films in

technology and fundamental studies in physics, chemistry and electronics. The term "film" usually means a three dimensional structure with one dimension (thickness) much smaller than the other two. Films of thickness in the 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, e.g. Deby screening, dislocation spacings, mean free path of charge carriers, etc.

The thin film physics and technology are relatively newer than crystals and crystal growth. The studies on thin films began only around the start of this century. While reduction in the device size has been a matter of major concern for thin film studies, the thin film characteristics themselves frequently exhibit all together quite curious properties depending on film thickness - the quantum size effect is a striking example. Numerous research papers have been published on attempts to understand various properties of semiconductors (both bulk and thin film) such as optical, magnetic, thermoelectric, photoconductivity and photovoltaic effects, etc. The thin film research has made extraordinary and rapid advancement in recent years to an extent that exotic structures like diamond films and nano-crystals have started coming to the forefront of research.

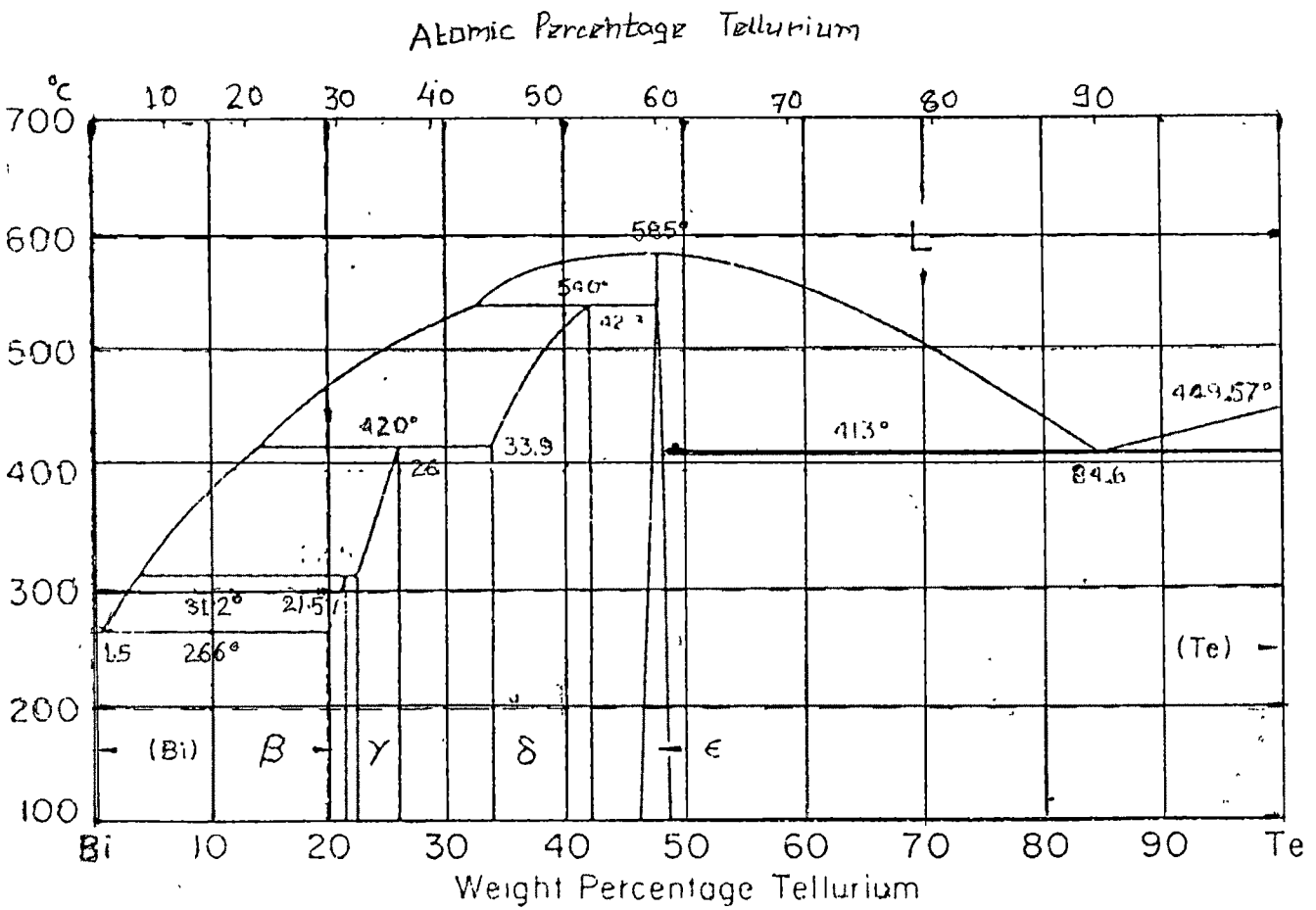
The compound semiconductors may be categorized in terms of the band gap : Wide and Narrow band gap semiconductors. Again the band gap

can be direct or indirect. Typical of wide band gap compounds are GaP, InP, AlSb, GaAs, etc. whose band gaps are greater than 0.5 eV and less than 3 eV (Those with band gaps greater than 3 eV have insulating or near insulating characteristics). Whereas compounds like InSb, PbSe, SnTe, PbTe, etc. have narrow band gaps down to 0.16 eV (InSb). The group V-VI compounds, to which the materials in the present study belong, have narrow band gaps. Whereas the wide gap semiconductors find most of the applications in electronic circuit devices, electrooptical and optoelectronic devices, etc., the narrow gap semiconductors have but restricted range of applications which nevertheless are very important.

The $V_2$ -$VI_3$ ( V = Bi, Sb; VI = Se, Te ) binary compounds and their pseudobinary solid solutions are known to find applications ranging from photoconductive targets in T.V. cameras to I.R.Spectroscopy [2]. These compounds have band gaps : Eg~ 0.2eV, ~0.35 eV and ~0.16eV for $Sb_2Te_3$, $Bi_2Se_3$ and $Bi_2Te_3$, respectively. There are also a few applications for temperature control of Laser diodes[3], optical recording system[4] and strain gauges[5]. Among these $Bi_2Te_3$ is the most potential material for thermoelectric devices such as thermoelectric generators, thermocouples, thermocoolers and I.R.Sensors with the best figure of merit near room temperature [3,6-9]. $Bi_2Te_3$ finds applications also in electronic, microelectronic, optoelectronic and electromechanical devices [10-11]. There have been various studies on the optical and electrical properties of single

crystals and thin films of $Bi_2Te_3$ [12-15]. Its single crystals can be grown by vapour phase technique[2]. They have also been grown by Bridgman-Stockbarger method and zone melting method [11]. Various workers have reported chemical etching of $Bi_2Te_3$[11,16,19]. There is also a report on microhardness of $Bi_2Te_3$ single crystals[2].

Bismuth telluride [$Bi_2Te_3$] occurs at 50 at. % of each of the elements in the system as indicated by the phase diagram in Fig.1[20]. Its melting point is 573 °C and its density, 7.7 gm/cc[21] . $Bi_2Te_3$ and its pseudobinary compounds are highly anisotropic and crystallize into homologous layered structures parallel to the c-axis [22]. The basic unit cell is rhombohedral, but a hexagonal unit cell is often used in its crystal-structure studies. We have used rhombohedral coordinate system for identifying the crystallographic planes [11]. Bismuth telluride possesses the symmetry elements : (a) the three-fold rotation axis [111] (b) three reflection planes containing the three-fold axis (c) three two-fold (binary) axes $[1\bar{0}1]$, $[\bar{1}10]$ and $[0\bar{1}1]$, normal to the three fold axis and bisecting the angle between the reflection planes and (d) a centre of symmetry. The plane normal to the three-fold rotation axis [ the (111) plane ] is also the cleavage plane and is sometimes identified as the c plane. $Bi_2Te_3$ has the space group $R\bar{3}m$[11] with lattice parameters: a = 4.3852 Å, c = 30.483 Å giving c/a = 6.9513 [23]. Its detailed structure is shown in two perspectives in Fig.2. The structure consists of 15 layers stacked along the C axis and presents the combination of 3-layer stacks of


Atomic Percentage Tellurium
°C
10
20
30
40
50
60
70
80
90
700
600
500
400
300
200
100
585°
420°
413°
449.57°
33.9
26
84.6
31.2°
21.5
1.5
266°
(Te)
(Bi)
β
γ
δ
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Bi
10
20
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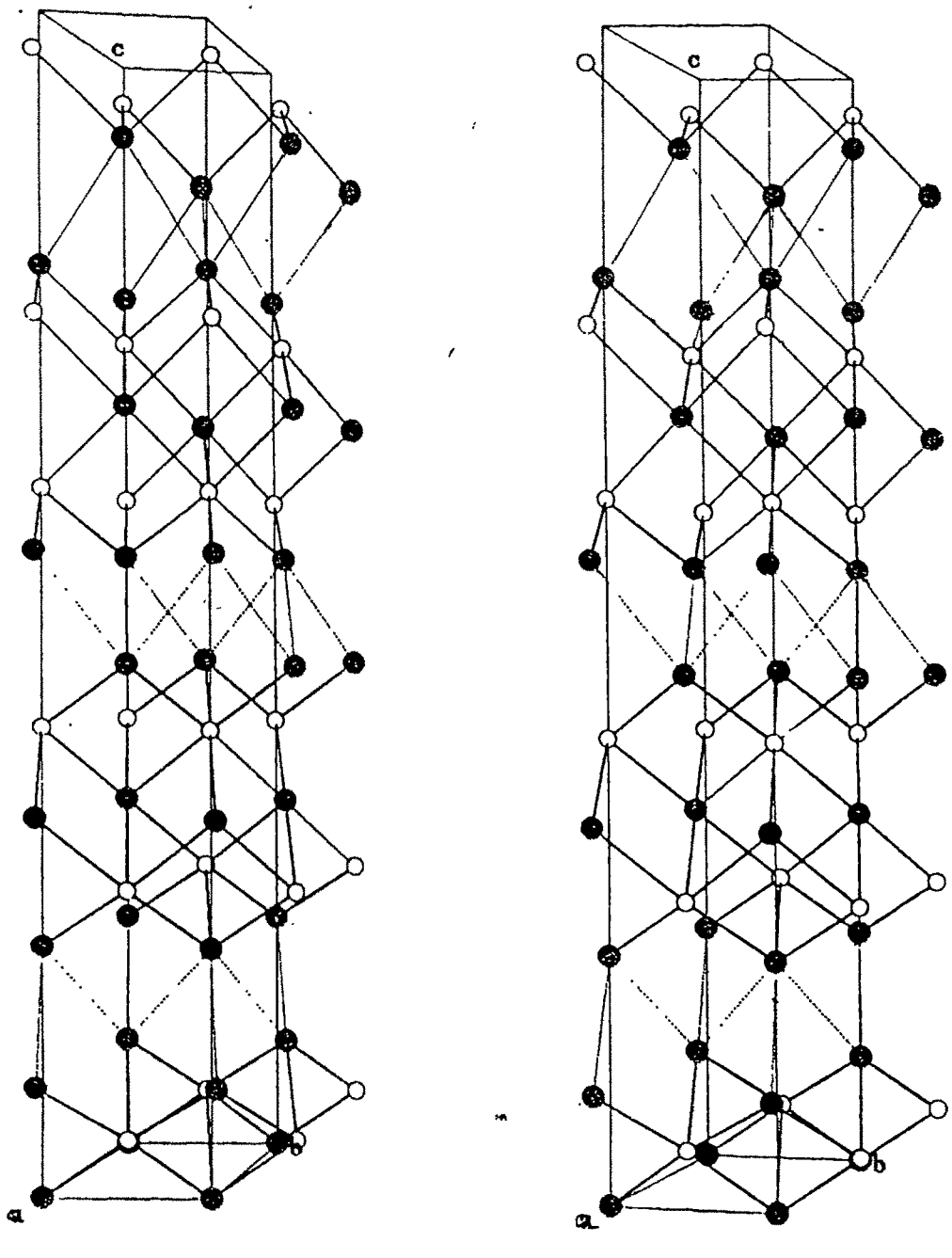
40
50
60
70
80
90
Te
Weight Percentage Tellurium

FIG. 1




Te ● BiO

FIG.2

(Te-Bi-Te-Bi-Te) composition[24]. It is a p-type semiconductor and has a direct band gap of 0.16 eV. At room temperature , the thermoelectric power perpendicular to the c-axis is 218 μV/K [ 7 ]. Its electrical resistivity is of the order of 1.6 x $10^{-5}$ ohm. m[ 7 ] . At room temperature, the Hall coefficient and carrier concentration are 0.42 x $10^{-6}$ $m^3$/A.sec. and 1.75 x $10^{25}$ $m^{-3}$, respectively [7,14 ]. Its Vickers microhardness is about 448 MPa. Electrical conductivity and thermoelectric power of its thin films increase with thickness and attain constant values of 0.3 x $10^5$ $ohm^{-1}$ $m^{-1}$ and 200 μV/K, respectively, at the thickness of ~2000 Å[13]. The thickness dependence has been explained in terms of the size effect. The absolute value of TCR and resistivity activation energy are 40 x $10^{-4}$ $°C^{-1}$ and 0.0287 eV, respectively, at room temperature [13].

Anisotropy of carrier density and its composition dependence in $Bi_{2-x}In_xTe_3$ has been studied by Kutasov et al [ 24 ], Horak et al [ 25] and Pancir et al [ 26 ] . Jansa et al [ 27 ] have studied reflectivity and transmission of $Bi_{2-x}In_xTe_3$ crystals in the infrared region. Horak et al [ 28 ] have studied the relation between structure, bonding and nature of point defects in layered crystals of $Bi_{2-x}In_xTe_3$. They have also reported their results on electrical conductivity, Hall coefficient, concentration of antisite defects and free carriers.

Adding the neighbouring group elements to $Bi_2Te_3$ has been observed to interestingly modify its properties; e.g., addition of Se in different concentrations has been found to influence scattering mechanism and hence the thermoelectric efficiency [29]. Addition of Sb increases the figure of merit of $Bi_2Te_3$ to be useful as a room temperature thermoelectric material [30]. Addition of Sn has been reported to affect I.R. reflectivity [31]. While in general there is a good amount of work reported on the tansport properties of the Sb, Sn and Se doped $Bi_2Te_3$ crystal, there are scarce reports, if any, on their mechanical properties and electronic and optical properties of their thin films in particular. Hence the present work on $Bi_2Te_3$ crystals doped with Sb, Sn and Se at the level of 4 at. % of each was undertaken. The materials in thin film form have also been studied.

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