CHAPTER – 5

GENERAL INFORMATION ON Bi_2Te_3

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Apart from the intensive research still going on onthe primitive elemental semiconductors Ge and Si at present much more attention is being paid to compound semiconductors, viz. binary, ternary and quaternary. 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, and in general electronic properties. For the study of basic semiconducting properties, it is of primary importance that these properties be measured on bulk single crystals which are also required directly or indirectly for device fabrication. Because of this, the field of crystal growth carries no less siginificance than the crystals themselves. In most of the applications the semiconductors are used in the form of single crystals or thin films or both at a time.

Whereas crystal study dates as long back as 18^{th} century, the studies on thin films began only around the start of this century. At present 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. While reduction in the device size has been a matter of major concern for thin film

studies, the thin film characteristics frequently exhibit all together quite curious properties depending on film thickness- the quantum Hall effect is a striking example. Numerous research papers have been published in attempt to understand various properties of semiconductors such as optical, magnetic, thermoelectric and photovoltaic effects etc. The research has made extraordinary and rapid advancement in recent years. This is to an extent that exotic structures like dimond films and nanostructures 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. Typical of wide band gap compounds are GaP, InP, GaAs etc. whose band gaps are greater than 0.5 eV and less than 3 eV. Whereas compounds like InSb, PbSe, SnTe, PbTe etc. have band gaps down to 0.25 eV or less. The V - VI compounds to which the materials in the present study belong have narrow band gaps. 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. [1]. These compounds have band gaps : $E_g \sim 0.2$ eV, ~0.35 eV and ~ 0.16 eV for Sb_2Te_3, Bi_2Se_3 and Bi_2Te_3, respectivcely. There are also a few applications for temperature control of laser diodes [2], optical recording system [3] and strain gauges [4]. Among, these Bi_2Te_3 is the most potential

matrerial for thermoelectric devices such as Peltier cooler, thermocouples and I R sensors with best figure of merit near room temperature [3,5-8] Bi_2Te_3 finds applications also in electronics, microelectronic, optoelectronic and electromechanical devices[9-10]. There have been reports on phase diagram and electrical properties of In_2Te_3 - Bi_2Te_3 solid solutions (e.g. A.J.Rosenberg et al. 1961) [11] . There have also been various reports on the optical and electrical properties of single crystals and thin films of Bi_2Te_3 [12-15]. Their single crystals are usually grown by Bridgman -Stockbarger method [10]. Various workers have reported chemical etching of Bi_2Te_3 [10,16-19]. There is also a report on microhardness of Bi_2Te_3 single crystals[1].

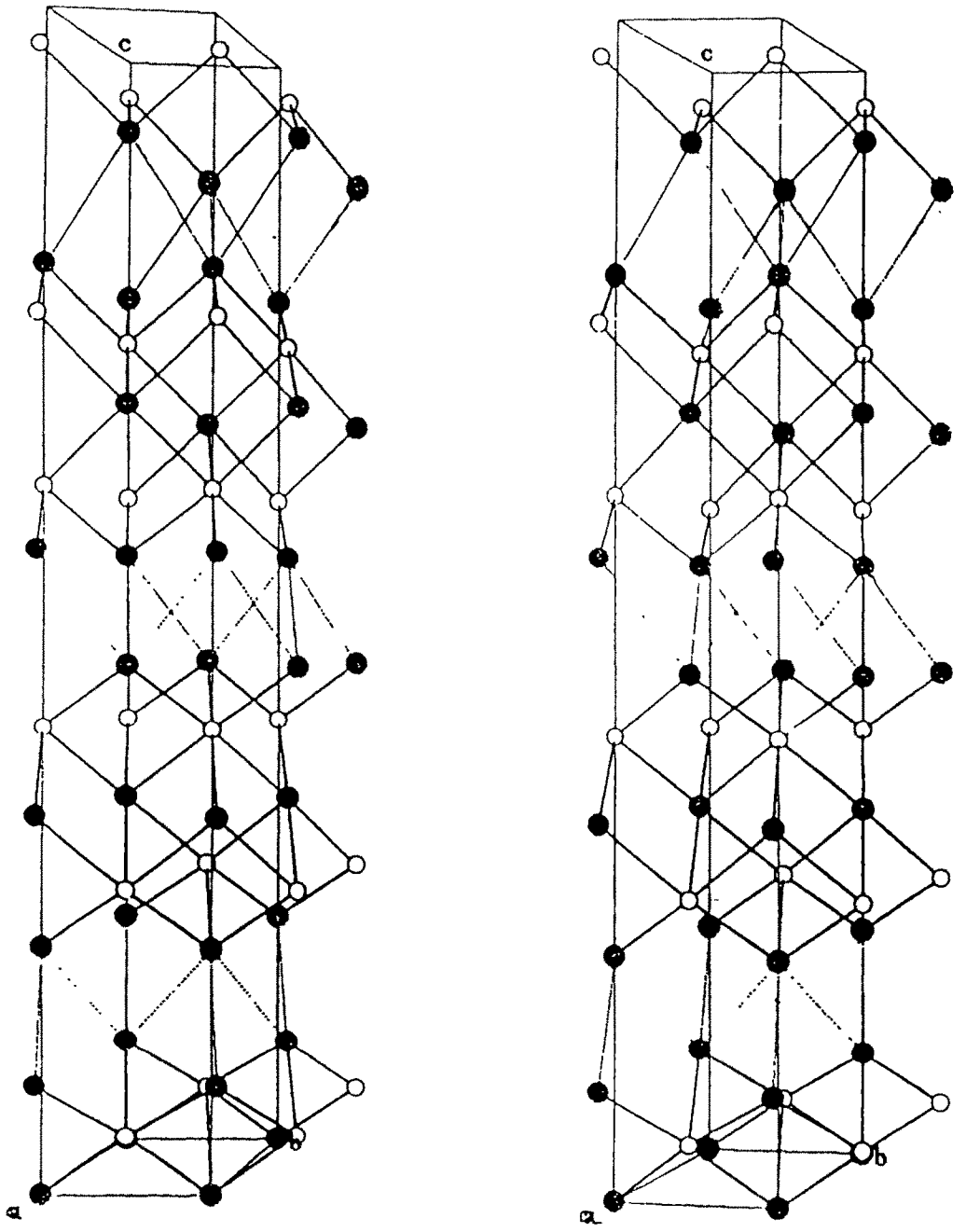
The Bi_2Te_3 semiconducting compound occurs at 50 at % of each of the elements in the system as indicated by the phase diagram in Fig.1 [20]. Its melting point is 573 ^{0}C and its density 7.7 gm/cc[21]. Bi_2Te_3 and its pseudobinary compounds are highly anisotropic and crystallize into homologous layered structures parallel to the c- axis[22]. The basic unit cell is rhombohedral but a hexagonal unit cell is often used in crystal structure study.The unit cell possesses the symmetry elements : (A) a three fold rotation axis (111), (B) three reflection planes containing the three fold axis (C) three- two fold (binary) axes (101), (110) and (011), normal to the three fold axis and bisecting the angle between the

Atomic Percentage Tellurium
°C
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
90
Bi
Te
(Bi)
(Te)
L
449.57°
413°
420°
585°
500°
312°
266°
β
γ
δ
ε
84.6
33.9
26
21.5
1.5
Weight Percentage Tellurium

Fig. 1

mirror planes and (D) a centre of symmetry. Bi_2Te_3 has space group $R\bar{3}m$[10] with lattice parameters of a= 4.3852 Å and c = 30.483 Å giving c/a = 6.9513 [23]. Its detailed structure is shown in two perspectives in Fig.2. It consist of 15 layers[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[6]. Its electrical resistivity is of the order of 1.6 x 10^{-5} ohm-m at room temperature. The Hall coefficient and carrier concentration are 0 42 x 10^{-6} m^3/Asec and 1.75 x 10^{25} m^{-3} , respectively [6,14]. Its microhareness is about 40 Kg/mm^2. 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 film thickness ~ 2000Å[13].The thickness dependence has been explained in terms of size effect. The absolute value of TCR and activation energy are 40 x $10^{-4}/^0C$ and 0.0287 eV,respectively, at room temperature[13].

The formation of $Bi_{2-x}In_xTe_3$ mixed crystal was reported for the first time by Rosenberg et al [11] in 1961. These authors found a high solubility of In_2Te_3 in Bi_2Te_3 (up to x = 0.25) and measured latttice parameters and their dependence on x. Horak et al [26] have studied relation between structure, bonding and nature of point defects in layered crystals of $Bi_{2-x}In_xTe_3$. They have also reported work electrical conductivity, Hall constant, concentration of antisite defects and free



Te ● BiO

FIG.2

carriers. Anisotropy and carrier density and its composotion dependence in $Bi_{2-x}In_xTe_3$ have been studied by Kutasove et al [25], Horak et al.[26], and Pancir et al. [27], Jansa et al. [28] have studied reflectivity and transmission of $Bi_{2-x}In_xTe_3$ crystals in IR region. P. Lostak et al. [29] have studied thermoelectric power of $Bi_{2-x}In_xTe_3$ under 20 GPa pressure. Thus while in general there is a good amount of work reported on the transport properties of $Bi_{2-x}In_xTe_3$ crystals,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 $Bi_{2-x}In_xTe_3$ crystals with x= 0.1 to 0.5 was undertaken. The material in the thin film form has also been studied.

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