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Elaboration and characterization of MOCVD $(Bi_{1-x}Sb_x)_2Te_3$ thin films

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The V_2VI_3 binary compounds such as Bi_2Te_3, Sb_2Te_3, and their alloys are narrow band gap semiconductors with homologous layered-crystal structure. Their electrical and thermoelectrical properties have been extensively studied because of their potential applicability in thermoelectrical devices [1–3]. Thin films of $(Bi_{1-x}Sb_x)_2$ Te_3 have already been grown by several techniques: sputtering deposition [4], flash evaporation [5, 6], and molecular beam epitaxy [2]. However, no work has been reported on $(Bi_{1-x}Sb_x)_2Te_3$ thin films prepared by MOCVD process. Aboulfarah *et al.* [7] have grown thin films of $(Bi_{1-x}Sb_x)_2Te_3$ by MOCVD using trimethylbismuth, triethylantimony, and diethyltellurium as organometallic sources and obtained good results concerning resistivity (16.60 $\mu\Omega$ m) and thermoelectrical power (235 ΩV/K) for $x_v = 0.75$ and Venkatasubramannian *et al.* [8] have studied the MOCVD Bi_2Te_3 and Sb_2Te_3 on GaSb substrate. Many authors have investigated the properties of $(Bi_{1-x}Sb_x)_2Te_3$ thin films and single crystals. Völklein *et al.* [5] have reported on the transport properties of $Bi_{0.5}Sb_{1.5}Te_3$ films deposited onto SiO_2 substrates and their dependence on various annealing conditions and Dillner *et al.* [6] have reported on transport measurements of $Bi_{0.5}Sb_{1.5}Te_3$ films on SiO_2/Si substrates. Aboulfarah *et al.* [9] have studied the effect of VI/V ratio on electrical and thermoelectrical properties of *p*-type $(Bi_{1-x}Sb_x)_2Te_3$ and shown that all properties are improved when the ratio exceeds 3. Hyung-Wook Jeon *et al.* [10] have studied the effect of Sb_2Se_3 addition to Bi_2Te_3-Sb_2Te_3 pseudo-binary alloy grown by Bridgman method. The thermoelectrical properties of $(Bi_{1-x}Sb_x)_2Te_3$ single-crystal solid solutions grown by the T.H.M method have been studied by Caillat *et al.* [11].

The aim of this letter is to report the optimal growth conditions, and the effect of the growth temperature and the partial pressure P_v of the group V elements on electrical and thermoelectrical properties of these semiconductors.

Thin films of $(Bi_{1-x}Sb_x)_2Te_3$ are grown by using MOCVD technique. Trimethylbismuth (TMBi), Triethylantimoiny (TESb), and diethyltellurium (DETe) are used, respectively, as bismuth, antimony, and tellurium organometallic sources. The experiments are performed in horizontal reactor at atmospheric pressure. The TMBi, TESb, and DETe sources are at 5 °C, 20 °C, and 20 °C respectively. Hydrogen is used as carrier gas with a flow rate equal to 6 slm in order to obtain a laminar flow. The VI/V ratio ($R_{VI/V}$ = DETe partial pressure/TMBi partial pressure + TESb partial pressure)) is kept constant and equal to 3. The antimony vapor composition ($X_v = P_{TESb}/(P_{TMBi}+P_{TESb})$) is fixed at 82.5%. The growth temperature is varied from 360 to 470 °C during the deposition process and the partial pressure of the group *V* elements ($P_{TMBi}+P_{TESb}$) is varied from 0.8×10^{-4} to 1.5×10^{-4} atm. An X-ray diffractometer Philips, using monochromatic CuKα ($\lambda = 1.54051$ Å) is employed to obtain diffraction patterns. The measurements are carried out in the range of 5– 30° with several scans in order to increase the accuracy of measurement. Surface morphology is examined by scanning electron microscopy (SEM) and the composition of the deposited layers is measured by means of the energy dispersive X-ray (EDX) microanalyzer. Seebeck coefficients are calculated from the variation of electromotive force with temperature gradient (ΔT). Hall measurements are carried out by using Van Der Pauw's method; the measurements have been made over temperature from 100 to 450 K.

The influence of the growth parameters P_v and temperature T_c, on the growth rate of *p*-type $(Bi_{1-x}Sb_x)_2Te_3$ has been studied. The growth rate as a function of P_v for different temperatures is shown in Fig. 1. It can be seen that the growth rate increase with increasing temperature due to the best cracking of DETe and increase also linearly with P_v because the growth is controlled by the

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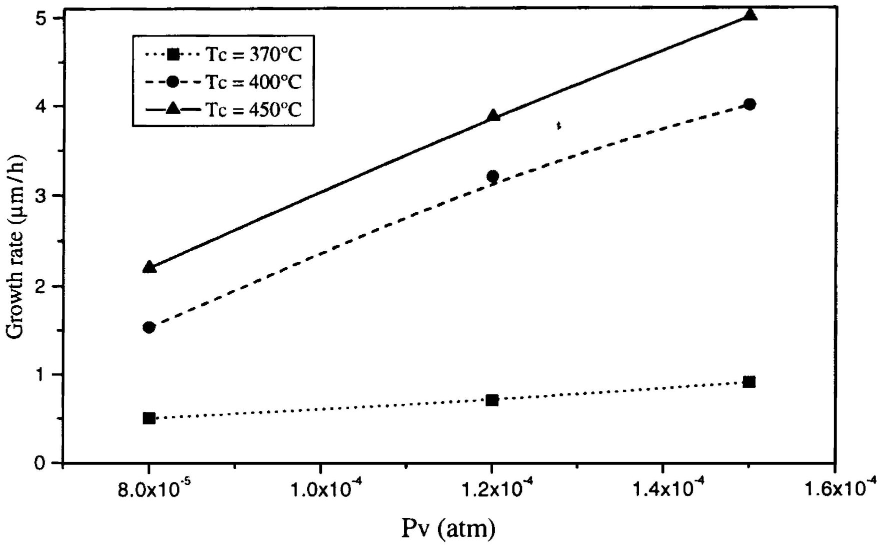

Figure 1 Dependence of growth rate on P_v at a fixed growth temperature.

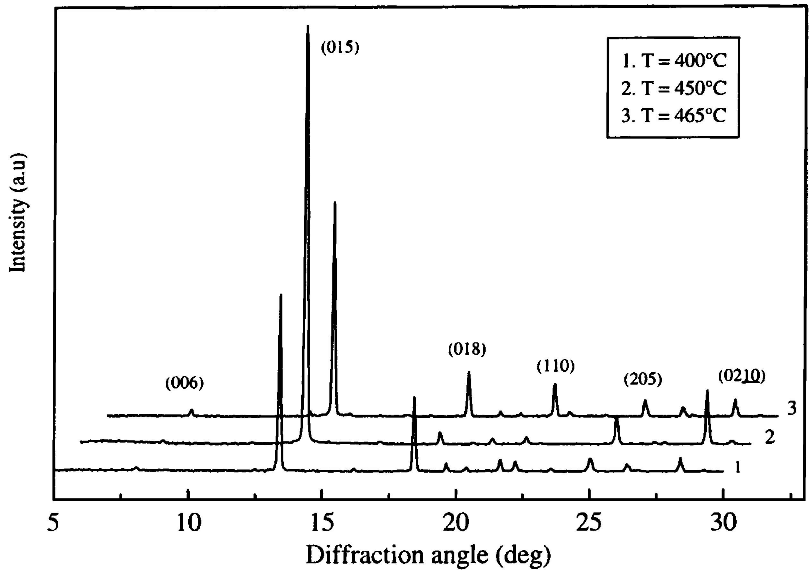

Figure 2 X-ray diffraction pattern of films deposited at different temperatures T_c.

V elements. This result is the same as that obtained for III/V (GaAs) materials [12] where the growth rate is controlled by the III element (TMGa).

In Fig. 2, we present the X-ray diffraction pattern (XRD) $(Bi_{1-x}Sb_x)_2Te_3$ thin films grown by MOCVD on pyrex substrate at different growth temperatures T_c. The deposited layers exhibited a polycrystalline structure which is explained by the presence of (0 1 5) and (1 1 0) peaks. The plane indices are obtained by comparing the intensities and positions of the peaks with those of Bi_2Te_3 and Sb_2Te_3 obtained by ASTM charts. Our results are in good agreement with Joraide *et al.* [13] and Noro *et al.* [4] on the same materials.

The Seebeck coefficient (S) measurements show that all samples are p-type. Fig. 3 shows the variation of the Seebeck coefficient measured at 300 K *versus* growth temperature. The high S obtained at high $T_c > 440$ °C can be explained by the anisotropic thermoelectric characteristics of $(Bi_{1-x}Sb_x)_2Te_3$ which have been evaluated on the basis of orientation distribution of the crystallites [14]. The value of S decreases from 240 to 164 μV/K when the carrier concentration increases from 4×10^{19} to 2×10^{20} cm^{-3} as expected from classical behavior. This result is in the same order of magnitude as that reported by Mongellaz [15] on the corresponding materials grown by T.H.M.

The influence of growth temperature on the electrical resistivity (ρ) measured at room temperature has been investigated and is shown in Fig. 4. It is observed that ρ increases up to a maximum at 410 °C and decreases with increasing T_c.

Fig. 5 shows the variation of the component of the resistivity for thin films at $T_c = 440$ and 465 °C as a function of absolute temperature T. ρ increases with increasing temperature, which is due to the influence of temperature on carriers concentration and Hall mobility.

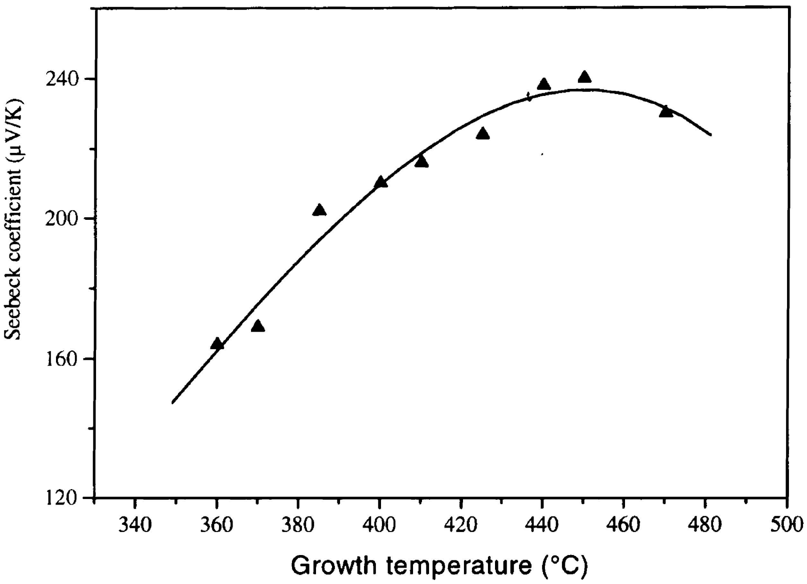

Figure 3 Experimental dependence of Seebeck coefficient on growth temperature.

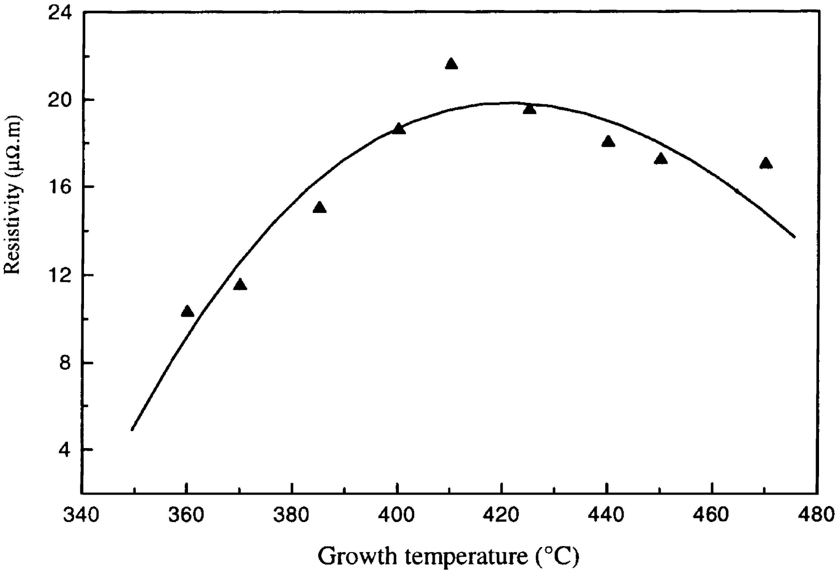

Figure 4 Effect of growth temperature on the electrical resistivity.

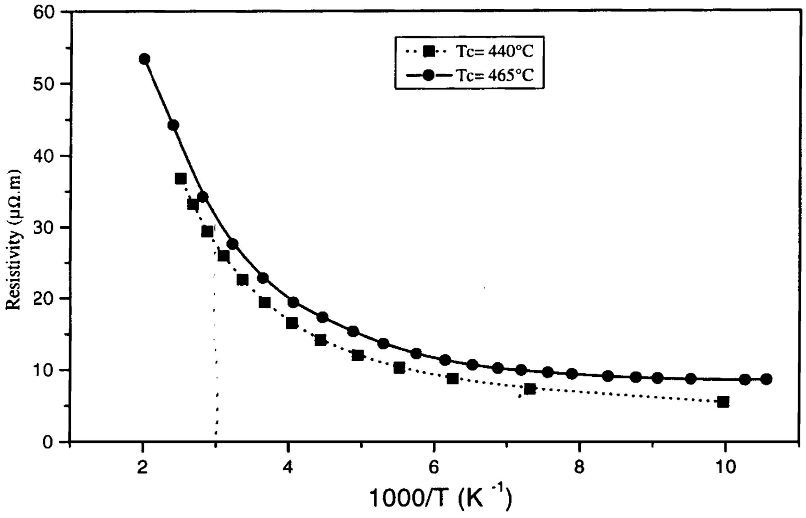

Figure 5 Variation of the electrical resistivity as a function of the reciprocal of the absolute temperature.

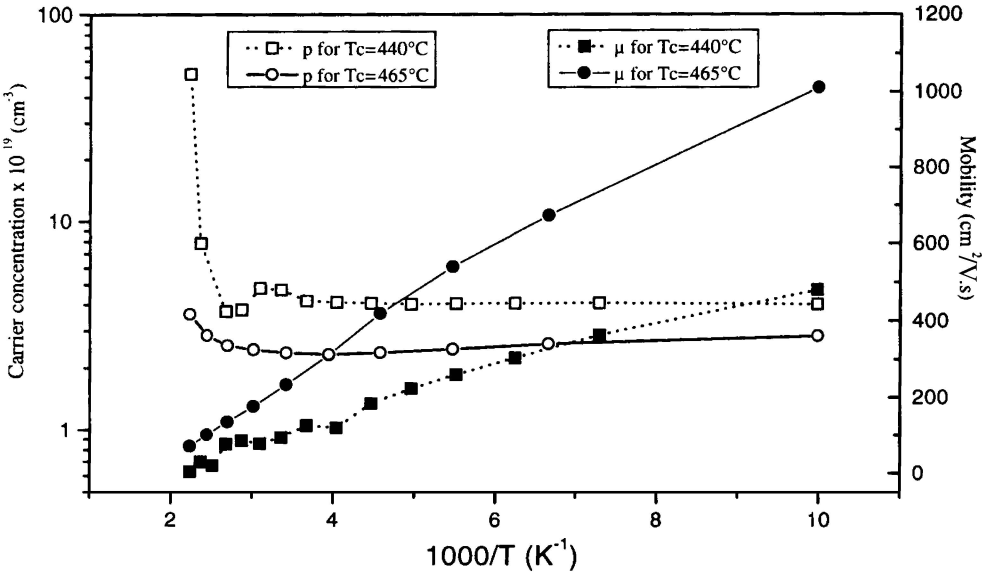

Figure 6 Carriers' concentration and Hall mobility as a function of the reciprocal of the absolute temperature.

Fig. 6 shows the carriers concentration p and the Hall mobility $\mu(\rho = 1/pe\mu_\mathrm{p}$, where e is the electronic charge) as a function of the reciprocal of the absolute temperature. p is still constant with increasing temperature from 100 to 300 K. Above 300 K, p increases with increasing temperature. The Hall mobility is typically lower than that of bulk sample of the corresponding materials. The reason is that a high concentration of defects leads to the formulation of potential barriers (strong scattering) near the boundaries of crystallites.

In conclusion, we have determined the optimal growth conditions for MOCVD method and studied in some details the effects of the growth temperature and the partial pressure on $(\mathrm{Bi}_{1-x}\mathrm{Sb}_x)_2\mathrm{Te}_3$ thin films. It is observed that the Seebeck coefficient increases from 164 to 240 μV/K when the temperature is increased from 360 to 450 °C and the growth rate increases with increasing P_v at a constant temperature.

The obtained electrical and thermoelectrical results are very promising to develop a thermoelectric device based on these materials and suggest the great potential of the MOCVD method to produce good materials with high performances used in thermoelectric applications.

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