MOCVD growth of Bi_2Te_3-Sb_2Te_3 layers. Effect of growth parameters on the electrical and thermoelectrical properties.

B. Aboulfarah, D. Sayah and A. Mzerd
Université M[ed] V Agdal, Faculté des Sciences, Département de Physique, Laboratoire de Physique des Matériaux, Rabat, Maroc.

A. Giani and A. Boyer
Centre d'Electronique et de Micro-Optoélectronique de Montpellier (CEM2), UM II, UMR 5507 CNRS, Place E. Bataillon, 34095 Montpellier cédex 05, France.

The growth of $(Bi_{1-x}Sb_x)_2Te_3$ thin films by metal-organic chemical vapour deposition (MOCVD) using trimethylbismuth, triethylantimony and diethyltellurium as bismuth, antimony and tellurium sources respectively is investigated on pyrex substrates. The electrical and thermoelectrical properties of this material are also measured over the growth temperature range 360-470°C. The studies are also made on the effect of VI/V ratio on these properties in the variation range 2-9. Polycrystalline structure is confirmed by X-ray diffraction, and it is observed that the intensity of the preferred orientation is higher at 450°C. The measurement of Seebeck coefficient shows that all samples have p-type conduction. The best value of this parameter is obtained for high growth temperature (240µV/K). The good result obtained for $(Bi_{1-x}Sb_x)_2Te_3$ thin films revealed the great potential of MOCVD method which is an industrial technique to produce good materials for device applications (sensors and thermopiles).

I. INTRODUCTION

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, 2, 3]. Thin films of $(Bi_{1-x}Sb_x)_2Te_3$ 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. Giani et al. [7] have reported on the MOCVD growth of Bi_2Te_3 thin films, and Venkatasubramannian et al. [8] have studied the MOCVD Bi_2Te_3 and Sb_2Te_3 on GaSb substrate. Aboulfarah et al. [9] have studied the MOCVD growth of Sb_2Te_3 thin films, they have reported on the effect of VI/V ratio on electrical and thermoelactrical properties of this material, they have also studied the growth of $(Bi_{1-x}Sb_x)_2Te_3$ films [10]. Many authors have investigated the physical 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. Hyung-Wook Jeon et al. [11] have studied the effect of Sb_2Se_3 addition to Bi_2Te_3-Sb_2Te_3 pseudo-binary alloy grown by the Bridgman method. The thermoelectric 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. [12]. The authors have showed a maximum in the figure of merit $Z=3.2\ 10^{-3}\ K^{-1}$ for the solid solution $Bi_{0.45}Sb_{1.55}Te_3$.

II. EXPERIMENTAL DETAILS

Thin films of $(Bi_{1-x}Sb_x)_2Te_3$ are grown by using MOCVD technique. Trimethylbismuth (TMBi), triethylantimony (TESb) and diethyltellurium (DETe) are used respectively as bismuth, antimony and tellerium organometallic sources. The experiments are performed in a horizontal reactor at atmospheric pressure. The TMBi, TESb and DETe sources are maintained at 5, 20 and 20°C respectively. Hydrogen is used as carrier gas with a flow rate equal to 6slm in order to obtain a better cracking [7]. The growth temperature is varied between 360 and 470°C during the deposition process. The VI/V ratio ($R_{VI/V}$ = DETe partial pressure/ (TMBi partial pressure + TESb partial pressure)) is also varied between 2 and 9. The partial pressure of the group V elements (Bi and Sb) is kept constant and equal to $1.2x10^{-4}$ atm when the growth temperature and VI/V ratio are varied. An X-ray diffractometer Philips, using monochromatic CuKα (λ = 1.54051Å) is employed to obtained diffraction patterns. The measurements are carried out in the range of 5 to 30° with several scans in order to increase the accuracy of the 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) microanalyser. Seebeck coefficients are calculated from the variation of electromotive force with temperature gradient (ΔT). The Van Der Pauw technique is used at 300°K to evaluate the samples resistivity, Hall mobility and carrier concentration.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the X-ray diffractograms of $(Bi_{1-x}Sb_x)_2Te_3$ thin films for three different growth

temperature (Tc). All patterns are similar and the difference between them might be considered to be the high intensity of the preferred orientation (015) observed for Tc = 450°C. 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, this last result is in good agreement with Joraide et al. [13]. Fig. 2 shows the X-ray patterns of $(Bi_{1-x}Sb_x)_2Te_3$ films for three values of the VI/V ratio and Tc = 450°C. It is observed that the preferred orientation is the same and it's intensity increases with increasing the ratio.

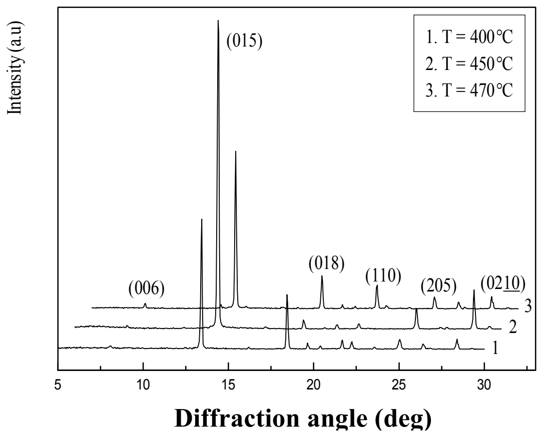

FIG. 1 : X-ray difractograms of MOCVD $(Bi_{1-x}Sb_x)_2Te_3$ For different Tc.

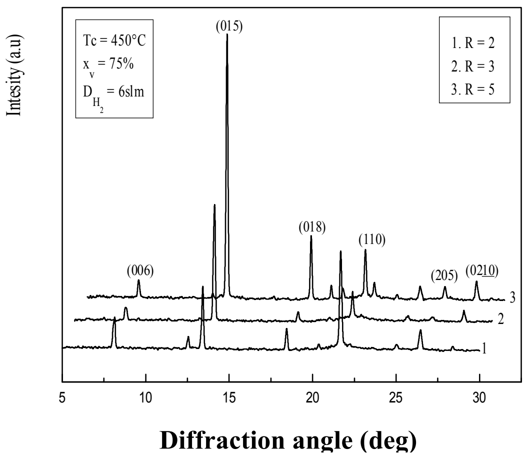

FIG. 2 : X-ray diffraction of $(Bi_{1-x}Sb_x)_2Te_3$ thin films as a function of $R_{VI/V}$.

Fig. 3 illustrates the variation of the Seebeck coefficient (S) of the thin films as a function of the growth temperature, it is observed that all samples have p-type conduction. The Seebeck coefficient has a maximum at a growth temperature near 450°C. The same behaviour of Seebeck coefficients have been observed by Noro et al. [4] on Bi-Sb-Te-Se thin films. The maximum value obtained of S (240µV/K) is better and closed to that reported by Giani et al [14] on flash evaporated p-type $Bi_{0.5}Sb_{1.5}Te_3$. The electrical resistivity (ρ) in dependence of the growth temperature is shown in Fig. 4. The appearance of a maximum in ρ is a direct result of the temperature dependence of the carrier concentration (p) and carrier mobility (µ). The initial increase in ρ is due to the decrease in p with increasing temperature, while the subsequent decrease reflect the increase in mobility.

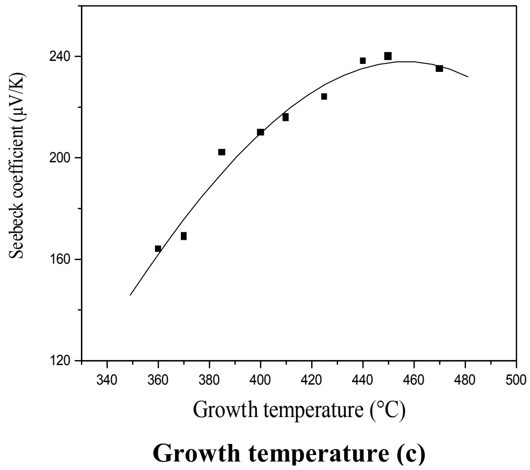

FIG. 3 : Variation of Seebeck coefficient as a function of Tc.

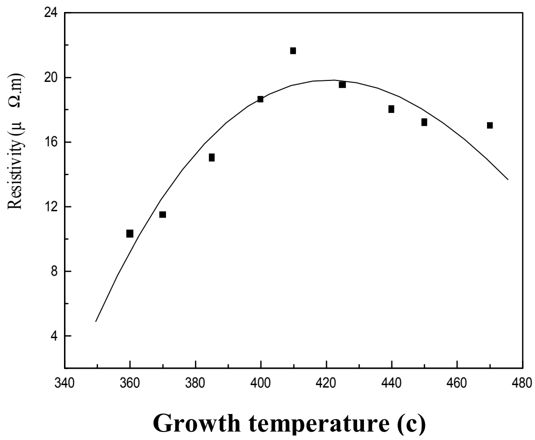

FIG. 4 : Electrical resistivity versus growth temperature Tc.

Fig. 5 shows the evolution of the carrier concentration (p) and mobility (µ) of the deposited layers as a function of the growth temperature. As the temperature increases, the carrier concentration decreases and the mobility increase to a maximum value (120 cm²/V.s). This last value is two or tree times lower than that of single crystals and this can be due to the polycrystalline structure of the materials and a strong boundaries scattering. The high concentration of defects leads to the formulation of potential barriers near the boundaries of the crystallites. The same behaviour of p and µ versus growth temperature had been reported for InAsSb grown by MOCVD by A. Giani et al. [15].

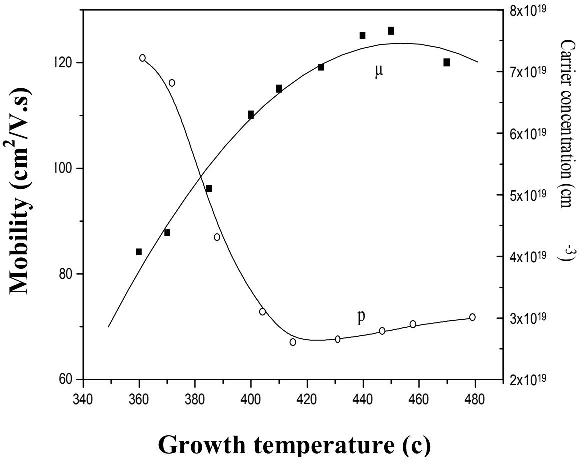

FIG. 5 : Tc dependence on p and μ.

Fig. 6 shows the dependence of the growth rate of $(Bi_{1-x}Sb_x)_2Te_3$ as a function of VI/V ratio for tree different growth temperature. It is observed that the growth rate become constant when $R_{VI/V}$ greater than 3 and increases with increasing temperature. This can be due to the best organometallic cracking observed at high temperature.

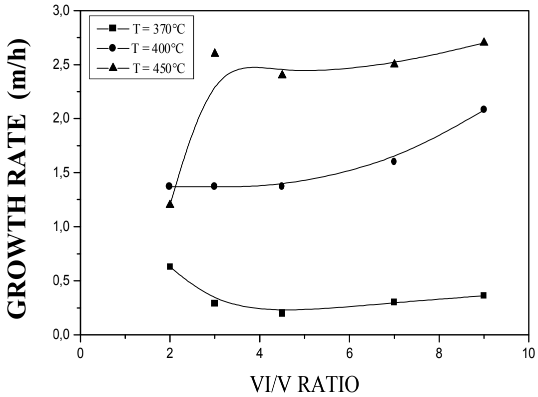

FIG. 6 : Growth rate versus VI/V ratio.

Fig. 7 shows the variation in Seebeck coefficient versus VI/V ratio for different temperature. S increases gradually with increasing the ratio and temperature, when VI/V ratio exceed 5 S become constant and varied with temperature. The same behaviour of S versus the ratio has been observed by Aboulfarah et al. [9] on MOCVD-growth Sb_2Te_3 thin films. The electrical resistivity (ρ) in dependence of VI/V ratio for different temperature is shown in fig. 8. It is observed that ρ increases to a maximum for $R_{VI/V} = 5$ and decrease when R increased.

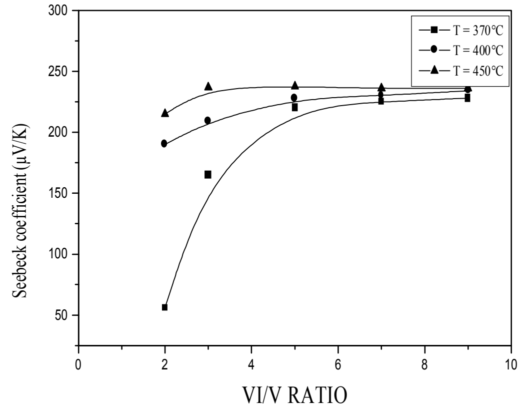

FIG. 7 : Seebeck coefficient Vs. $R_{VI/V}$ for different Tc.

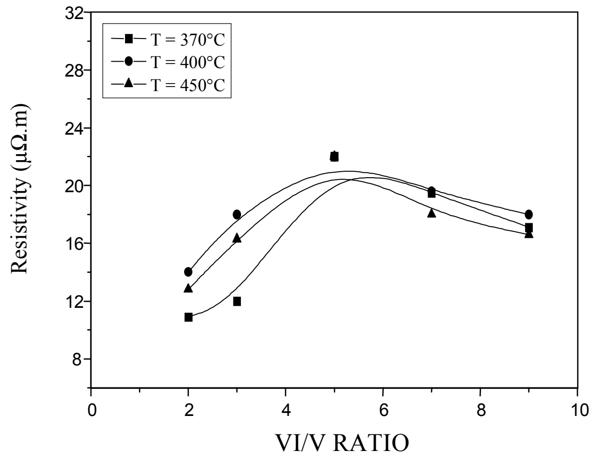

FIG. 8 : Electrical resistivity as a function of $R_{VI/V}$.

Fig. 9 shows the variation of the carrier concentration as a function of VI/V ratio. A noticeable decrease of p for all temperatures is observed. The behaviour of Hall mobility as function of the ratio is indicated in Fig. 10. For all temperatures the mobility increases with increasing the ratio. The best value of mobility is found equal to 120 cm²/V.s for Tc = 450°C, for this growth temperature, the layer must contain lower numbers of grain boundaries which permit a better mobility of the carriers.

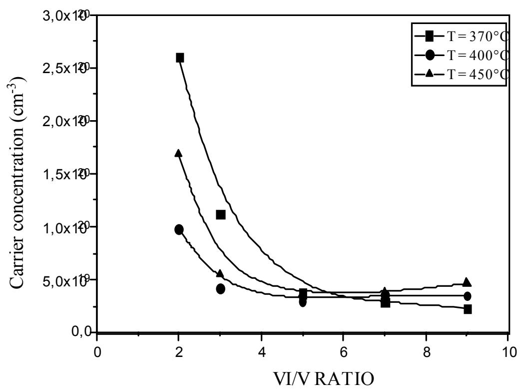

FIG. 9 : VI/V ratio dependence on carrier concentration.

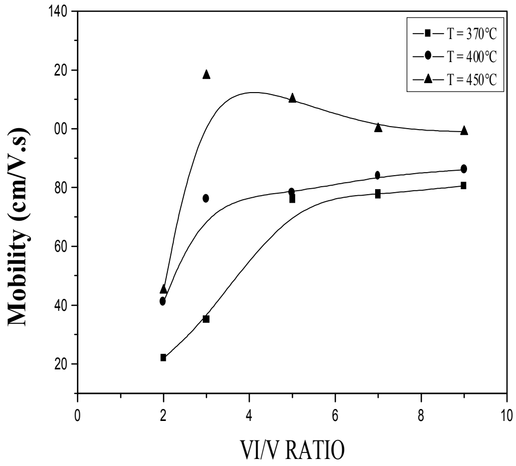

FIG. 10 : Carrier mobility versus $R_{VI/V}$.

IV. CONCLUSIONS

MOCVD growth of p-type $(Bi_{1-x}Sb_x)_2Te_3$ on pyrex substrate is investigated. The growth parameters are studied to obtain a good crystallinity. The electrical and thermoelectrical properties of the layer are shown to be strongly dependent on growth temperature and VI/V ratio. The best results are found for VI/V ratio greater than 3. In the variation range of these parameters, the results obtained for both Seebeck coefficient and resistivity are better and in the same order of magnitude as those of the same single crystals materials. The good results obtained for p-type $(Bi_{1-x}Sb_x)_2Te_3$ thin films suggest a significant potential of MOCVD method to produce good materials for thermoelectric devices.

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