Growth and characterization of Sb_2Te_3 thin films prepared by MOCVD technique in horizontal reactor.

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In this paper the electrical and thermoelectrical performances of p-type Sb_2Te_3 elaborated by metal organic chemical vapour deposition (MOCVD) in horizontal quartz reactor on pyrex glass substrate are discussed. The quality of the deposited layers is controlled by X-ray diffraction, Scanning Elecrtron Microscope (SEM), Energy dispersive X-ray spectroscopy (EDX), and Hall effect. The deposition optimal conditions are : substrate temperature equal to 450°C, the pressure ratio R= VI/V is varied from 1 to 13 and TESb partial pressure is about $1x10^{-4}$ atm. It is found that the electrical properties of Sb_2Te_3 change remarkably with VI/V ratio and exhibited a polycrystalline structure. The measurement of the Seebeck coefficient (115μV/K) and the mobility (196cm^2/V.s) leads us to confirm the significant potential of the OMCVD method to obtain a good material promising for thermoelectric applications.

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 a high thermoelectric figure of merit $Z=S^2\sigma/k$, where S is the Seebeck coefficient, σ is the electrical conductivity and k is the thermal conductivity. These semiconductors have been extensively studied in recent years because of their promising applications especially for thermoelectrical devices [1,2], thermal [3] and humidity [4] sensors using respectively seebeck and peltier effects. Giani et al[5] have grown Bi_2Te_3 on pyrex substrates by using MOCVD technique in a horizontal quartz reactor. They have also studied in some details the electrical and thermoelectrical properties of Bi_2Te_3. Venkatasubramanian et al.,[6] have studied the OMCVD Bi_2Te_3 and Sb_2Te_3 on GaAs substrate and used their superlattice structures for the thermoelectrical applications. Dauscher et al.,[7] have elaborated Bi_2Te_3 thin films by using pulsed laser deposition (PLD). They have showed that a congruent transfer of stoichiometry occurs from the target to the substrate on several cm^2 and a good crystallinity is achieved. Magri et al.,[8] have investigated the properties of electro-deposited bismuth telluride films and showed that the films composition is dependent on the electrolyte composition and the current density.

We report in this paper the results of the electrical and thermoelectrical properties of Sb_2Te_3 thin films prepared by OMCVD method.

II. EXPERIMENTAL DETAILS

In this work Sb_2Te_3 thin films are grown by using OMCVD technique in horizontal quartz reactor. Triethylantimony (TESb) and Triethyltellerium (TETe) are used respectively as antimony and tellurium sources. In order to avoid the possibility of any premature decomposition (TESb) and (TETe) sources are both maintained at 20°C. Hydrogen is used as carrier gas with a flow rate equal to 3 slm in order to obtained a good results. This is due to a better cracking efficiency for 3 slm found by Giani et al.,[5]. The substrate temperature is fixed at 450°C during the deposition process and controlled by a thermocouple directly in contact with the substrate holder. The VI/V ratio ($R_{VI/V}$= TETe partial pressure/ TESb partial pressure) varied between 1 and 13. An X-ray diffractometer Philips, using monochromatic CuKα radiation (λ=1.54051Å) is employed to obtained diffraction patterns. The samples are measured in the range of 5 to 30° with several scans in order to obtain the measurements with accuracy. Surface morphology and cross-sectional view are examined by scanning electron microscope (SEM). The composition of the deposited layers is measured by means of the energy-dispersive X-ray (EDX) microanalyser. To measure Seebeck coefficients, heat is applied to the sample which is placed between two small perfectly parallel brass cylinders. The temperature difference between these two cylinders is measured using thermocouples and a sensitive Keithley digital thermometer. The potential difference is obtained at the position of the two thermocouples using a sensitive digital multimeter. The van der Pauw technique is used at 300K to evaluate the sample resistivity, mobility and carrier concentration.

III. RESULTS AND DISCUSSIONS

X-ray diffraction pattern (Fig.1) compared with ASTM charts showed that the deposited layers are growing in $(0,0,0,l)_H$ and exhibited a polycrystalline phase characterised by $(1,0,\bar{1},5)$ line . The same line is observed by Mandouh[9] on vacuum deposited Sb_2Te_3 thin films and disappeared with annealing at 473K.

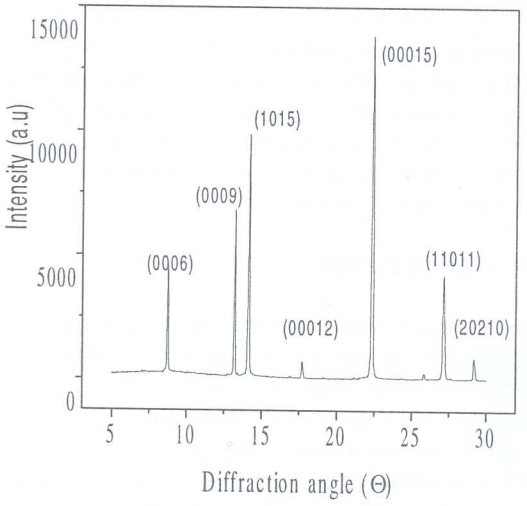

FIG.1. X-ray diffraction spectra of Sb_2Te_3 thin film at VI/V ratio (R= 7) and substrate temperature T_S= 450°C.

The surface morphology and crystallinity of the deposited thin films on amorphous substrate are found to be strongly dependent on the VI/V ratio, and its aspect seemed quite different. The SEM micrograph shown in Fig.2 is of

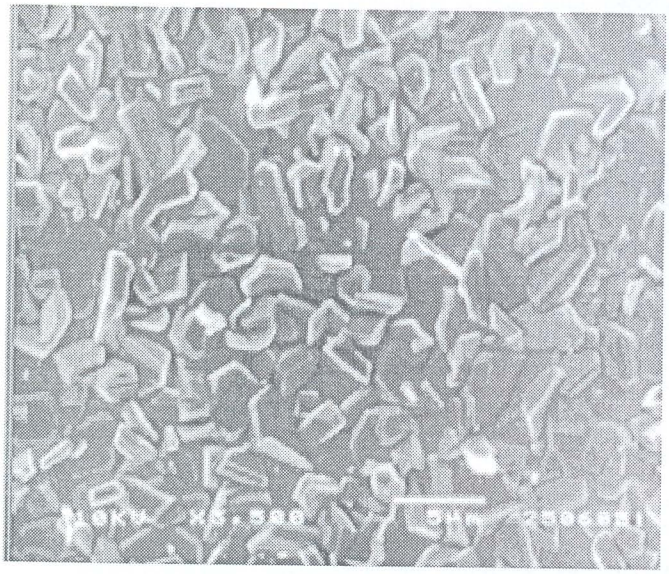

FIG..2. SEM micrograph of Sb_2Te_3 on amorphous substrate (T_S= 450°C and R= 7).

Sb_2Te_3 layer deposited at 450°C and VI/V ratio = 7. It is observed that all crystallites are not symmetrical in shape and showing a hexagonal platelet inclined and display little tendency to adopt a single preferred orientation. This is in good agreement with the X-ray data data and the crystallites are randomly oriented with respect to the amorphous substrate. The cross - sectional view (Fig.3) shows that the depositedlayer is dense and compact and the thickness is 1μm.

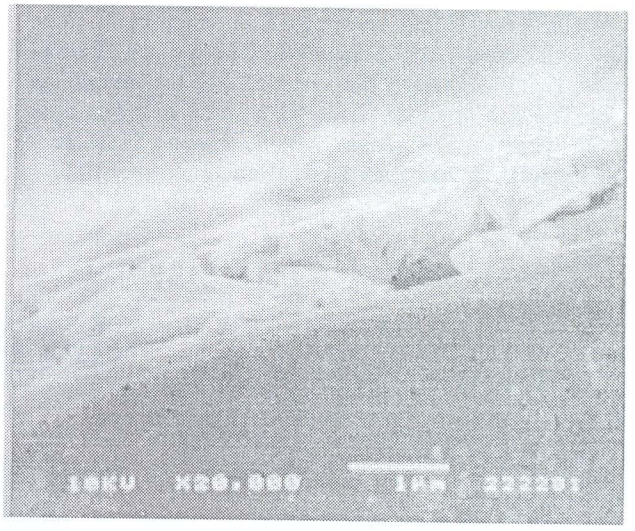

FIG..3. Cross-sectional view of Sb_2Te3 (T_S= 450°C and R= 7).

EDX analysis showed that the compound is usually stoichiometric contrary to the results obtained on Bridgman Sb_2Te_3[10] where progressive loss of Te occurs and the sample composition contains excess Sb atoms which replace Te and this is explained by the higher melting point of Sb than that Sb_2Te_3. The good stoichiomerty in MOCVD films is due to the presence of Te in the vapour phase which composes the losses of the Te in material during the growth process. To avoid non stoichiometry in epitaxial growth of thin films of Bi_2Te_3[11] and Sb_2Te_3[12] in molecular beam epitaxy technique, the authors have deposited their layers in the presence of excess tellurium.

In this paper, thermoelectrical power measurement is made perpendicular to the c-axis. Fig.4 illustrates the variation of the Seebeck coefficient of Sb_2Te_3 as a function of VI/V ratio. The initial abrupt increase in S is explained by the reduction in defect density or by the carriers compensation during the incorporation of tellurium.

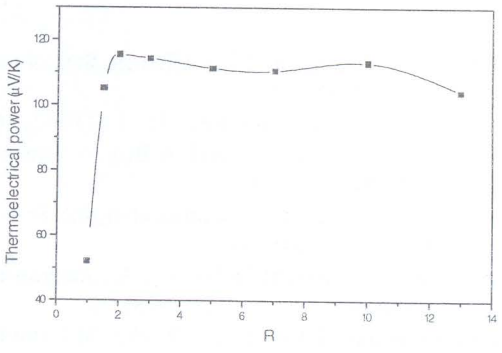

FIG.4.Variation of thermoelectric power S of Sb_2Te_3 thin films at VI/V ratio (R= 7) and substrate T_S= 450°C.

The Seebeck coefficient values for R $\geq$ 3 are in the same order of magnitude as that reported by Mzerd et al.[10] on p-type Sb_2Te_3. Fig.5 shows the variation of the resistivity for Sb_2Te_3 as a function of the VI/V ratio. It is observed that the resistivity decreases with increasing in R in a manner similar to that reported by Giani et al.,[5] on Bi_2Te_3.

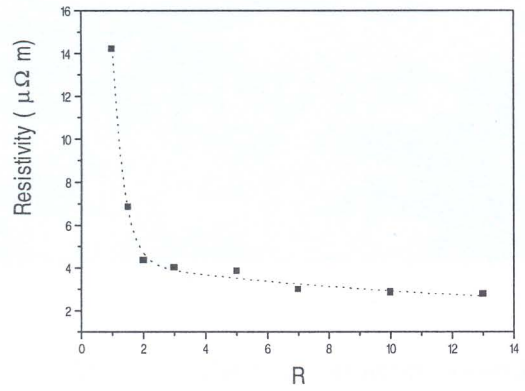

FIG. .5. Variation of the resistivity with VI/V ratio for Sb_2Te_3 thin films at substrate T_S= 450°C.

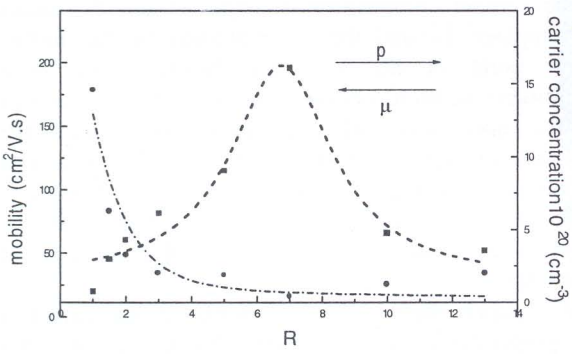

FIG..6. Variation of carrier concentration p and mobility μ with VI/V ratio for Sb_2Te_3 thin films at substrate T_S= 450°C.

Fig.6 shows the evolution of the mobility μ and carrier concentration p as a function of the VI/V ratio. Exceeding VI/V= 3 all properties are improved. It is observed that the mobility increases gradually contrary to the carrier. concentration until an maximum occurs. Exceeding VI/V = 7, this mobility decreases with increasing ratio due to the lower cracking efficiency.

IV. CONCLUSIONS

In this work we have studied in some detail the growth of thin films Sb_2Te_3 on amorphous substrate by MOCVD method in horizontal quartz reactor by using Triethyltellerium as a precursor. It is found that the growth kinetics is controlled only by TESb partial pressure. This pressure is quite different from the reactor pressure during the deposition. As grown thin films are examined by X-ray, SEM and EDX in order to determine their stability and quality. It is found that the deposited layers are stoichiometry and are in the orientation of $(000l)_H$ with the presence of polycrystalline phase(10$\bar{1}$5). It is observed that the electrical and thermoelectrical properties are shown to be dependent on VI/V ratio and best value of mobility is found equal to 196 cm^2/V.s for VI/V ratio equal 7. The decrease in carrier concentration with increasing VI/V is due the cracking efficiency of the gases in the reactor or the carriers are scattered by imperfections such as grain boundaries. This phenomenon is observed by Giani et al.,[5] on Bi_2Te_3 for flow ratio equal 3slm. This work is actually in progress and new results, particularly on photo stimulated V_2VI_3 for reducing growth temperature, will be achieved and published later.

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