Optimal crystal growth conditions of thin films of Bi_2Te_3, Sb_2Te_3 semiconductors and their alloys $Bi_xSb_{2-x}Te_3$. Applications to the thermal sensors

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We have grown stoichiometrically thin films of the narrow band-gap semiconductor Bi_2Te_3 by molecular beam epitaxy in an ultra-high vacuum on single-crystal substrate Sb_2Te_3 prepared by Bridgman technique. The quality of deposited layers is controlled by X-ray diffraction, scanning electron microscope (SEM) , secondary ion mass spectroscopy (SIMS) depth profiling and energy dispersive X-ray (EDX) microanalyser. It is observed that the stoichiometry of the deposited layers depended on substrate temperature and flux ratio. In addition all the deposited layers are single-crystal in the orientation of their substrates with a small shift due to the stress in layer. We have also studied the optimal growth conditions of Bi_2Te_3(n) and Sb_2Te_3(p) layers onto amorphous substrates and the thermoelectric properties of $Bi_xSb_{2-x}Te_3$ alloys as a function of the bismuth concentration x. The optimal value of S (thermoelectrical power) is obtained at x=0.1. The improvement of S in comparison with that of Sb_2Te_3 results in the reduction in antisite defects or carrier compensation. Thermopile and pressure sensors based on [$Bi_{0.1}Sb_{1.9}Te_3$ (p)- Bi_2Te_3 (n)] are constructed. These [p-n] active junctions constitute the sensitive elements of both the thermopiles and the vacuum gauges. In comparison with the (Bi-Sb) couple, an improvement in the sensitivity by factor 2.8 is achieved. Thermal simulation based on COSMOS/M software confirmed the experimental findings.

I. INRODUCTION

The V_2VI_3 binary compounds such as Sb_2Te_3 and Bi_2Te_3 are narrow band-gap semiconductors with the homologous layered-crystal structure. Their electrical and optical properties have been extensively studied because of the potential applicability to efficient thermoelectric devices [1,3]. Mzerd et al.,[4] have studied the effect of heat treatment on electrical properties of Sb_2Te_3 single crystal and showed that the mobility is improved with annealing and at low temperature. They have also studied the semiconducting behaviour and showed that the impurities are responsible for the deviation from stoichiometry and affect the electrical properties.

Temperature and pressure are the most important physical parameters which must be supervised and controlled in many industrial processes. In recent years, considerable attention has been devoted to Sb_2Te_3 and Bi_2Te_3 and their alloys because of their potential applications in the fabrication of thermoelectrical devices based on the Seebeck effect, such as thermal sensors [2,5], hyperfrequency power sensors and wide band radiation detectors[6]. Following the previous work on these materials, we have extended the application to the new active elements in the thermopile [$Bi_{0.1}Sb_{1.9}Te_3$ (p)- Bi_2Te_3 (n)] in order to increase the sensitivity, owing to the higher thermoelectric power of the [p-n] junction. Before manufacturing the thermopile and vacuum gauge, thermal simulation based on finite elements is achieved by using COSMOS/M software. This simulation permits us to carefully consider the design of the sensor in order to obtain a sensor with high sensitivity in temperature and pressure[7].

II. EXPERIMENTAL DETAILS

A. Preparation of Sb_2Te_3

Sb_2Te_3 single-crystal substrates are grown by a gradient freeze method in a Bridgman apparatus by using the pellets of the elements Sb and Te with 99.999% purity with corresponding stoichiometric composition. 40% Sb and 60% Te are mixed in a sealed evacuated tube (10^{-4} Torr) and are heated to 800°C in an electrical furnace and then cooled to form the starting ingot. The obtained ingot is then broken into grains and mixed in a sealed evacuated Bridgman quartz tube (10^{-4}Torr). The temperature gradient in the Bridgman furnace is about 1°C/h. The samples are taken from the natural cleavage faces of Sb_2Te_3 by carefully cleaving off a thin layer whose thickness is determined by a mechanical standard method. It is observed from the thermoelectrical power measurement over the temperature range from 100 to 300K that the substrate exhibited p-type conduction.

B. Growth of Bi_2Te_3 and $Bi_xSb_{2-x}Te_3$

Bi_2Te_3 and $Bi_xSb_{2-x}Te_3$ thin films are deposited using the molecular beam epitaxy from three effusion cells (Bi, Sb and Te). These compounds are obtained by condensation of the Bi, Sb and Te molecular beams on single-crystal substrate Sb_2Te_3 for epitaxy and on an amorphous substrate, Al_2O_3 for the thermopile, and on polyimide film (Kapton) for the pressure sensor in an ultra-high vacuum chamber. The optimal deposition conditions are as follows:

- For the epitaxy of Bi_2Te_3 on p-type Sb_2Te_3, the substrate temperature and ratio flux are varied from 100 to 350°C and from 2 to 6 respectively, with an excess of tellurium which yield n-type material.
- For Bi_2Te_3 and $Bi_xSb_{2-x}Te_3$ on amorphous substrate, the substrate temperature is approximately 260°C

with the flux ratios Fr = Te/Bi and Fr = Te/(Bi+Sb) greater than three. The deposition rates of Bi and Te for Bi_2Te_3 are respectively 1.12 and 4.12Ås^{-1} and those of Bi, Sb and Te for $Bi_{0.1}Sb_{1.9}Te_3$ are respectively 0.13, 1.25 and 4.12s^{-1}.

C. Description of the thermopile and vacuum gauge

The thermopile (Fig.1) is based on aluminium (1mm) and

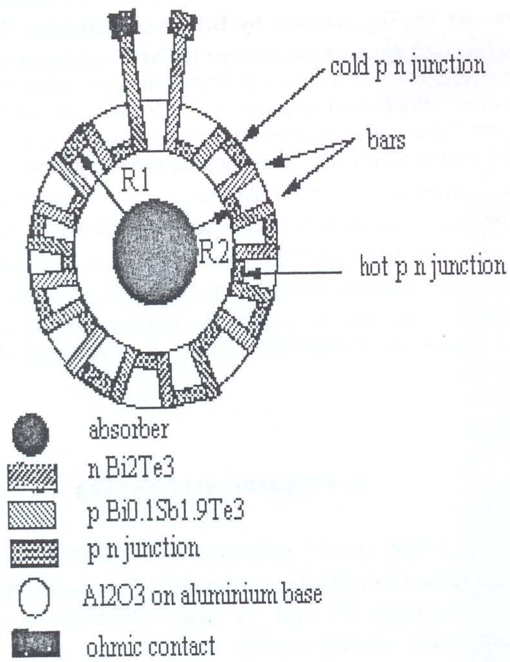


FIG.1. Schematic drawing of ($Bi_{0.1}$ $Sb_{1.9}$ Te_3) thermopile.

steel disk (0.7mm) covered respectively by an thin electrical insulating Al_2O_3 (50µm) and an enamel film (50µm). The thermopile consists of 2N semiconductors (small bars in Fig.1) which are alternately arranged to form N individual junctions in series. The absorber transforms the energy of the laser beam into heat energy, which is

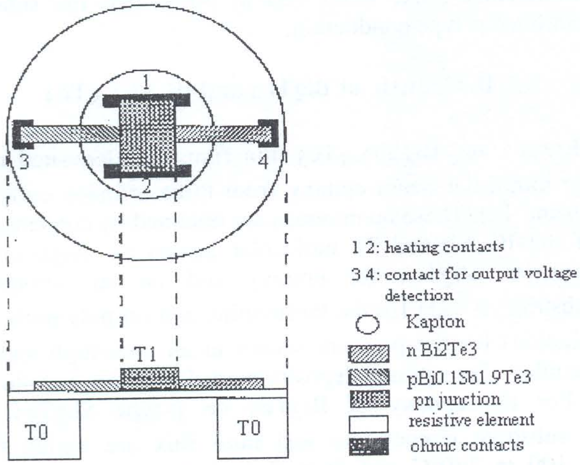


FIG.2. Schematic drawing of ($Bi_{0.1}$ $Sb_{1.9}$ Te_3- Bi_2Te_3) vacuum gauge.

evacuated by conduction in the metal disk. This acts as a mechanical and thermal link between the absorber and the thermostat, which is kept at room temperature by a water-cooled radiator. The thermopile measures the temperature difference ΔT produced in the disk. Its hot and cold junctions are distributed over two isothermic circles of radius R_1= 13mm and R_2= 9mm for reasons of symetry. The pressure sensor (Fig.2) consists of a resistive element R, which constitutes two superposed layers Bi_2Te_3 and $Bi_{0.1}Sb_{1.9}Te_3$ and the two perpendicular thermocouple arms. The Kapton supporting membrane acts as the thermal insulator of R. The resistive element R is heated using an a.c electrical power supply applied to the contacts 1 and 2. The temperature measurement is performed owing to the thermocouple contacts 3 and 4. In both cases the active thermoelements are deposited through two complementary masks of nickel.

III. RESULTS AND DISCUSSIONS

High resolution X-ray diffraction (XRD) patterns are obtained by using a Philips diffractometer (CuK$_\alpha$ radiation, λ= 1.5418Å). Typical X-ray diffraction spectra of Bi_2Te_3 thin films on Sb_2Te_3 as a function of substrate temperature are shown in Fig.3. By comparison of the relative intensities of Bi_2Te_3, it is observed that the relative

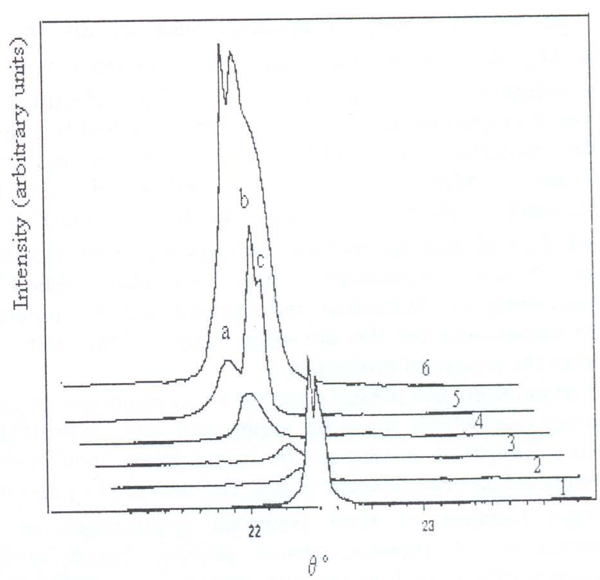


FIG..3. .X-ray diffraction spectra of separated radiation CuKα_1 and CuKα_2 of layer and substrate as a function of substrate temperature at flux ratio Fr= 4.5. (1.substrate, 2.Ts= 200°C, 3.Ts= 280°C, 4.Ts= 300°C, 5.Ts= 310°C, 6.Ts=330°C).

intensity of the $(00015)_H$ peak is greater than the other peaks and varied with increasing temperature. It is also observed that the layer peaks appear before those of the substrate (Fig.4) and shifted to lower angles with respect to the position given in ASTM charts. As the mismatch in the Bi_2Te_3/Sb_2Te_3 system is quite large, 3% (a_H is 4,38Å for Bi_2Te_3 and 4.25Å for Sb_2Te_3) the deposited films are certain to be replete with dislocations in order to accommodate the resulting strain.

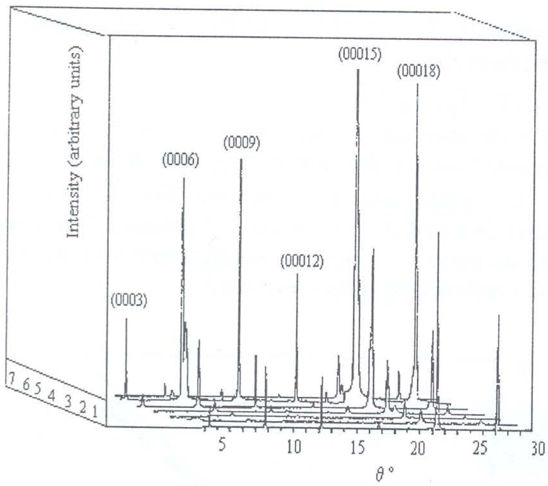


FIG.4. X-ray diffraction spectra of Sb_2Te_3 and deposited layer Bi_2Te_3 as function of substrate temperature at flux ratio Fr= 4.5. (1.substrate, 2.Ts= 200°C, 3.Ts= 280°C, 4.Ts= 300°C, 5.Ts= 310°C, 6.Ts=330°C, 7.Ts= 350°C).

As the mismatch in the Bi_2Te_3/Sb_2Te_3 system is quite large, 3% (a_H is 4,38Å for Bi_2Te_3 and 4.25Å for Sb_2Te_3) the deposited films are certain to be replete with dislocations in order to accommodate the resulting strain. Examination of SIMS spectra (Fig.5) of Bi_2Te_3/Sb_2Te_3 system in optimal growth conditions (Ts= 310°C, Fr= 4.5)

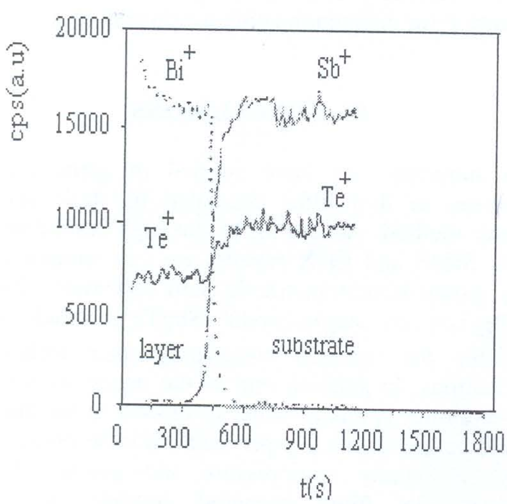


FIG.5. SIMS depth profile of layer and substrate elements (Bi, Te and Sb) for Ts= 310°C and Fr= 4.5.

reveals that Bi atoms do not diffuse into the substrate. The thickness is uniform and the interface is relatively abrupt. It is also observed that the Te and Bi profiles are uniform across the deposited layer.

To express the calculated values of sticking coefficient Ks(x), which is the most significant parameter of semiconductor growth by molecular beam epitaxy method, we have used the experimental results of EDX analysis and previous calculation[8] . Fig.6 and Fig.7 show respectively the variation in sticking coefficient Ks (Te, Bi) of the elements that composed Bi_2Te_3 as a function of Ts and Fr . It is observed that Ks (Bi) is independent of Ts and this is explained by the fact that all effused Bi atoms are stuck on the substrate but Ks (Te) is very sensitive to variation in Ts.

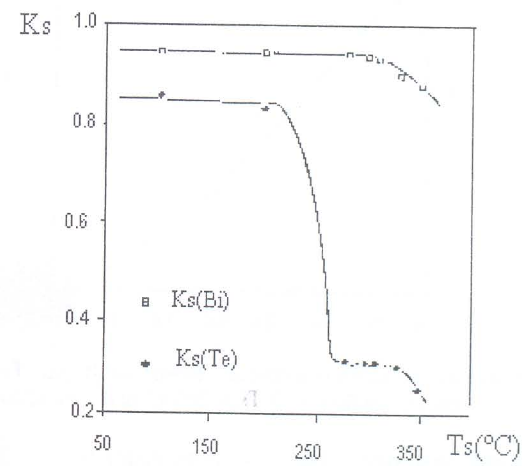


FIG. 6. Variation of sticking coefficients Ks (Te, Bi) as a function of substrate temperature at Fr= 4.5.

At low temperature Ks(Te) is about equal to unity, which means that the temperature is not sufficient to desorb the excess of Te and this is in good agreement with SEM observations[8], X-ray diffraction results and EDX analysis. When Ts is increased to 280°C, the layer desorbs the excess of Te and keeps only the amount necessary to have stoichiometry until 330°C.

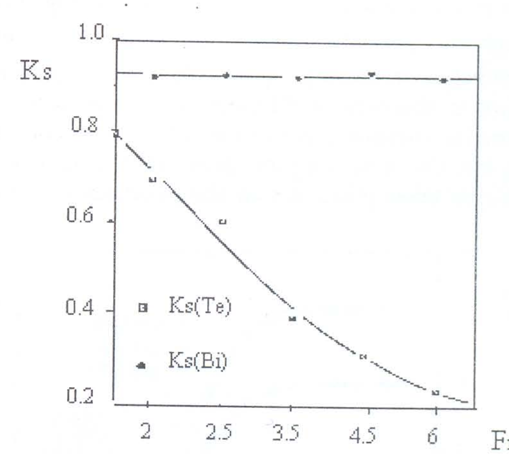
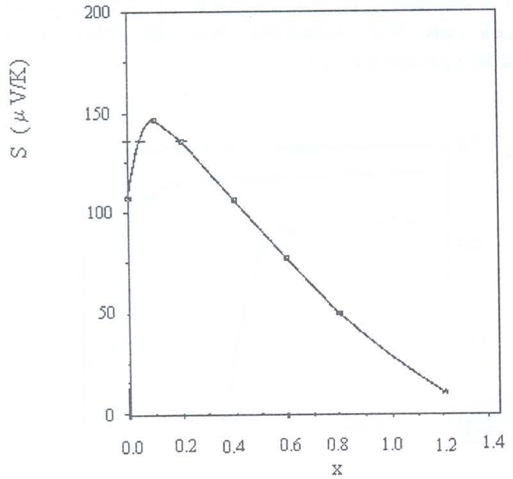


FIG.7. Variation of sticking coefficients Ks (Te, Bi) as a function of flux ratio at Ts= 310°C.

Fig.8 illustrates the variation of the thermoelectrical power of $Bi_xSb_{2-x}Te_3$ as a function of the molar fraction x for the thickness e= 4200Å. The initial increase in S is explained by the reduction in defect density (antisites) or by the carriers compensation during the incorporation of the bismuth[5].

Included in this study are the tests of the two thermopiles using a SYNRAD CO_2 laser with a maximum power of 23W[9]. The temperature gradient ΔT between the hot and cold junction is detected and is proportional to the power received. It is observed that the gain in sensitivity of the two [$Bi_{0.1}Sb_{1.9}Te_3$ (p) - Bi_2Te_3 (n)] thermopiles on



Fg.8. Variation of thermoelectrical power of $Bi_xSB_{2-x}Te_3$ as a function of molar fraction x at Ts= 260°C and e= 4200 Å.

aluminium and steel disks, in comparison to the [Sb-Bi] thermopile, is 2.8±0.2 orders of magnitude[5]. Moreover thermal simulation based on COSMOS/M software confirmed that the sensitivity is increased sublinearly with the reciprocal thickness[5]. This result is in good agreement with those reported by Boyer et al.,[9] using a numerical solution of the heat-transport equation.

We have also studied the performance of a gauge achieved with the same materials ($Bi_{0.1}Sb_{1.9}Te_3$ (p)- Bi_2Te_3 (n)). The gauge is placed in vacuum chamber and a low biasing a.c. voltage is applied in order to heat the resistive element. A typical change (Fig.9) in $\Delta V= V_M-V_{init}$, where V_M is the measured voltage and V_{init} the initial voltage under the atmospheric pressure (with V_{init} = 1, 2 and 3mV respectively for heating power 10,34 and 52mW) versus pressure is observed at different heating powers . At low pressure the thermal loss by conduction and convection is negligible. On increasing the pressure the thermal loss by convection takes place and an abrupt decrease is observed.

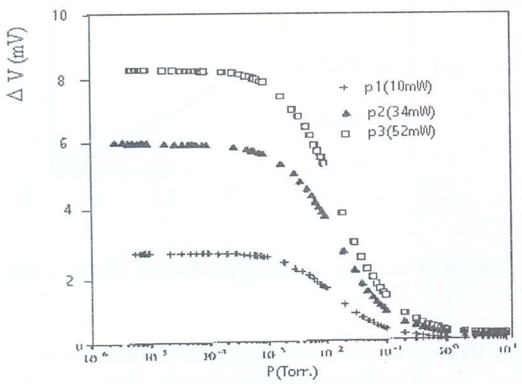


FIG. 9. Outpout voltage reponse ΔV of vacuum gauge vs. Pressure P for different heating a. c. powers (p_i).

This change ΔV is similar to that obtained by Volklein and Schnelle[10] in $Bi_{1-x}Sb_x$ (n-material) and Sb (p-material) films.

By using thermal simulation and experimental results, we have confirmed that the convection coefficient H depends on the pressure $H = f(P) = kAPT_g^{-1/2}$ according to Knudsen's formula:

$E = k\,A\,P\,(T - T_g)\,T_g^{-1/2}$.

where E is the thermal loss by convection, P the pressure, T_g the temperature of the surrounding gas, A the surface area of the gauge and k a constant. Fig.10 shows the linear dependence of H as a function of pressure. The slope of log(H) as function of log(P) is nearly equal to unity, this behaviour confirms the proposed model.

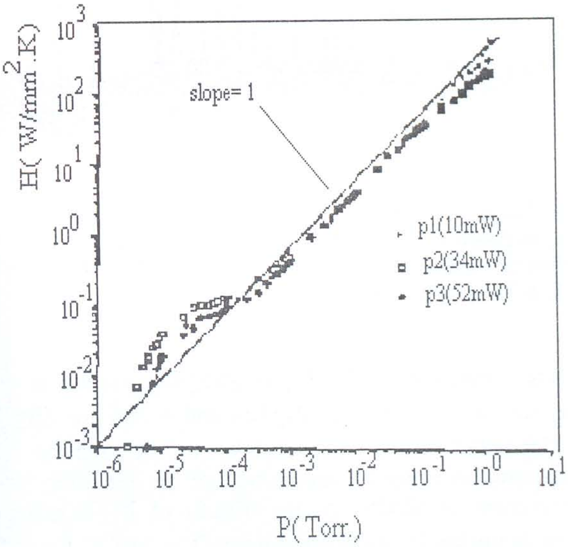


FIG.10. Variation of convection H as a function of pressure P for different heating a.c.powers (pi).

IV. CONCLUSIONS

In summary, we have studied in some detail the properties of thin films deposited by molecular beam epitaxy method. According to the high resolution XRD, SEM, SIMS and EDX results, we can suggest that we have grown stoichiometrically and epitaxially thin films of Bi_2Te_3 on single-crystal Sb_2Te_3, which will be available for research concerning their technological applications. In general, one of the necessary conditions for obtaining epitaxial films is known to be that misfit should be less than a few per cent[11]. It is observed that the stress is mostly compressive and greater than that observed in films prepared outside the optimal conditions[12,13]. We have also studied thermoelectrical properties of Bi_2Te_3 and its alloy $Bi_{0.1}Sb_{1.9}Te_3$ deposited on amorphous substrates. By applying thin film technology, we have developed a new vacuum gauge with high sensitivity in the pressure range 10^{-6}-10^1Torr. We have also obtained a good improvement in sensitivityof the thermopile. It is observed that all experimental results are confirmed by the thermal simulation.

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