THIN FILM MATERIALS BASED ON V-VI SEMICONDUCTORS AND BINARY SKUTTERUDITE FOR APPLICATIONS ON THERMOELECTRIC MICROSENSORS

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Abstract

The characteristics of Bi_2Te_3, Sb_2Te_3 and $(Bi_{1-x}Sb_x)_2Te_3$ alloy films growth by MOCVD will be presented. The values of Seebeck coefficient (α(T)) at room temperature for Bi_2Te_3, Sb_2Te_3, and $(Bi_{1-x}Sb_x)_2Te_3$ with x=0.77 are found to be –220 µV/K, +110 µV/K and +240 µV/K, respectively. In an other hand, the thermoelectric $CoSb_3$ films are deposited on oxidised Si(100) and ceramic Al_2O_3 substrates using magnetron dc sputtering technique.

To evaluate the efficiency of some elaborated films, we present results of gas and pressure micro-sensor

Introduction

The efficiency of thermoelectric materials is usually characterised by the dimensionless of the product ZT where Z is known as thermoelectric Figure of merit and T is absolute temperature (in Kelvin).

There are two differents approaches which can be used for preparing high ZT materials: (1) the multi quantum well structures (MQW) with quantum confinement effects and (2) the concept of reducing lattice thermal conductivity K (especially in high temperature applications) in PGEC (Phonon Glass Electron Crystal) systems. The concept of MQW is mainly dealt with thin films and superlattices [3-5]. $CoSb_3$) are studied mainly as bulk materials [6].

The Figure of merit Z or the potential of a material for thermoelectric applications is determined by [2]:

$Z= \alpha^2/\rho k$ (1)

$k = k_L + k_e$ (2)

Where α represent the Seebeck coefficient, ρ the electrical resistivity, and k the total thermal conductivity (the lattice (phonon part) k_L and electronic k_e contributions) [1-2]. The power factor, α^2/ρ, is typically optimized as a function of carrier concentration, through doping, to give the largest ZT.

From equation 1, the value of Z can be raised by decreasing k_L. It can also be raised by increasing α^2/ρ. However, $1/\rho$ (electrical condictivity) is related proportionaly to the Ke through the Wiedmann-Franz Law, and the ratio is essentially constant at a given temperature.

Experimental details

The MOCVD with an horizontal quartz reactor was used to elaborat a binary Bi_2Te_3 and Sb_2Te_3, and ternary $(Bi_{1-x}Sb_x)_2Te_3$ alloys on pyrex substrate with total H_2 gas flow rate of 6 litre/minute. All the films were prepared at a pressure of 700 Torr. The high purity (a few parts per billion) precursors for Bi, Sb and Te were Trimethylbismuth, Triethylantimony and Diethyltellurium, respectively [7-8]. The deposition rate for all the films was of the order 0.34 μm/h and the final thickness deposited in all cases was around 600 nm.

DC-magnetron sputtering technique with an ultra high vacuum chamber with a base pressure less than 10^{-9} mbar was used to growth binary skutterudite $CoSb_3$. The films were deposited on oxidised Si(100) and ceramic Al_2O_3 substrates under argon atmosphere. During deposition, the chamber pressure was at $7x10^{-3}$ mbar while the substrate temperature was kept at 200°C and 20°C. The applied dc-power in the sputtering target was 150W. The rate of deposition was kept at around 6.3nm/min and the final thickness for $CoSb_3$ films was about 190nm.

Results and discussion

Figure 1 shows the X-ray diffractogram of a typical $(Bi_{1-x}\,Sb_x)_2Te_3$ thin film with x = 0.77. The presence of (006), (015) and (110) plans confirms the polycristalline structure of the thin layers.

The composition of the deposited Bi_2Te_3 and Sb_2Te_3 films is measured by means of the energy dispersive X-ray (EDX) microanalyser.

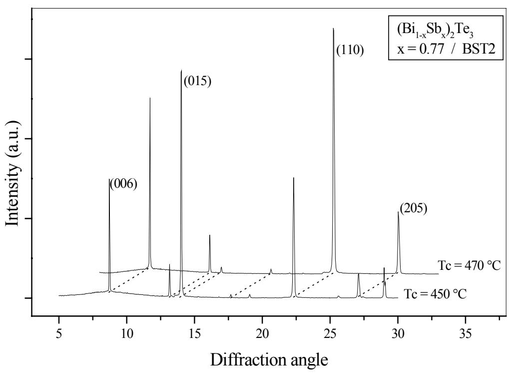

Fig 1: X-ray diffraction diagram of $(Bi_{1-x}Sb_x)_2Te_3$ Thin film elaborated at Tc =450°C and TC = 470°C

An annealing at 350°C for 3 hours under argon atmosphere does not have any influence on the quality of crystallisation of the skutterudite $CoSb_3$ films (figure 2).

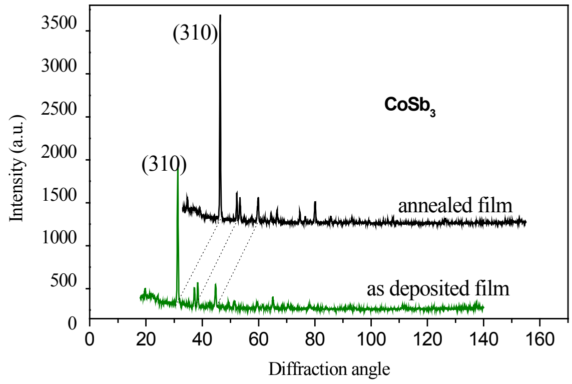

***Fig 2**: X-ray diffraction diagram of $CoSb_3$ Thin film elaborated*

The lattice parameter of the cubic cell is found to be around a = 9.0358 Å which is very close to the value of the bulk materials reported earlier by Fleurial et al. [30] (a = 9.0385 Å).

From the X-ray diffraction, it can be seen that the polycrystalline grains in the films exhibit a strong preferred alignment of the cubic (310) axis perpendicular to the substrate surface which indicates the skutterudite phase of $CoSb_3$ only.

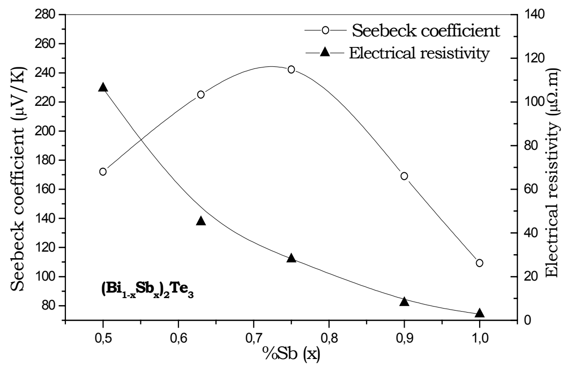

***Fig 3**: Seebeck coefficient and electrical resistivity of $(Bi_{1-x}Sb_x)_2Te_3$ Thin film as function of %Sb (x).*

Figure 3 illustrates the variation of the Seebeck coefficient and electrical resistivity of $(Bi_{1-x}Sb_x)_2Te_3$ thin films as a function of the antimony composition x in the layers. It is observed that for $x \leq 0.30$,

The room temperature values of Seebeck coefficient (α), Hall mobility (μ), electrical resistivity (ρ), and carrier concentration for optimal n-type Bi_2Te_3 and p-type Sb_2Te_3

and BiSbTe p-type ternary $(Bi_{1-x}Sb_x)_2Te_3$ (x=0.77) films, are presented in the table 1.

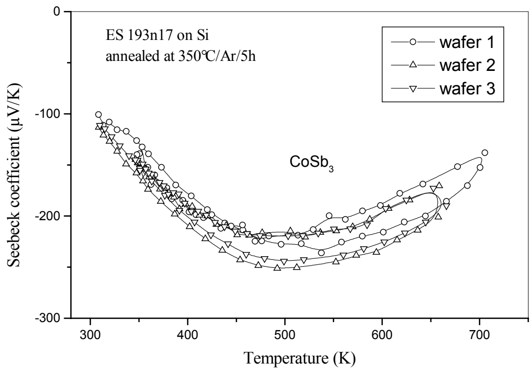

Fig4: Reproductibility of temperature dependence of seebeck coefficient of $CoSb_3$ thin film deposited on silicon substrate.

The variation of the Seebeck coefficient (α) is shown in Figure 4 for the annealed $CoSb_3$ films on two different substrates in the temperature range between 300 and 700 K.

The value of α in the as-deposited film is found to be near zero at 300K. After the first measuring cycle up to 700K and also for the sample annealed at 350°C, the maximum value of -250 µV/K is attained.

The sensor design that can work as gas detection or pressure sensor is presented in Figure 5. This sensor is made of a resistor (heating element) and an integrated thermocouple deposited on a thermally isolated membrane. In both cases the active thermoelement is deposited through two complementary masks of nickel. Thus n-Bi_2Te_3 and p-$(Bi_{1\_x}Sb_x)_2Te_3$ basic materials are realised by MOCVD under optimal growth conditions setting in previous section.

We have found the measure of temperature in the centre of the active zone in the resistance as a function of an injected current by using three different means: an infrared camera, a discrete thermocouple, and the integrated thermocouple.

For the infrared camera, we have determined the emission of the materials Bi_2Te_3 and $(Bi_{1-x}Sb_x)_2Te_3$ compared to the blackbody one which is equal to 1. The material one has been measured and equal to 0.61. the good function of this thermocouple is accuracy verified. The measure obtained by thermocouple type E on contact with the resistance field presents a difference in comparison with that of infrared camera. This difference increases with the heating courant: it is due to the heating dissipation that crosses through the thermocouple by conduction. It unfortunately plays the role of a heat sink.

Generally, the rule of variation of the resistance temperature is I^2. This means the heating by Joule effect of the charge.

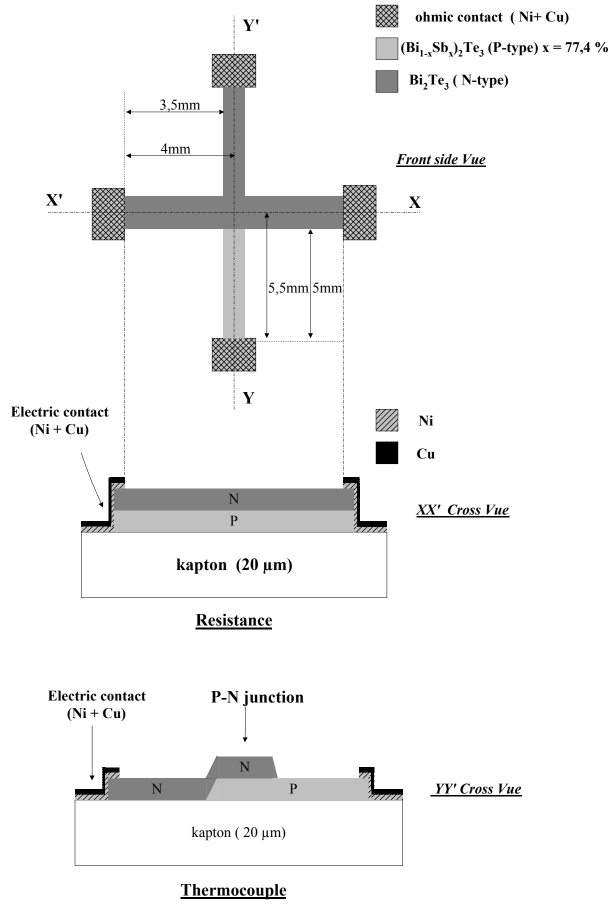

Fig 5: Schematic design of gas and pressure micro-sensor using n-type Bi_2Te_3 and p-type $(Bi_{1-x}Sb_x)_2Te_3$ for x=0.77 films.

In Figure 6 we represent the tension variation (V_{pr} - V_{atm}) of the sensor for different powers of heating. V_{pr} is the thermoelectric tension got by the thermocouple at a pressure value and V_{atm}

the tension measure at atmospheric pressure.

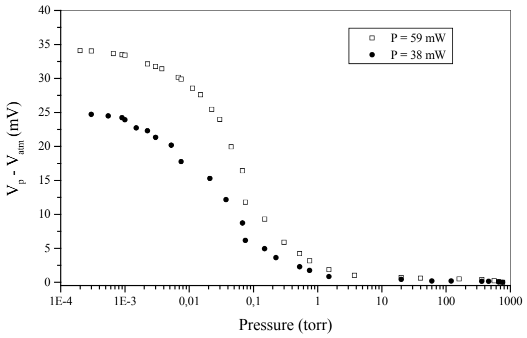

***Fig 6**: V(mV) (1) variation as function of the pressure in the chamber*

From 10^{-4} to 10^{-2} torr, the resistance changes from the heat caused by thermal radiance. The response of sensor in this part is constant. From 10^{-3} to 10 torr, the changes of heat are caused by convection, the coefficient H approaches to the Knudsen formula and it is a function of the pressure [10-11]. From 10 to 760 torr, the response of the sensor is saturated because the exchanges caused by convection are constants.

Figure 7, shows the V(mv) voltage variation as function of time.

$V_t = V_{max} (1-e^{-t/\tau})$

where $V_t = V$ at time t, and τ=time constant of sensor.

when $t = \tau$, (t = one time constant) :

$V_\tau = V_{max}(1-e^{-1}) = V_{max}(0.63)$

So, one time constant or reponse time is the time it takes for the V(t) to reach 63% of its maximum value Vmax. τ = 600ms.

Conclusion

The BiSbTe thin films are prepared by MOCVD technique. From the room temperature Seebeck coefficient (α) measurement, the values of α for Bi_2Te_3, Sb_2Te_3, and $(Bi_{1-x}Sb_x)_2Te_3$ with x=0.77 are found to be –220 µV/K, +110µV/K and + 240 µV/K respectively.

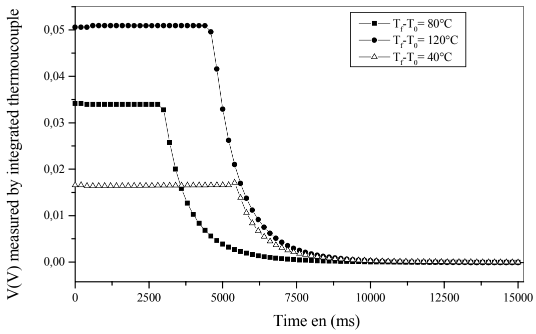

***Fig 7**: Variation of thermocouple voltage as function of the time (ms)*

The $CoSb_3$ films with relatively high Seebeck coefficients can be prepared by dc magnetron sputtering using compound targets. The preparation process has to be carefully optimized, For the pressure sensor, the optimal sensibility is observed for the pressure range: 10^{-4} to 10 torr. The response time of the sensor, about 600 ms, does not vary with the injected electric power. Good sensibility is due to high thermoelectric power of the thin films and the good reproducibility is obtained.

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