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Epitaxial growth of thin films of V_2VI_3 semiconductors

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Epitaxial growth conditions of V_2VI_3 semiconductors have been studied using the molecular beam epitaxy technique, which was applied to the growth of Sb_2Te_3 on Bi_2Te_3 substrates. These substrates were prepared by gradient freeze method in a Bridgman apparatus. Ingots were cleaved along the (0001) plane. The deposition conditions have been studied as a function of two parameters: substrate temperature and flux ratios of the two elements. The quality of these epilayers was controlled by SEM and X-ray diffraction. Epilayers of good quality have been obtained for the first time.

1. Introduction

Until now the best materials for thermoelectric devices at room temperature have been built up with elemental or alloyed semiconductors such as Bi_2Te_3 or Sb_2Te_3. They are characterized by a band gap width lower than 300 meV and a high thermoelectric efficiency [1, 2]. The crystals have the same rhombohedral space group $R\bar{3}m$ and the crystal structure can be described by layers of atoms according to the sequence $-Te^{(1)}-Bi-Te^{(2)}-Bi-Te^{(1)}-$. They are perpendicular to the *c*-axis. Bismuth and tellurium atoms are connected by strong ionic-covalent bonds, but adjacent tellurium are connected by Wan der Waals bonding [ ]. This situation entails an easier cleavability of these compounds and an anisotropy of the mechanical and thermoelectrical properties.

This characteristic led to a study of the ability of these compounds to grow epitaxially along the $\langle 0001 \rangle$ axis.

In a recent work [4], multiple beam epitaxy (MBE) growth of these compounds was studied using amorphous substrates. Deposition characteristics, such as sticking coefficient, incident-atomic fluxes, ratio and temperature range for stoichiometric deposition, were determined. These parameters particularly defined for Sb_2Te_3 were $F(\mathrm{Te})/F(\mathrm{Sb}) > 2$ and $180 < T_s < 270$.

The aim of the present work was to study the growth of Sb_2Te_3 thin films on Bi_2Te_3 with $\langle 0001 \rangle$ orientation, considering the lattice mismatch in the (0001) plane to be smaller than 3%.

2. Experimental procedure

The substrates used for deposition were prepared by directed vertical Bridgman crystallization. The single-crystalline ingots were cleaved and cut parallel to the (0001) planes so that slides of 0.5 cm^2 surface area and 0.2–0.5 mm thick were obtained.

V_2VI_3 compounds deposition was realized in an MBE system, the residual pressure being less than 10^{-9} torr (1 torr = 133.322 Pa), the effusion heaters, 15 cm distant from the substrate and their axes angle being 8°. The antimony and tellurium used were of 99.999% purity. Their incident flux ratios $F(\mathrm{Te})/F(\mathrm{Sb})$ were established from the deposition rate measured on a quartz balance.

The deposition rate changed from 0.056 $nm\,s^{-1}$ to 0.06 $nm\,s^{-1}$ for antimony and from 0.19 $nm\,s^{-1}$ to 0.356 $nm\,s^{-1}$ for tellurium. The substrate temperature was maintained equal during vapour depositions and controlled by a thermocouple directly in contact with the substrate holder. The layer thicknesses were 300 nm on average. They were studied by X-ray diffraction and scanning electron microscopy (SEM).

3. Results

First, we investigated the feasibility of this process and determined the orientation of the epilayers. Fig. 1 shows the X-ray diffractogram obtained with a Bi_2Te_3 oriented (0001) single crystal used as a substrate in Sb_2Te_3 vapour deposition. Thin and strong lines were observed corresponding to the (0006), (00015) and (0018) reticular planes.

After some preliminary vapour depositions, extensive research was undertaken concerning films obtained with a constant substrate temperature, T_s, equal to 310 °C and with incident flux ratios $F(\mathrm{Te})/F(\mathrm{Sb})$ from 2.0–6.7.

From antimony and tellurium concentrations given by analysis of the layers, the variation of the atomic $X = \mathrm{Te}/\mathrm{Sb}$ ratio as a function of the incident flux ratio

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F(Te)F(Sb) was studied, and the results are summarized in Fig. 2. It can be seen a Sb_2Te_3 single-phase layer is obtained with an incident flux ratio F(Te)/F(Sb) larger than or equal to 4.5. The X-ray diffraction diagram of a film 300 nm thick, deposited under such conditions (F(Te)/F(Sb) = 6.7) is presented in Fig. 3. The lines first observed in Fig. 1a related to the planes (0 0 0 6), (0 0 0 1 5), (0 0 0 1 8) of the substrate are still present, with an additional line for 13.10° which can be attributed to the (0 0 9) plane in the Sb_2Te_3 X-ray diagram.

The weak angular difference between the equivalent crystalline planes of the layer and the substrate, results in an apparent single line. That difference can be observed, with more attention, line by line. Fig. 4 gives an example for the line (0 0 1 5). The Sb_2Te_3 c parameter is smaller than that of Bi_2Te_3, thus the layer diffraction lines are observed to have a bigger angle [5]. The $\theta = 22.36°$ and 22.45° lines correspond, respectively, to the substrate K_{α_1} and the layer K_{α_2} diffraction, whereas the stronger central line with $\theta = 22.40°$ results from the addition of the substrate K_{α_2} ($\theta = 22.41°$) and the layer K_{α_1} ($\theta = 22.31°$) diffractions.

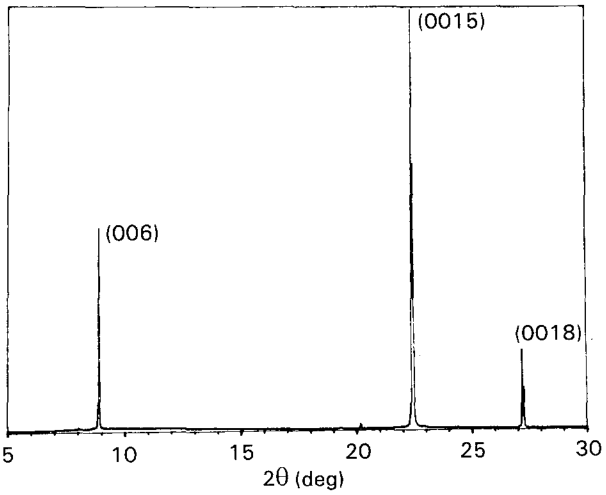

Figure 1 Diffractogram of Bi_2Te_3 with the orientation (0 0 0 1).

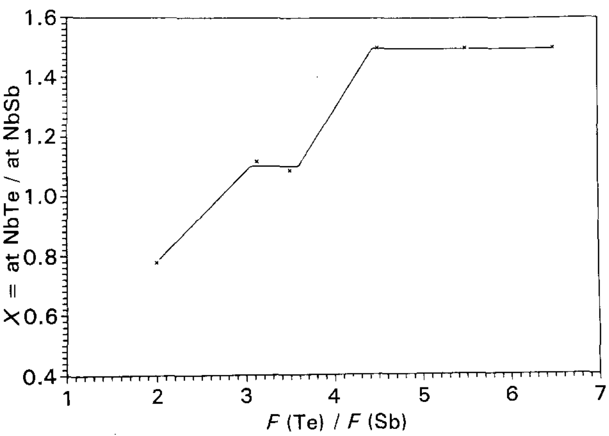

Figure 2 Variation of the atomic (Te/Sb) ratio as a function of incident fluxes.

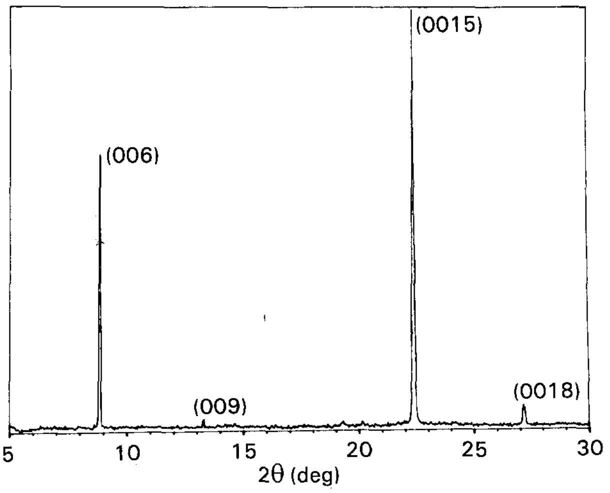

Figure 3 Diffractogram of a Sb_2Te_3 epilayer on a Bi_2Te_3 substrate.

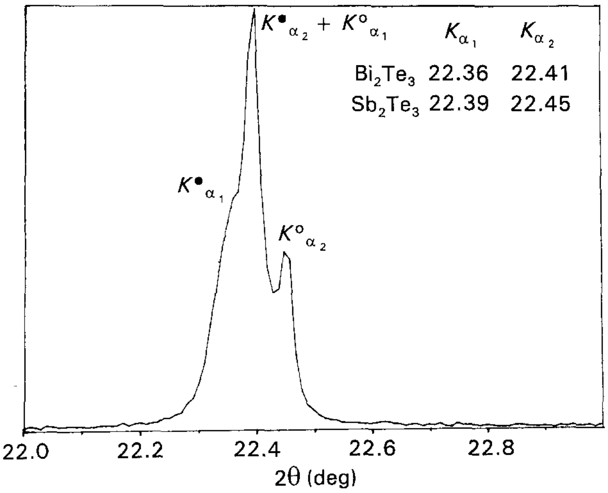

Figure 4 The (0 0 0 1 5) diffraction plane with the indication of (○) Sb_2Te_3 and (●) Bi_2Te_3.

Optimization of the process was studied by varying the experimental conditions (fluxes and temperatures). For incident flux ratios F(Te)/F(Sb) slower than 4.5, the SEM atomic analysis results indicate that the layers contain antimony in excess and, consequently, a ratio situation is confirmed by X-ray diffraction pattern analysis. Fig. 5 shows the X-ray diffraction pattern of a layer 360 nm thick, deposited with $T_s = 310\,°C$ and an incident flux ratio equal to 3.5. Sb_2Te_3 phase characteristic lines are observed with three new extra lines for $\theta = 12.89°$, 22.80° and 26.80°. Those lines result from the diffraction of the planes (0 0 0 7), (0 0 0 1 2) and (0 0 0 1 4) of the phase SbTe. It was shown previously [4] that SbTe, BiTe and BiSe are isomorphous. The hexagonal lattice parameters of the compound SbTe are $a = 0.426$ nm and $c = 2.387$ nm. The precise crystalline structure has not been determined up to now, but we can suppose that it is very similar to that of BiTe [6], so it can be regarded as a hexagonal layered structure in which a unit cell is a sequence of two five-layer groups ($Te^{(1)}$–Sb–$Te^{(2)}$–Sb–$Te^{(1)}$) linked to adjacent layers of antimony (Sb–Sb) [5]. That structure differs from Sb_2Te_3 only in the number and sequence of layers. The lattice mismatch between SbTe and the substrate should be low enough to allow the crystallization of SbTe to the detriment of Sb_2Te_3, according to the

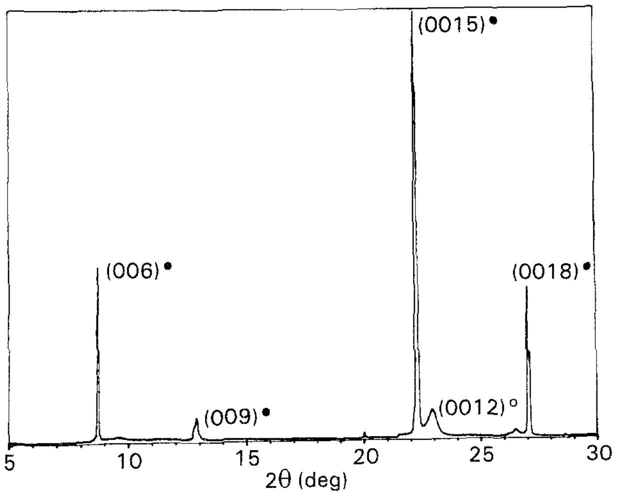

Figure 5 X-ray diffraction diagram of a layer 360 nm thick. (●) Sb_2Te_3, (○) SbTe.

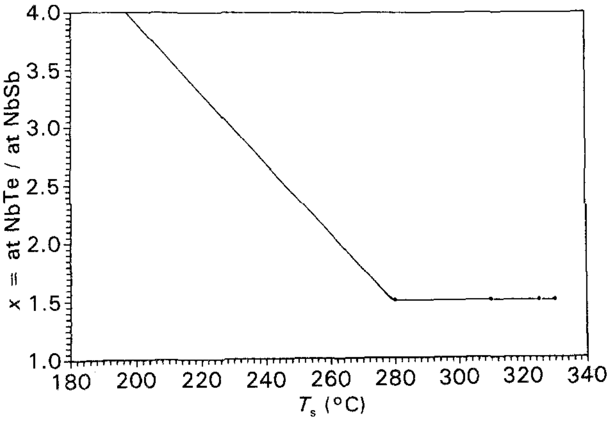

Figure 6 The variation of the layer stoichiometric X = Sb at Te/Sb at Sb at % as a function of the substrate temperature.

comparative effused antimony quantity during the layer-formation process.

Another series of experiments was carried out with different substrate temperatures from 200–330 °C with incident flux ratios constantly equal to 4.5. The variation of the layer stoichiometric X = Sb at Te/Sb at % as a function of the substrate temperature is shown in Fig. 6. The corresponding X values ($= 1.5$) for Sb_2Te_3 are obtained with substrate temperatures equal to or bigger than $T_s = 280\,°C$. This result is verified by the X-ray diffraction diagram whose profile is similar to Fig. 1b and c. When the temperature, T_s, is lower than 280 °C, the layers contain tellurium in excess, as is indicated by an X value bigger than 1.5. Thus, the X-ray diffraction diagrams present exclusively the atomic antimony and tellurium diffraction lines.

From SEM quantitative analysis results, as well as the layer thicknesses, the antimony and tellurium sticking coefficients were calculated. Their variation as a function of T_s, the incident flux ratio being constantly equal to 4.5, is shown in Fig. 6. The antimony sticking coefficient is always near 1 over the whole

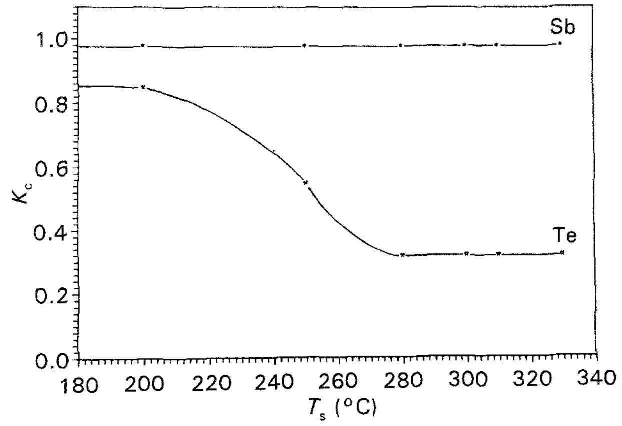

Figure 7 The antimony sticking coefficient as a function of temperature.

temperature range studied, whereas the tellurium sticking coefficient decreases very rapidly from 0.35 ($T_s = 200\,°C$) to 0.32 ($T_s = 280\,°C$), Fig. 7.

Extra experiments were carried out at $T_s = 280\,°C$ and flux ratios lower than 4.5 (F/F 3.0 and 3.5). Either X-ray diffraction diagrams or SEM quantitative analysis results indicate the formation of both phases SbTe and Sb_2Te_3 in those cases. This result is identical to that observed with the same flux ratios in the case of layers deposited at $T_s = 310\,°C$.

4. Conclusion

Growth conditions of epilayers of Sb_2Te_3 on Bi_2Te_3 substrates were studied using a molecular beam epitaxy apparatus. The stability range of the layers was determined as a function of temperature and flux ratio. It was shown that the better samples were obtained for the conditions of substrate temperature 310 °C, and flux ratio, $F(Te)/F(Sb) \geq 4.5$.

The samples were characterized by X-ray analysis, they are oriented along the $\langle 0001 \rangle$ axis like the substrate. This work is a first step in obtaining such p-n junctions built on thermoelectric materials.

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