Comparative studies between the growth characteristics of Bi$_2$Te$_3$ thin films deposited on SiO$_2$, Si(100) and Si(111)

M. Ferhat $^a$, B. Liautard $^a$, G. Brun $^a$, J.C. Tedenac $^a$, M. Nouaoura $^b$, L. Lassabatere $^b$

$^a$ LPM, cc003, URA 407, Université Montpellier II, Place E. Bataillon, F-34095 Montpellier Cedex 05, France
$^b$ LAIN, cc088, URA 1881, Université Montpellier II, F-34095 Montpellier Cedex 05, France

Received 10 February 1996; accepted 14 February 1996

Abstract

Thin films of Bi$_2$Te$_3$ on SiO$_2$, Si(100) and Si(111) were deposited using a hot wall epitaxy (HWE) system. The growth conditions were optimized by the criterion of the highest mobility. XRD and SEM analysis show that the films obtained were stoichiometric and present a good morphology. No difference was observed between layers deposited on Si(100) and on Si(111): the layers were not sensitive to the initial orientation of silicon. The electrical measurements performed at room temperature show that the quality of layers deposited on SiO$_2$ was better than the quality of layers deposited on Si(100) and Si(111). The figure of merit obtained in the case of the SiO$_2$ substrate was $Z = 1.9 \times 10^{-3}$ K$^{-1}$, which is close to those reported for the monocrystal. The study of the first growing stage shows that the difference obtained between the substrates can be explained by the degree of reactivity of their surfaces.

1. Introduction

The need for small thermoelectric coolers, power generators and thermal sensors is increasing in the field of micro- and optoelectronics. Such devices can be used to provide safe operating temperatures for discrete or integrated components, laser diodes [1,2], electrochemical devices, [3], optical recording systems [4,5] and thermal sensors [6].

Until now, the best materials for thermoelectric applications at room temperature were Bi$_2$Te$_3$ and its alloys with Sb$_2$Te$_3$ and Bi$_2$Se$_3$. They are narrow bandgap semiconductors with layered structures.

Many authors have investigated the properties of thin films of Bi$_2$Te$_3$ produced by different techniques and deposited on various substrates.

Francombe's work [7] on films obtained by dc sputtering from a Bi$_2$Te$_3$ cathode on glass substrates indicates a metastable single phase characterized by a composition that ranges from Bi$_2$Te$_3$ to approximately BiTe, depending on the substrate temperature during growth. Goswami and Koli have studied the semiconducting properties of Bi$_2$Te$_3$ and Bi$_2$Se$_3$ films, vacuum deposited from bulks, on glass substrates [8]. Resulting from incongruent evaporation of the compound material they present a lack of stoichiometry.

George and Bradeep [9] have reported the electrical properties of Bi$_2$Te$_3$ thin films from liquid nitro-
gen with temperature to 300 K. Their carrier concentration was $1.25 \times 10^{20} \text{ cm}^{-3}$ at room temperature, one order of magnitude greater than the optimal value for thermoelectric applications, probably because of the non-stoichiometry of the deposited layer.

The effect of the film thickness and deposition temperature on thermoelectric power and electrical resistivity of $\text{Bi}_2\text{Te}_3$ thin films, prepared by vacuum evaporation on glass substrates is reported by Damadora et al. [10]. More recently Boikov et al. [11,12] used hot wall epitaxy (HWE) to grow both n- and p-type $\text{Bi}_2\text{Te}_3$ thin films on $\text{BaF}_2$ and clean mica. They obtained films with electrical properties approaching those reported for bulk.

The present paper reports on the structural and semiconducting properties, at room temperature, of stoichiometric $\text{Bi}_2\text{Te}_3$ thin films prepared by HWE on different substrates ($\text{SiO}_2$, $\text{Si}(100)$ and $\text{Si}(111)$). By investigating the first stages of the thin films formation, we attempt to qualitatively explain the differences between films deposited on amorphous and monocrystalline substrates.

2. Experimental details

The hot wall epitaxy technique used in the present work has been described by Lopez Otero [13]. It essentially consists of a heated quartz liner with three independent furnaces. The substrate is placed on the top of the quartz liner. The whole system is contained in a vacuum chamber evacuated to less than $10^{-7}$ Torr. The main characteristic of this technique is the growth of thin films under conditions as near as possible to thermodynamical equilibrium and without significant loss of starting materials.

2.1. Source materials preparation

$\text{Bi}_2\text{Te}_3$ single crystals were grown by the gradient freeze method in a Bridgman apparatus. We started from Bi and Te pellets (purity 99.999%) and prepared a mixture made of 40% Bi and 60% Te corresponding to the stoichiometric composition. The mixture was placed in sealed evacuated tubes ($10^{-5}$ Torr) heated to 800°C in an electrical furnace and then cooled to form the starting ingot. This ingot was then broken into grains and introduced into a sealed evacuated Bridgman quartz tube, which was placed in the Bridgman furnace characterized by a temperature gradient of about 20 to 30°C/cm. Pellets cut from the so-produced ingot were then broken into grains (30–100 μm), which were introduced into the HWE system. The stoichiometry of the compounds so obtained was verified by XRD.

2.2. Substrate preparation

The strong dependence between the film quality and the water preparation conditions is well known [14,15]; an important step is the initial substrate cleaning. For $\text{SiO}_2$, $\text{Si}(100)$ and $\text{Si}(111)$ substrates, the usual preparation prior HWE deposition consists in three steps. First the substrates are degreased in trichloroethylene and rinsed in methanol. Then, they were immersed in concentrated HF (2 min) in order to remove the native oxide layer (case of silicon) and concentrated HC1 (case of $\text{SiO}_2$ substrates) to remove surface adsorbates. Finally, they were rinsed in 2-propanol, blown dried with nitrogen and inserted into the HWE apparatus (pressure around $10^{-7}$ Torr).

3. Results

3.1. XRD characterization

Fig. 1 and Fig. 2 present the X-ray diffraction pattern of $\text{Bi}_2\text{Te}_3$ thin films deposited on $\text{SiO}_2$ and

![Fig. 1. X-ray diffraction scan of $\text{Bi}_2\text{Te}_3$/SiO$_2$.](image-url)
Si(100) substrates, respectively. In each case, the optimal growth conditions (largest mobility) were used. These conditions were obtained after preliminary attempts with various source and substrate temperatures. In both cases, the optimal source temperature was found to be $T_{so} = 470^\circ C$, while the optimal substrate temperature was $T_{su} = 320^\circ C$ for the SiO$_2$ substrate and $T_{su} = 340^\circ C$ for the Si(100) substrate.

In the case of Bi$_2$Te$_3$/SiO$_2$ (Fig. 1), intense and thin lines are only observed for the (001) planes ($l = 3, 6, 15, 18$). In the case of Bi$_2$Te$_3$/Si(100), the previous (001) lines are still present, with additional ones, indicating many different orientations. The lattice parameters deduced from the diffraction angles were as follows:

- for Bi$_2$Te$_3$/SiO$_2$: $a = 4.434(2)$ Å and $c = 30.384(8)$ Å
- for Bi$_2$Te$_3$/Si: $a = 4.365(3)$ Å and $c = 30.238(8)$ Å

These values are close to those reported for bulk Bi$_2$Te$_3$ ($a = 4.385(2)$ Å, $c = 30.483(5)$ Å). The results of EDS analysis (59.28% Te and 40.72% Bi) confirm that deviation from stoichiometry, if present, is very small. The same samples were observed by SEM (Fig. 3 and Fig. 4). The micrograph of Fig. 3

![Fig. 2. X-ray diffraction scan of Bi$_2$Te$_3$/Si(100).](image)

![Fig. 3. SEM micrograph of the Bi$_2$Te$_3$ surface deposited on SiO$_2$.](image)

![Fig. 4. SEM micrograph of the Bi$_2$Te$_3$ thin film surface deposited on Si(100).](image)

![Fig. 5. Variation of Hall mobility versus substrate temperature for $T_{so} = 470^\circ C$.](image)
Table 1

<table>
<thead>
<tr>
<th>Type</th>
<th>$T_{so}$ (°C)</th>
<th>$T_{su}$ (°C)</th>
<th>$\rho$ (Ω · cm)</th>
<th>$R_h$ (cm$^3$/C)</th>
<th>$\mu$ (cm$^2$/V · s)</th>
<th>$p$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Te$_3$/SiO$_2$</td>
<td>p</td>
<td>470</td>
<td>320</td>
<td>$2.08 \times 10^{-3}$</td>
<td>$3.53 \times 10^{-1}$</td>
<td>169</td>
</tr>
<tr>
<td>Bi$_2$Te$_3$/Si</td>
<td>p</td>
<td>470</td>
<td>340</td>
<td>$1.30 \times 10^{-3}$</td>
<td>$2.96 \times 10^{-2}$</td>
<td>22.7</td>
</tr>
</tbody>
</table>

corresponds to Bi$_2$Te$_3$ thin film on silica; it shows several crystallites of hexagonal form bounded by twin boundaries and oriented such as their $c$-axis was perpendicular to the substrate plane. In the case of deposition on the silicon substrate, Fig. 4 shows a different morphology: crystallites are hexagonal but smaller than previously and without preferential orientation.

3.2. Electrical results

An important and universally accepted characteristic of the electrophysical properties of V$_2$VI$_3$ thermoelectric materials is $\mu_0((m^*/m_0)^{3/2}$ in which $\mu_0$ is the drift mobility in absence of degeneracy, $m^*$ the effective mass of carriers and $m_0$ the electron mass.

This parameter is directly related to the figure of merit $Z$, which characterizes the thermoelectric quality of the material [16], and is given by the relation $Z = S^2\sigma/K$ in which $S$ is the Seebeck coefficient, $\sigma$ the electrical conductivity and $K$ the thermal conductivity. The growth conditions were then optimized by the criterion of the highest mobility.

Table 1 presents the electrical properties of the best layers grown under optimal conditions.

In the case of layers deposited on silica (SiO$_2$) substrates, strong correlation between the Hall mobility and the growth conditions was observed (Fig. 5 and Fig. 6).

Fig. 5 presents the variation of the Hall mobility versus the substrate temperature for fixed source temperature ($T_{so} = 470°C$). The Hall mobility increases when decreasing the source temperature from 360 to 320°C.

On the other hand, by maintaining the substrate at 320°C and varying the source temperature from 360 to 470°C (Fig. 6), we observe a noticeable increase of the Hall mobility from 12 to 169 cm$^2$/V · s; in parallel, the carrier concentration varies from $p = 9.6 \times 10^{19}$ to $p = 1.22 \times 10^{19}$ cm$^3$.

For $T_{so} = 470°C$ and $T_{su} = 320°C$, we found the thermoelectric factor of merit $Z = 1.9 \times 10^{-3}$ K$^{-1}$ with $\sigma = 4.8 \times 10^4$ Ω · m, $S = 200$ μV/K and $K$ estimated to 1 W/mK.

In the case of silicon, the highest Hall mobility observed for $T_{so} = 470°C$ and $T_{su} = 340°C$ was equal to 22.7 cm$^2$/V · s. The mobility is always smaller than in the case of deposits on silica. The carrier concentration was higher by one order of magnitude ($p = 10^{20}$ cm$^{-3}$) than the values needed for the thermoelectric optimum figure of merit. On the other hand, no simple correlation between the growth conditions and the electrical properties was observed, but we noted that the Hall mobility and the carrier concentration have opposite behaviour when the substrate temperature increases.
4. Discussion

The results obtained for Bi$_2$Te$_3$/SiO$_2$ were better than for Bi$_2$Te$_3$/Si(100) or Si(111). On silica substrates, because the layers were uniformly oriented (0001) and with a bigger crystal size, the Hall mobility is higher and the results are more reproducible. On silicon (100) or (111), crystal growth conditions are disturbed and lead to layers with smaller crystallites and without any dominating orientation; the substrate orientations of silicon have no significant effect on the growth mechanism.

This observation can be directly connected to a higher partial tellurium pressure; the decomposition of Bi$_2$Te$_3$ according to the reaction Bi$_2$Te$_3$(s) = 2BiTe(g) + $\frac{1}{2}$Te$_2$(g) is known to be incongruent [17], then, for high condensation temperatures (> 300°C) the main process governing the growth of Bi$_2$Te$_3$ is the re-evaporation of Te. The layer composition is then slightly deficient in tellurium, leading to an increase of the carrier concentration. This tendency could at most result in the formation of films with a composition of around BiTe and not Bi$_2$Te$_3$ as previously observed by several authors [7,9,18].

The use of the HWE technique in which the thermodynamical conditions are close to the equilibrium and the study of the first growing stages, on silica and silicon, could allow us to have the best understanding of the observed results.

5. First growing stages

The growth and the quality of thin films deposited by evaporation under vacuum are strongly related with the first stages of the growth and are essentially governed by four mechanisms:

- the molecules and atoms adsorption (sticking coefficient);
- the species migration on surfaces (diffusion length on surface);
- the nucleation and formation of stable islands;
- coalescence and growth of these islands.

We previously observed that the density of misoriented crystallites is greater on silicon than on silica. This induces a drastic decrease of the electrical properties.

To explain this result, we studied the first growing stages of Bi$_2$Te$_3$ thin films on Si(100) and SiO$_2$; the two orientations Si(111) and Si(100) giving the same results but only the second case was considered. We performed a series of experiments, using the two substrates under the same conditions for several deposition times: 1, 2, 7, and 10 min. In both cases, the XRD patterns after 10 min ($e = 34$ nm on Si and $e = 24$ nm on SiO$_2$) exhibit a good orientation along the c-axis and correspond to the composition Bi$_2$Te$_3$.

Fig. 7 and Fig. 8 present the SEM photographs relevant to the two previous corresponding cases. In both cases, the growth begins by a 3D nucleation, due to the growth on amorphous substrates (SiO$_2$) or to the high lattice mismatch ($\Delta a/a = 30\%$ for Bi$_2$Te$_3$/Si(100)) but the density and the distribution of islands is quite different. The comparison between the two sequences also shows that the nucleation is faster in the Si case; after one minute of deposition on silica we do not see any nuclei (Fig. 8). When we increase the deposition duration, nuclei appear but only in some regions.

The high density of islands in the silicon case can be explained by a high nucleation site density or otherwise by the difference in the surfaces reactivity. The species incorporation onto surfaces is not only related to the growth conditions ($T_{so}$ and $T_{sw}$) but also to the nature and density of the surface nucleation sites (steps, dangling bonds or other defects.
etc.), which strongly affect the atom surface diffusion lengths.

It is well known that the use of a fluoridric solution for the cleaning of silicon substrates removes native oxides but also gives a surface saturation by hydrogen bonds Si–H [19]. The heating of the substrates at a temperature above 500°C can lead to hydrogen desorption and therefore to the formation of dangling bonds giving a reactive surface. Recently, Franklin et al. [20] demonstrated that bismuth atoms can be absorbed on silicon surfaces have a high diffusion length and therefore constitute a uniform monolayer; hydrogen can play a reactive surfactant role [21] by reducing the species diffusion length on the surface.

In our case, Bi₂Te₃ sublimation occurs in accordance to the reaction Bi₂Te₃(s) = 2BiTe(g) + ½Te₂(g). Consequently, the growth mechanism of thin films is essentially governed by the kinetics of BiTe species diffusion and chalcogen evaporation. As the diffusion length of BiTe molecules is less than the diffusion length of Bi atoms, then the nuclei density is more important on the reactive surface of silicon than on the inert silica.

Amorphous silica substrates present a non-reactive surface and the nucleation can only occur on mechanical damage; this can be an explanation of the non-uniformity of the nuclei distribution. The surface inertness enhances the surface mobility of the molecules, which can therefore easily reach the more thermodynamically favourable site; the crystallites are better defined and the crystalline quality is better. The same good quality observed in the case of Bi₂Te₃ thin films deposited on a kapton support [22] confirms the role of the surface reactivity of the substrate.

6. Conclusion

We optimized the growth conditions for Bi₂Te₃ thin layers on various substrates using HWE equipment. The films obtained on Si(111), Si(100) and amorphous SiO₂ were analyzed by XRD, EDX and SEM. The optimal growth parameters were determined by electrical measurements; the best quality layers were obtained for $T_{so} = 470°C$ and $T_{su} = 320°C$ for silica, and $T_{so} = 470°C$ and $T_{su} = 340°C$ for silicon. Thin films deposited on silica present better structural and electrical properties than films deposited on silicon. In the silicon case, no difference was observed between the crystallographic orientation (100) and (111); the layer qualities are not sensitive to the substrate orientation.

The investigations of the first growing stages of Bi₂Te₃ thin films show a strong correlation between the layers’ properties and the substrate surface. In the silicon case, the high density of nuclei is very favourable to the growth of non-oriented crystallites which will play the role of diffusion barrier for the electrons and so reduces the electrical properties of the layers.

References
