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Growth of polycrystalline GeTe films on $Pb_{1-x}Sn_xTe$ (x = 0, 0.05 or 0.2) and BaF_2 substrates

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Phase composition, microstructure and orientation were investigated for GeTe films grown on BaF_2 and $Pb_{1-x}Sn_xTe$ (x = 0, 0.05 or 0.2) substrates by hot wall epitaxy.

Polycrystalline films of germanium telluride are of interest for thermal converters[1] and data storage medium preparation.[2] They can be produced by physical vapour transport techniques. Among them is hot wall epitaxy (HWE), which is based on the evaporation and subsequent deposition of films in a quasi-isolated volume.[3] The HWE technique controls deposition parameters, film stoichiometry and morphology. Here, we report the application of HWE to the growth of GeTe films on PbTe, $Pb_{1-x}Sn_xTe$ and BaF_2 substrates of different orientations. The film composition, microstructure, and electrophysical properties are also reported.

The GeTe films were grown on BaF_2 (111), PbTe (311), and $Pb_{1-x}Sn_xTe$ (100), (220) (x = 0.05, 0.2) substrates. The BaF_2 substrates were prepared by cleaving in air just before the film growth procedure. The PbTe and $Pb_{1-x}Sn_xTe$ substrates were produced from single crystals by cutting along the given planes. After the cutting procedure, the damaged surface layers were deleted by grinding with 5 μm Al_2O_3 powder followed by chemical lap polishing (CLP) in an alkaline solution of $K_3Fe(CN)_6$. After the CLP, the wafers were rinsed in distilled water and then in ethanol.

A two-phase $Ge_{0.505}Te_{0.495}$ alloy was used as a source material. HWE was performed in a UVN-71 PZ chamber described elsewhere.[4] The following deposition conditions were varied: source temperature T_1 = 683–1043 K, substrate temperature T_2 = 423–643 K and deposition time t = 10–80 min. For all the films, the microstructure (morphology and crystallite size), thickness, phase composition and electrophysical properties were characterised. The microstructure was studied by scanning electron microscopy (SEM) on a JEM 2000 FX II (Jeol) microscope. Film thickness was derived from the interference structures obtained with a MII-4 optical microscope, as well as from Talystep profilometer data. The X-ray diffraction studies were performed on a DRON-4 diffractometer using CuKα radiation in a 2θ range of 22–95°. The X-ray patterns were interpreted using the PDF-2 database. In order to study the film texture, a DRON-3 diffractometer (CuKα source) was employed to perform φ-scanning at fixed 2θ (29.82°) and χ (38°) angles. Electrophysical properties of the films (Hall mobility, carrier concentration and Zeebeck coefficient) were also investigated. The influence of the growth temperature on the interface interdiffusion was studied by SNMS on an INA-3 mass spectrometer (Leybold, Germany).

The study of the film growth rate at different substrate and source temperatures was performed for GeTe/BaF_2 films. The mean linear film growth rate v was calculated using the equation $v = d/t$, where d is the film thickness, and t is the deposition time. The obtained data are presented in Table 1. Our experi-

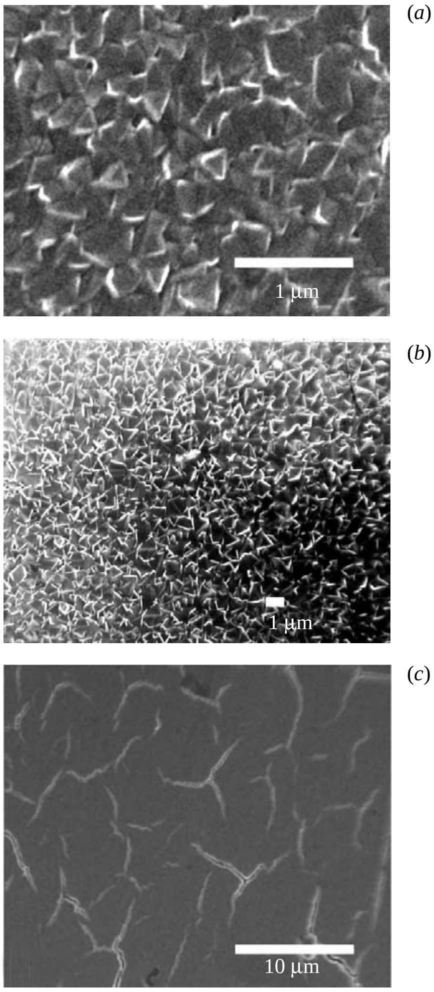

Figure 1 SEM images of the following films: (*a*) GeTe/$Pb_{0.95}Sn_{0.05}Te$, 1.8±0.1 µm in thickness; (*b*) GeTe/PbTe, 7.0±0.4 µm in thickness; (*c*) GeTe/$Pb_{0.8}Sn_{0.2}Te$, 2.1±0.1 µm in thickness.

ments show that the film growth rate does not depend on the substrate temperature T_2 in the given range of experimental parameters, whereas the dependence of the logarithmic growth rate on the inverse source temperature T_1 is linear, indicating the limiting role of the evaporation process.

The GeTe films obtained at substrate temperatures < 573 K have mat surfaces, whereas those deposited at a higher temperature (643 K) are mirror-like. SEM analysis showed that all films are polycrystalline and inclusions-free. GeTe/PbTe and GeTe/$Pb_{1-x}Sn_xTe$ mat films consist of well-defined triangular crystallites; their facets are oriented parallel to the substrate surface [Figure 1(*a*),(*b*)]. In the case of GeTe/BaF_2 films, the shape of the crystallites is not clearly defined. For the mat films, the shape of the crystallites does not depend on film thickness.

For the mirror-like GeTe films, the surface is smooth and the crystallites do not form [Figure 1(*c*)]. The formation of smooth mirror-like films may be explained by the closeness of the substrate temperature to the GeTe + Te eutectic one.[5] Hence, it may be supposed that at this temperature the films grow in the presence of a Te-rich liquid phase. However, both SEM and X-ray diffraction patterns show the absence of elemental Te in the films, which means that the volume of the liquid phase is negligibly small.

All the films deposited at substrate temperatures < 603 K consist of a stable rhombohedral α-GeTe phase independent of the substrate nature. At higher substrate temperatures, those films which were deposited on PbTe and $Pb_{1-x}Sn_xTe$ substrates include both α-GeTe and metastable cubic β-GeTe; this may be explained by the orienting influence of the substrate. In this case, the growth temperature of the films is close to the $\alpha \rightarrow \beta$ phase transition temperature for GeTe,[5] so that the crystalline structure of the substrate ($Fm3m$) causes the stabilisation of cubic GeTe. The intensities of (00*n*) X-ray diffraction peaks for all samples are sufficiently higher than those observed for bulk germanium telluride. This is an indication of the (001) texture, which is also supported by the triangular shape of the crystallites (Figure 1). In addition, the films are textured parallel to the substrate surface.

Table 1 Mean linear growth rates for GeTe/BaF_2 films.

Source temperature, T_1/K	Substrate temperature, T_2/K	Mean linear growth rate, v/m s^{-1}
698±5	423±5	$(1.16\pm0.12)\times10^{-9}$
698±5	523±5	$(1.02\pm0.10)\times10^{-9}$
715±5	523±5	$(1.58\pm0.16)\times10^{-9}$
715±5	563±5	$(1.53\pm0.15)\times10^{-9}$
715±5	603±5	$(1.56\pm0.15)\times10^{-9}$

Table 2 Zeebeck coefficients for GeTe in GeTe/PbTe films.

Source temperature, T_1/K	Substrate temperature, T_2/K	Zeebeck coefficient, α_{mean}/µV K^{-1}
715±5	603±5	140±12
715±5	523±5	90±9
715±5	423±5	95±10

The non-stoichiometric excess of tellurium within the films may be evaluated using the Zeebeck coefficients values. At a constant source temperature T_1, the partial pressure of tellurium in the evaporation zone does not change during the film growth procedure. The data on the Ge–Te system[5] show that at a constant Te pressure the decrease of the substrate temperature should lead to an increase of the non-stoichiometric excess of tellurium (up to the boundary of the homogeneity range), this causing the decrease of the Zeebeck coefficient value.

The Zeebeck coefficient α was measured for GeTe/PbTe films obtained at three different substrate temperatures. Three samples were analysed for each temperature, then the α value was calculated by averaging the obtained data. The results are presented in Table 2. The obtained values of the Zeebeck coefficient show that the film composition remains within the homogeneity range of GeTe independent of the substrate temperature.[6] The concentration of non-stoichiometric Te in the films at the substrate temperature $T_2 = 423–523$ K is higher than that at $T_2 = 603$ K.

The carrier concentration of GeTe films correlates with the data for bulk GeTe, whereas the values of the Hall mobility (15–60 cm^2 V^{-1} s^{-1}) are typical of A^4B^6 polycrystalline semiconductors.[5]

One should take into account that interdiffusion may take place during the preparation of heterostructures at high temperatures. This can give rise to a shift of the film–substrate interface position and cause certain changes in electrophysical properties. The SNMS studies performed in GeTe films showed that no detectable film–substrate interdiffusion was observed in the above ranges of temperatures and deposition times.

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