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Designing epitaxial GeSbTe alloys by tuning the phase, the composition, and the vacancy ordering

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In this study, we present a significant advance in the growth of epitaxial GeTe-Sb2Te3 alloys on Si(111)-(3×3)R30°-Sb reconstructed surface by means of Molecular Beam Epitaxy. By employing X-ray diffraction and Raman spectroscopy, we show how phase, composition, and vacancy ordering can be tailored by tuning the growth parameters such as Ge and Te elemental fluxes as well as the substrate temperature. The effect of each parameter on the GeSbTe composition and phase is also discussed. A very surprising finding is that GeSbTe alloys are more ordered when grown at lower substrate temperatures. In addition, it was possible to fabricate ordered GeSbTe even for substrate temperatures as low as 120°C. In situ high-energy electron diffraction is employed to monitor the crystallinity and surface roughness of GeSbTe films at different stages of growth. Thus, we identify the deposition parameter ranges whereby high structural quality GeSbTe with flat surfaces can be obtained. Published by AIP Publishing.

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INTRODUCTION

Phase-change materials (PCMs) and, in particular, GeTe-Sb2Te3 (GST) alloys, have recently gained ground in the technology market by progressing from being simply a promising 3-dimensional (3D) memory concept to actual production.1,2 Such a breakthrough exploits the strong electrical contrast exhibited between the amorphous and crystalline phases of GST. The main technique used to fabricate PCM thin films in industry is sputtering. However, in the last decade, Molecular Beam Epitaxy (MBE) has gained in importance in the academic research context. MBE’s main advantage is that epitaxial quasi single-crystalline PCM layers can be obtained. This achievement has made it possible to investigate the material properties for which spatial perfection is of crucial importance. For example, the first experimental studies of GeTe3,4 and GST5 band structure by angle-resolved photoemission spectroscopy have been performed, helping to verify the theoretical predictions.6,7 It has been further demonstrated that quasi single-crystalline GST, with ordered stacking of intrinsic vacancies, has a larger resistivity range. This is one order of magnitude higher if compared to the polycrystalline cubic GST, thus producing a promising material for the realization of memory cells with the larger programming windows.8

In the recent years, there has been a growing interest in the use of textured PCMs for memory applications due to the enhanced performance of textured GeTe/Sb2Te3 superlattices.9 Given this interest, accurate growth studies of epitaxial and textured PCM could lead to better device implementations.

EXPERIMENTAL RESULTS

Since then, more attention has been given to the epitaxial growth of PCM also by using other fabrication methods such as pulsed laser deposition,10–13 sputtering,9,14,15 and metal-organic vapor phase epitaxy,16,17 with this last method allowing the fabrication of crystalline nanostructures.18–20 GST alloys present, in addition to an amorphous (a-) phase, two crystalline (x-) ones: a stable trigonal (t-GST) phase and a metastable cubic rocksalt-like (c-GST) phase. The latter is the phase most relevant for memory applications. The alloy contains, depending on composition, a large number of intrinsic Ge/Sb vacancies (up to 25%). The two x-phases, in addition to the stacking (rhombohedral and cubic), display a different arrangement of vacancies. These are randomly distributed in the Ge/Sb cation layers of c-GST and periodically arranged into van der Waals gaps (vdW) in between two adjacent Te layers in t-GST. Recently, it has been demonstrated that an intermediate ordered c-GST can be found between the two x-phases.8,21,22 In the experiment described below, we carried out growth engineering by MBE in quasi single-crystalline GST to achieve unprecedented control over structural order, phase, and composition.
and $\Phi_{Te} = 0.252\, \text{nm/min}$. For the lowest $T_{sub} = 120\, ^\circ\text{C}$, a tuning of the fluxes to $\Phi_{Ge} = 0.122\, \text{nm/min}$, $\Phi_{Sb} = 0.128\, \text{nm/min}$, and $\Phi_{Te} = 0.235\, \text{nm/min}$ was necessary to avoid amorphous growth.

Figure 1(a) shows the superposition of X-ray diffraction (XRD) profiles (symmetric $\omega-2\theta$ scans) around the GST(222). Each curve corresponds to a sample grown at different $\Phi_{Ge}$, where the reported flux values are normalized to the lowest one ($\Phi_{Ge} = 0.069\, \text{nm/min}$). An intense sharp peak at $3.6\, \text{Å}^{-1}$ and a broad one are detected and attributed to the main Te-Te and vacancy layer (VL) periodicities, respectively. Both the GST and the VL peak (VLp) shift for decreasing $\Phi_{Ge}$ toward higher and lower $Q$, respectively, indicating a change in the main composition, as demonstrated elsewhere. From the distance between the two peaks, the lattice parameter $c_0$ is extracted and plotted in Fig. 1(b). It is clear that within the $\Phi_{Ge}$ range explored, for increasing $\Phi_{Ge}$ composition varies from GST225 to GST326, i.e., towards a more Ge-rich composition. Bulk values for $c_0$ of GST225 and 326 compositions are reported as a Ref. 23.

Interestingly, the blue curve in Fig. 1(a), corresponding to the lowest $\Phi_{Ge}$, shows not only a more pronounced VLp if compared to the others, but also a second VLp at about $Q = 2.9\, \text{Å}^{-1}$. This is a clear indication that at low $\Phi_{Ge}$, ordered VLs between Te-Te layers can be easily formed. A representative scanning transmission electron microscopy (STEM) micrograph is shown in Fig. 1(c) and displays the presence of vdW gaps with a width of 2.7 and 2.9 Å, as indicated in the integrated profile. The image is only an example of hundreds of micrographs showing on average the same result, indicating the fact that the sample (corresponding to the blue curve) is in its t-phase. Please note that in the ordered c-phase, the vacancy gaps between Te-Te layers have a larger width (3.3–3.5 Å); thus, they are defined as VL (not yet vdW gaps). 8, 24

For investigating the phase of the grown samples, Raman spectroscopy is a highly efficient characterization tool [Fig. 1(d)]. From the spectra, the modes appearing in two different energy ranges are used for the identification of c- and t-phases. The most evident differences between c- and t-GST consist in the modes appearing in the low energy range (30–50 cm$^{-1}$) and in the highest one (160–175 cm$^{-1}$). From the literature, it is calculated and observed that in the low energy range t-GST shows two distinct modes, while c-GST shows a broad mode. In the highest energy range, however, in the t-phase the characteristic cubic mode at ~160 cm$^{-1}$ turns off and a higher energy mode at ~170 cm$^{-1}$ turns on. This mode is attributed to the formation of ordered vdW gaps between Te-Te layers. 22 By comparing the spectra, it emerges that the yellow and blue curves in Fig. 1(d) are assigned to c- and t-GST, respectively, while the green curve corresponds to the mixed phases.

In a ternary alloy, the three constituent elements are interdependent. Indeed, by varying the $\Phi_{Ge}$, the flux ratios between the elements ($\Phi_{Te}/Ge$ and $\Phi_{Sb}/Ge$) change as a result. In this experiment, while $\Phi_{Te}/Sb$ remains constant at 1.9, $\Phi_{Te}/Ge$, and $\Phi_{Sb}/Ge$ change from 2.8 to 5.4 and 1.5 to 2.8, respectively. These results suggest that the excess Te, not required...
for the compositional arrangement, plays an important role in the ordering process. In order to validate this assumption, a series of samples were grown at different $\Phi_{Te}$.

By increasing $\Phi_{Te}$ [red to blue curve in Fig. 2(a)], XRD curves visibly change. $\Phi_{Te}$ values are normalized to the lowest value of 0.18 nm/min. Within the second order profiles (2.8–3.8 Å⁻¹), the VLp shape, i.e., FWHM and intensity, changes upon $\Phi_{Te}$ increases. A clear shift toward lower $Q_z$ for increasing Te flux is also visible and corresponds to a change of sample composition from GST124 to 225, as reported in Fig. 2(c). However, as the VLp consists of multiple peaks that can be fitted using multi Gaussian curves to account for compositional disorder, we consider the main composition arising from the most intense contribution. The FWHM reduction and intensity increase in the VLp with increasing $\Phi_{Te}$ indicate an increase in the vacancy ordering degree. This is particularly evident at the highest flux [blue curve in Fig. 2(a)], being also characterized by multiple orders of VLps. The sharp GST peak around 3.0 Å⁻¹ consistently shifts toward higher $Q_z$, an indication of smaller average Te-Te layer distance for increasing ordering, as expected when VLs deplete completely to form vdW gaps. The Raman spectra for the samples of Fig. 2(a) are shown in Fig. 2(b). The red curve is in accordance with a c-phase, while the sample grown at the highest $\Phi_{Te}$ is a t-phase. Again, the intermediated curves can be considered as being due to mixed phases.

Sample surface quality is highly important for any kind of device development; therefore, Fig. 3 shows high-energy electron diffraction (RHEED) images corresponding to the samples grown at $T_{sub}$ = 250 °C with different $\Phi_{Te}$, as indicated by labels, to understand the effect of Te excess on the roughness. Three different stages of the growth are shown: beginning of the deposition after 90 s [images in Figs. 3(a), 3(d), 3(g), and 3(l)], the intermediate stage at which interesting changes in the growth dynamics are observed [see time label in Figs. 3(b), 3(e), 3(h), and 3(m)] and the end of the growth after 2 h [Figs. 3(c), 3(f), 3(i), and 3(n)]. The RHEED images along the azimuth (1 1 2) are shown for the first three samples (from row one to three) and along (1 1 0) for the last one, for completeness. Initial Si(111)–(3 × 3) R30°-Sb reconstructed surfaces are reported in the upper panel for both azimuths (see labels), showing well defined RHEED reconstruction patterns with Kikuchi lines indicating the high quality of the substrate surface.

In all the images of Fig. 3 acquired after 90 s deposition [Figs. 3(a), 3(d), 3(g), and 3(l)], it can be observed that GST is already deposited on the substrate, since the Si reconstruction is no longer visible.

The RHEED patterns appear streaky in Figs. 3(d), 3(g), and 3(l), an indication of a smooth surface. If we look carefully at the RHEED streaks in Fig. 3(g), an intensity modulation is visible and could indicate that the growth is actually proceeding by coalescence of large flat islands. This is completely different from the initial stage of deposition of the sample grown with $\Phi_{Te}$ = 3.3. The RHEED pattern shows intense spots superimposed on a streaky pattern, an indication of a growth process dominated by three-dimensional structures. Interestingly, for the same sample, during deposition (15 min) in Fig. 3(b), the film growth process seems to change, with a consistent spotty pattern reduction favoring a smooth growth. At the end of the growth in Fig. 3(c), the film shows a very good streaky pattern, an indication of a smooth film. The GST samples grown with intermediate fluxes ($\Phi_{Te}$ of 2.3 and 1.3) display a streaky RHEED pattern till the end of the growth. The sample grown with the lowest flux ($\Phi_{Te}$ = 1) shows, instead, a change in the growth regime after 30 min, as can be seen by comparing the RHEED patterns in Figs. 3(i) and 3(m). Weak spots appear on top of the streaks, an indication of roughening of the surface during the growth. Also in this case, the film quality recovers significantly toward the end of the growth. From the RHEED pattern, it is possible to identify the best growth window for $\Phi_{Te}$ between 1.3 and 2.3, in which high quality GST with different degrees of ordering [see Figs. 2(a) and 2(b)] can be obtained.

Another interesting consideration concerns the identification of all the RHEED streaks. From the streak position analysis along (1 1 2) and (1 1 0) azimuths, a clear 1 × 1 GST

![FIG. 2. GST samples grown at different $\Phi_{Te}$: (a) superposition of XRD profiles, expected positions of VLp are shown as guide for the eye for GST326, 225, and 124 from higher to lower $Q_z$; (b) comparison of Raman spectra; (c) lattice parameter as a function of $\Phi_{Te}$, bulk references can be found elsewhere.](image-url)
reconstruction can be identified. A red scale, with indicated Laue orders, is superimposed on the RHEED images in Figs. 3(i) and 3(n); n = 1 and m = 1 along azimuth (112) and (1T0) respectively, are also shown. Interestingly, by careful observation of the RHEED images taken along azimuth (112), additional weak streaks can be identified within the first order Laue diffraction for some samples [see Figs. 3(d) and 3(g)]. Nevertheless, these streaks are not equidistant from the 0 and 1st order, but actually correspond to the same distance of the m = 1 streak observed along the azimuth (1T0). In other words, a very faint contribution of streaks characteristic of one azimuth (⟨1T0⟩) is also visible along the other azimuth (⟨112⟩). It is known that the additional streaks are due to the contribution of in-plane 30° rotational domains, which are expected to contribute to the RHEED pattern. The in-plane reciprocal space map (not shown) performed ex situ at the end of the growth demonstrates that the GST films are fully relaxed.8

The effect of the variation of Tsub on the GST film composition and phase is investigated by XRD and reported in Fig. 4(a) (employed flux ratios are indicated in the figure), where the shift of both the GST reflection and its distance to the VLP again suggests a change in composition. In Fig. 4(c), the lattice parameter c0 is plotted as a function of Tsub. Stoichiometric GST326 and GST225 together with non-stoichiometric compositions were obtained (see bulk references in graph23). Raman measurements in Fig. 4(b) indicate that the samples grown at 250°C and 200°C are c-GST, with very pronounced modes; by contrast, the sample grown at 120°C, displays characteristic spectra of t-GST. The sample grown at 180°C shows a splitting of the low frequency mode into two. Since the high frequency trigonal mode has not been formed, we can tentatively assign the sample to a mixed phase.

It is reasonable to assume that when the Ge, Sb, and Te cell shutters are opened, for a given amount of UGe, the same amount of Te is quickly used to form Ge-Te molecules and that all the remaining UTe is used to form Sb-Te. The excess Te, which is highly volatile, desorbs. A schematic diagram comparing the fluxes values is given in Fig. 5 for the first and second series of experiments. In the first series, Ge and Sb are the growth limiting species while UTe determines whether the final GST composition is more Sb2Te3- or GeTe-rich. Increasing UTe for fixed substrate temperature leads to Sb2Te3-rich compositions: 225 and then 124, and concomitantly increases the vacancy ordering [see Figs. 2(a) and 2(b)]. Thus,
GST124, the most Sb$_2$Te$_3$-rich composition, is also the most ordered. This last point is intuitively understood considering that the GST alloys are composed of the binary GeTe and Sb$_2$Te$_3$. While the former (GeTe) does not contain vDW gaps, in the latter (Sb$_2$Te$_3$), such gaps are intrinsically present and separate each quintuple layer. Therefore, an excess of Te serves to ensure a good ordering.

In general, a decrease in $T_{sub}$ implies an increase in each element’s sticking coefficient. Ge is the element with the highest sticking coefficient whereas Te and Sb desorb easily. The element that is mostly affected by $T_{sub}$ changes is Te. Thus, by decreasing $T_{sub}$, there is an increase in the fraction of $\Phi_{Te}$, participating in the adsorption, leading, as in the previous case, to Sb$_2$Te$_3$-rich compositions which increase the ordering [this time going from 326 to 225, as shown in Figs. 4(a) and 4(b)]. In other words, with decreasing $T_{sub}$, both the effective $\Phi_{Te/Ge}$ and $\Phi_{Te/Sb}$ increase; again, this suggests that Te flux is the key point in the ordering process during growth, as in the other cases (tuning $\Phi_{Te}$ and $\Phi_{Ge}$ at fixed $T_{sub}$).

CONCLUSIONS

In conclusion, we have shown that composition and ordering in the MBE grown GST are not decoupled: Sb$_2$Te$_3$-rich compositions are easier to grow into their stable crystalline phase if compared to the GeTe-rich ones. A surprising result, as strongly counterintuitive, is that the GST alloys are more ordered if grown at lower $T_{sub}$. This is explained by an increase in the fraction of $\Phi_{Te}$ participating to the growth process at lower $T_{sub}$, Nevertheless, by directly changing the $\Phi_{Te}$, or indirectly, if $T_{sub}$ is modified, it has been possible to obtain different growth windows in which compositional tuning and different crystalline phases can be fabricated, even at $T_{sub}$ as low as 120°C. Such precision in the design of crystalline GST alloys is relevant for tailoring the GST properties by tuning composition, ordering, and the corresponding stacking.

RHEED is a powerful tool for identifying the growth windows in which high quality GST surfaces can be obtained. Regardless of the roughness at the initial stages of the growth, the more ordered is the GST sample, the better is the RHEED pattern at the final growth stage, i.e., streaky pattern with sharp intense lines. This finding suggests that when the GST is in the ordered t-phase, the coalescence of islands is more uniform when compared to the less ordered cubic phases.

We therefore think that such an advance in the material fabrication by employing MBE offers considerable potential for the development of more accurately controlled GST alloys.

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The authors declare no competing financial interest.

1M. Technology, see https://www.micron.com/products/advanced-solutions/3d-Xpoint-Technology for 3D XPoint™ Memory technology, an entirely new class of nonvolatile memory (2016).


