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Thermal annealing studies of GeTe-Sb$_2$Te$_3$ alloys with multiple interfaces

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A high degree of vacancy ordering is obtained by annealing amorphous GeTe-Sb$_2$Te$_3$ (GST) alloys deposited on a crystalline substrate, which acts as a template for the crystallization. Under annealing the material evolves from amorphous to disordered rocksalt, to ordered rocksalt with vacancies arranged into (111) oriented layers, and finally converts into the stable trigonal phase. The role of the interface in respect to the formation of an ordered crystalline phase is studied by comparing the transformation stages of crystalline GST with and without a capping layer. The capping layer offers another crystallization interface, which harms the overall crystalline quality.

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INTRODUCTION

Phase-change-material (PCM) based memory is a well established non-volatile electronic memory device. Its working principle is based on the switching between two well distinct phases, i.e. amorphous and crystalline, which are characterized by a striking change both in optical and electrical properties.

The most technologically relevant PCMs are GeTe-Sb$_2$Te$_3$ (GST) alloys. The established understanding of the GST switching process is based on melting of the metastable disordered crystal phase to obtain the amorphous one. The recrystallization is generated by annealing the amorphous phase above the crystallization temperature.

GST alloys present an amorphous (a-) and two crystalline (x-) phases: A metastable cubic (c-GST), which is the one technologically relevant, and a stable trigonal one (t-GST). The alloy contains enormous number of intrinsic Ge-vacancies (up to 25 % depending on composition). Cubic rocksalt structure (Fm-3m space group) is usually obtained by crystallizing the amorphous thin film, grown by techniques such as sputtering. One sublattice is fully occupied by Te atoms, and the other one by a random distribution of Ge, Sb and vacancy sites. The stable configuration of the x- phase belongs to a trigonal structure (space group P-3m1 or R-3m). The two x- phases, however, are similar to each other: They fundamentally consist of alternately stacked Te and Ge/Sb layers along the c-axis. Differences arise from the vacancies configuration depending on the phase. In the cubic crystal, they are randomly distributed in the Ge/Sb layers, while in the trigonal one, they are organized into periodic van der Waals gaps (vdW) in between two adjacent Te layers.

Crystallization of the GST alloy using thermal annealing is subject of extensive studies. In most of the cases the investigated material is polycrystalline. In 2014 Bragaglia et al. demonstrated that both the metastable c- and stable t-GST phases can be obtained by annealing an amorphous film deposited by molecular beam epitaxy (MBE) on a Si(111) substrate. The relevant point is that the obtained film was highly textured.

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The interest in textured GST-based material arise from the enhanced switching performances in terms of power consumptions and speed displayed by GeTe/Sb$_2$Te$_3$ superlattices (SLs) with a preferential texture along the (0001) out-of-plane orientation. The structural similitude of ordered stable GST alloys and SLs shows how critical it is to better understand the influence of thermal treatments on textured GST and the effect of interfaces during the crystallization process.

**EXPERIMENT**

Thin films of Ge$_2$Sb$_2$Te$_5$ and Ge$_3$Sb$_2$Te$_6$ with thicknesses of 20 and 30 nm were deposited via MBE on a Si(111) substrate passivated with Sb. The film was deposited at room temperature if intending to obtain the a- phase or at 250 °C for producing the c- phase. After c-GST deposition the samples are in situ transferred to the magnetron sputtering chamber (base pressure: 5 ×10$^{-8}$ mbar) and capped with ZnS-SiO$_2$. GST samples were introduced in a rapid thermal annealing (RTA) furnace under 1 bar nitrogen atmosphere and repeatedly annealed at increasing temperatures ($T_A$). The temperature was varied between 80 and 405 °C with a fixed RTA ramp at $T_A/10$ (°C/s). Once reached $T_A$ was maintained for about 10 min, in order to ensure the structural changes. Between two successive annealing steps, the sample structure was investigated by means of ex situ, X-ray diffraction (XRD).

XRD analysis is performed by fitting peaks with single Gaussian or multi-gaussian functions. Scanning transmission electron microscopy (STEM) was performed to better investigate the structural quality. The diffractometer used for characterization of the sample is a Panalytical X’ Pert PRO MRD system with Ge (220) hybrid monocromator, employing a CuK$\alpha_1$ ($\lambda = 1.540598$ Å) X-ray radiation. A JEOL ARM200F Field Emission Cs-corrected STEM/TEM, working at 200 kV, was adopted to obtain High Resolution (HR) micrographs of the sample. The HAADF STEM images were obtained with a convergence semiangle of 33 mrad, a nominal point resolution of 0.68 Å.

**RESULTS**

As shown by the profiles of Figure 1(a), the substrate and the film share an out-of-plane orientation relationship: for the metastable phase [111] Si || [111] GST and for the trigonal phase [111] Si || [00.1] GST, respectively. Note that cubic [111] direction corresponds to the [00.1] direction in trigonal axes. In both cases then, the GST film presents a high degree of texture in the out-of-plane direction. Symmetric $\omega$-2$\theta$ scans of samples as deposited in the a- phase and annealed at different temperatures ($T_A$) are plotted with an offset for better comparison. Peaks at $Q_z = 2.00, 4.01$ Å$^{-1}$ are attributed to the Si substrate while two narrow peaks ($Q_z = 1.81, 3.61$ Å$^{-1}$) are ascribed to the GST layer. The latter are multiple orders Bragg reflections of the GST film corresponding to the (00.15) and (00.30) planes, respectively and therefore give rise to the periodicity of the Te-Te sublattice. Three additional broader peaks ($Q_z = 1.44, 3.27$ Å$^{-1}$) appear, which are not Bragg reflections of the GST unit cell and correspond to the periodicity of the vacancy layers (VLp) or of the vdW gaps.

Please note that the diffraction maxima are indexed as (00.n) according to the trigonal unit cell for both c- and t-phases. See a dedicated study for the peak indexing attribution. In Figure 1(b) the crystal structures of c- disordered and ordered as well as t- phase of GST225 are shown (see labels) employing trigonal axes; the above mentioned periodicities are highlighted with red arrows.

The corresponding cubic and trigonal stackings are reported on the side. An intermediate ordered cubic phase is shown for sake of clarity, in order to underline the different degrees of vacancy ordering. In particular, t-GST presents the highest degree of vacancies which are distributed in such a way to form vdW gaps.

In addition to the fact that both c- and t-phases are obtained, it is important to underline how the ordering of vacancies takes place, appearing in the XRD profiles of metastable phase (135°C) first, and gradually increasing in intensity and decreasing in full width half maximum (FWHM) for higher $T_A$ [see VLp (00.21) development, as marked in blue in Figure 1].

Periodicity of VL can be obtained from XRD profiles, i.e. out-of-plane lattice parameter $c_0$, which is directly linked to the average composition of GST. In Figure 1(c) the evolution of $c_0$ when
FIG. 1. (a) XRD profiles of GST/Si(111) as deposited amorphous by MBE and crystallized by annealing at different $T_A$.
(b) Schematic showing the crystal structures of c-disordered and c-ordered (see labels) and t-GST225. Cubic and trigonal
stacking is reported on the side. (c) Lattice parameter $c_0$ evolution as function of $T_A$ for crystallizing a-GST225. This is
indication of compositional rearrangement upon annealing.

transforming from the cubic to the trigonal phase is shown. It is clearly visible that the sample
composition slowly changes from average GST225 value towards the GST124. Reference values can
be found elsewhere.\textsuperscript{11}

However, up to the complete crystallization at 130 °C strain effects could not be completely
ruled out, thus the estimation of the composition in the cubic phase is not precise, but it delivers
the information that the first crystallites have a GST225 composition. The change in composition
during annealing from a GST225 to GST124 can be ascribed to the constituent elements segregation, singularly or in binaries alloys, as reported in former studies.4,12

A further evidence of the ordering process has been given by HAADF STEM for a sample annealed at 170 °C for 1 h. In the micrograph of Figure 2(a), two sets of vacancy planes can clearly be identified: One is parallel to the substrate surface, the other is at an angle of 70° compared to the previous one. The VLs parallel to the substrate are oriented along the [111] direction and are measured by the ω-2θ XRD scans, as shown in Figure 1. The other set of VLs belong to the equivalent \{111\} family of planes. In a STEM cross section we can only observe two of these equivalent planes even if for symmetry reasons vacancy layers should occur in all four directions.

In Figure 2(b) a zoom on the vacancy planes at 70° rotated in respect to the substrate surface is shown, and an integrated line profile is extracted in order to highlight the Te-Te layers distance across the gap. Distances of 3.4-3.5 Å indicate that the VLs are not fully depleted; therefore they are not yet vdW gaps as in the trigonal phase. Such result is in agreement with former literature.12,13 In addition, the stacking (not shown) is that of the rocksalt phase (ABCABC). As opposed, the crystalline phase formed by annealing of a-GST at 110 °C for 10 min does not show any VLp in the XRD profile (as shown in Figure 1), and STEM analysis confirms that the sample is in a disordered rocksalt phase with vacancies randomly distributed. Further details of the microstructure can be found in a dedicated publication.14

From the annealing experiment shown in Figure 1 and the study of Bragaglia et al.,8 which systematically combines morphological and structural measurements, it emerges that the preparation of the Si(111) substrate, acting as a template, plays a fundamental role on the crystallization of a-GST. Crystallization is prevalently of heterogeneous nature, starting at the Si/GST interface, with consequent formation of a propagating front. Thus the interface between GST film and air15 is in comparison negligible. Homogeneous nucleation in the a-GST film could not be excluded within the investigations of the mentioned study, even if it is reasonably not dominant if compared to heterogeneous one.8

In order to clearly address this point, a study on the effect of additional interfaces to the Si/GST was performed. Note that this experiment is of relevance whenever a capping of samples is required to use in the temperature dependent spectroscopy16 and pump-probe experiments.17 A crystallization experiment is performed on two pieces of the same c-GST sample grown by MBE. The starting composition is 326. The only difference between the two samples is that one is capped by Zn-SiO2 and named “c-GST capped”, while the other is “c-GST uncapped”. In Figure 3 the XRD profiles of the samples as grown c-GST (see GST peaks of the already crystalline GST film) and annealed c-GST are plotted with an offset for sake of clarity. The two as grown metastable samples were annealed simultaneously at the same temperature for increasing T_A.

FIG. 2. (a) Cross-view [11.0] high resolution HAADF STEM micrograph of crystallized GST [00.1] oriented; two sets of vacancy planes can be identified: One is parallel to the substrate surface, the other is at an angle of 70° compared to the previous one. (b) Zoom on the vacancy planes at 70° in respect of the substrate surface. Vacancy layers are highlighted in green. Corresponding integrated line profile is displayed (in red).
FIG. 3. (a) XRD profiles of "c-GST_uncapped" as grown and annealed at different $T_A$; (b) XRD profiles of "c-GST_capped" as grown and annealed at different $T_A$; (c) VLp FWHM evolution for capped (blue) and uncapped (black) samples. Filled symbols stay for c-GST, empty for t-GST phase.

After each annealing, ex situ XRD was performed on both samples. In Figure 3(a) the profiles of "c-GST_uncapped" are shown. The c- to t-GST transition takes place at 265 $^\circ$C, with a trigonal phase characterized by high structural quality according to the presence of many superior order peaks, with an increase in peak intensity and a decrease of its FWHM. On the contrary, for "c-GST_capped" [see Figure 3(b)] first the c- to t-GST transition temperature is around 370 $^\circ$C, much higher than in the case of the uncapped sample (100 $^\circ$C difference); second, the crystalline quality of the t-GST is lower if compared to the case without capping, as can be seen by the asymmetric shape, low intensity and larger FWHM of the peak. For even higher $T_A = 405$ $^\circ$C, the peaks become even more asymmetric, indication of possible segregation or more compositional disorder.

To strengthen this last point, in Figure 3(c) the VLp FWHM evolution as a function of $T_A$ is plotted for the uncapped (black) and capped (blue) samples. In particular the peak chosen for the analysis is the (00.27) for "c-GSTUncapped" and (00.11) for "c-GST_capped". The FWHM of the VLp peak related to the uncapped sample shows a plateau till 225 $^\circ$C with an abrupt decrease till a value of 0.45$^\circ$ for the t- phase. On the contrary, the capped sample shows a plateau till 265$^\circ$C and then starts gradually to decrease, indication of the fact that ordering is increasing in the sample, nevertheless the minimum value of 0.9$^\circ$ in the trigonal phase is higher than the previous case. This corroborates the assumption that in uncapped samples ordering is faster and in addition the sample spontaneously transforms into a higher quality t- phase if compared to the capped case. This result is in agreement with a recent STEM based study on epitaxial samples, in which it is shown that
by properly choosing the substrate and the capping layers, it is possible to promote or prevent the vacancies ordering in the rocksalt structure or the conversion into the trigonal phase. The study of periodicity evolution upon annealing is now discussed. In Figure 4, the average distance between Te-Te layers (d_{GST}) and the periodicity of the vacancy layers ($\Lambda_{VL}$), in other terms the size of the GST unit building blocks, are plotted as function of $T_A$. As expected, the periodicity decreases for increasing $T_A$. Both capped and uncapped samples reach a minimum value around 3.45 Å. If we look at the $\Lambda_{VL}$ periodicity instead, interesting information is found. The uncapped sample shows a decrease of lattice periodicity with maximum change of 12 %, while instead the evolution of $\Lambda_{VL}$ in case of the capped sample goes in the opposite direction, increasing consistently till a value of 22 Å, with a total percentage change of 8 % once the trigonal phase is obtained. The capped sample presents less change in composition if compared to the uncapped, which drifts from an average GST326 into GST225 composition. According to our previous study, desorption really starts to play a role for $T_A$ above 300 °C, which is not reached for the “c-GST, uncapped” sample. In addition, the fact that both samples present a percentage of compositional change, may indicate that segregation of the material might also play an important role in order to lower the energy of the system in the t-phase.

CONCLUSIONS

In conclusion, we have shown that thermal annealing of a-GST films deposited on a crystalline substrate induces crystallization, which starts preferentially at the interface and leads to a well ordered structures. The material transforms from a-phase to an ordered metastable rocksalt structure with vacancies organized in layers and finally the stable trigonal phase is obtained. This finding demonstrates that it is possible to create an ordered crystalline GST layer using thermal annealing, a simple and inexpensive technique, paying only attention to carefully treat the crystalline surface prior to physical deposition.

The effect of the presence of an additional interface on the crystallization process has been investigated. A comparison between the phase transformation from ordered c- to t- GST for a sample with and without a capping layer shows that higher structural quality in terms of texture and vacancy ordering is obtained for annealing without capping layer. This result gives indication that for studies requiring annealing experiments or crystallization for which preservation of the structural quality is mandatory no capping facilitates the interpretation of the results.

In former studies it was shown that upon transition from disorder to ordered c-GST and then to t-GST relevant resistance variations occurs and that the resistivity window can be enlarged if quasi-single-crystalline is used instead of polycrystalline GST. The possibility to enlarge the resistivity window by simply controlling the formation of the crystalline phases (by tuning of the order of the vacancies) is of fundamental relevance for the development of multilevel phase change data storage.
Here we show that, by properly choosing the substrate and the capping layers, it is possible to promote or delay vacancy ordering in c-GST or its conversion to t-GST, therefore to tune the vacancy ordering in a controlled fashion.

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