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Real-space imaging of atomic arrangement and vacancy layers ordering in laser crystallised $Ge_2Sb_2Te_5$ phase change thin films

Andriy Lotnyk*, Sabine Bernütz, Xinxing Sun, Ulrich Ross, Martin Ehrhardt, Bernd Rauschenbach

Leibniz Institute of Surface Modification (IOM), Permoserstr. 15, D-04318 Leipzig, Germany

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ABSTRACT

In this work, the local structure of metastable $Ge_2Sb_2Te_5$ (GST) phase change thin films crystallised by laser irradiation of amorphous GST films is studied by state-of-the-art aberration-corrected scanning transmission electron microscopy (Cs-corrected STEM). By analysing simulated and experimental atomic-resolution Cs-corrected STEM images, a structure model for metastable GST is proposed. The GST lattice is described by a distorted rock-salt like structure with an ordered Te sublattice at the 4(a) site and a disordered sublattice of Ge, Sb and vacancies at the 4(b) site, where only a distorted octahedral atomic arrangement of Ge and Sb atoms exists without layered ordering of intrinsic vacancies. Additionally, no evidence for the presence of either tetrahedral Ge atoms in the GST lattice or an amorphous component at the grain boundaries is found. Moreover, a formation of vacancy layers in metastable GST in <111> direction under the influence of focused electron beam irradiation is observed. These vacancy layers vanish during repeated scanning of the electron beam over these defects. The gained outcomes of this study shed new insight into understanding the atomic arrangement and phase change mechanism in GST thin films as well as the control of disorder in phase change materials.

1. Introduction

Phase change materials (PCMs), such as Ge–Sb–Te alloys, are of high interest due to their technologically eminent optical and electronic properties. Among the Ge–Sb–Te based PCMs, $Ge_2Sb_2Te_5$ (GST) is a well-known compound and the most used PCM. GST is utilized in optical storage media such as DVD-RW [1,2]. GST thin films are also among the main candidates for next generation non-volatile random access memory (PC-RAM) devices [3–6]. The operating principle of PCM based devices relies on the ultrafast reversible transformation between the disordered amorphous and the metastable crystalline phases which is accompanied by strong changes in optical and electrical properties [2,7–9]. Previous experimental and theoretical studies indicated a certain similarity in the crystal structures of amorphous and metastable GST phases [10–17]. It was also argued that the fast and reversible phase change is due to this intrinsic structural similarity between the two phases [18]. Thus, a detailed knowledge of the atomic arrangement in metastable GST is of paramount importance for a better understanding of the phase change mechanism and the unique property contrasts of GST alloys upon the phase transition.

On the basis of X-ray diffraction data it was proposed that the metastable GST phase has possessed a cubic rock-salt like structure (NaCl) with the 4(a) site being occupied by Te atoms and the 4(b) site being occupied by 40% Ge and 40% Sb as well as 20% vacancies (Vs), forming mixed GeSb/V lattice sites [19]. Previously, extended X-ray absorption fine structure studies have shown that Ge and Sb atoms in the GST lattice are displaced off-centre resulting in a net dipole moment [10]. Therefore, GST was found to also exhibit ferroelectric properties [20,21]. However, an ordered GST lattice at the 4(b) site based on high-resolution TEM studies was proposed [22]. In addition, ab-initio calculations have suggested that metastable GST consists of two well-defined 3D repeating units (Te-Ge-Te-Sb-Te- and -Te-Sb-Te-Ge-) possessing rock-salt symmetry with highly ordered and layered vacancy positions [18] which is in agreement with recent first principles calculations suggesting the ordering of vacancies on {111} planes [23]. The distribution of intrinsic vacancies is believed to play an important role in the ultrafast phase transition [14]. Moreover, a coexistence of octahedral and tetrahedral Ge sites in the GST lattice was also reported

* Corresponding author.
E-mail address: andriy.lotnyk@iom-leipzig.de (A. Lotnyk).

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[24–26]. Thus, the atomic arrangement in the GST lattice is not well-understood and still under discussion. In addition, there are no reports on real-space imaging of atomic arrangement in laser crystallised GST thin films by e.g. Cs-corrected annular dark-field STEM (ADF-STEM). In contrast to the above-mentioned investigation methods, atomic-resolution Cs-corrected STEM can provide information about the local structure of functional materials in real-space with a point resolution as low as in the picometre scale [27–34]. It should be pointed out that atomic-resolution Cs-corrected TEM investigations of metastable GST have been reported by Liu et al. [26]. The work of Liu et al. claims to observe ordered tetrahedrally coordinated Ge atoms which is in contradiction to density functional theory (DFT) calculations performed by Raty et al. [16]. This may be due to the fact that the metastable GST phase in the work of Liu et al. was prepared by heating of amorphous GST in a vacuum furnace at 200 °C for 2 h [26]. This temperature is close to the transformation temperature to the stable layered GST high temperature phase and may induce the formation of tetrahedral Ge in some grains as was also observed in our previous work, where the crystalline GST was produced by heating at 200 °C for only 30 min [35]. In addition, stable vacancy layers (VLs) can exist in GST produced as such, which is also predicted by theoretical simulations [23]. Consequently, the local structure of thermally and laser crystallised GST can be significantly different.

Since a detailed knowledge about the real structure of PCMs is the key for a better understanding of the high crystallisation speed and the significant property contrasts, we aim in this work to study the atomic structure of the laser crystallised metastable GST phase by a combination of atomic-resolution Cs-corrected STEM imaging and theoretical image simulations methods in order to directly reveal the atomic arrangement in the GST lattice. Particularly, questions such as on the presence of tetrahedral Ge, off-centre located Ge and Sb and ordering of vacancies on {111} planes as well as electron beam induced creation of VLs in a GST structure are addressed in our paper.

2. Experimental

The metastable GST phase was obtained by laser irradiation of amorphous GST films. The latter were deposited by pulsed laser deposition at room temperature onto Si substrates covered by a thin layer of SiO_2. The thicknesses of the amorphous GST thin films were in the range between 80 nm and 100 nm. Femtosecond (fs) and nanosecond (ns) single laser pulses ($\lambda = 248$ nm) with pulse durations of 500 fs and 20 ns, respectively, were applied in the crystallisation experiments in order to generate the metastable GST phase. Laser fluences of 19 mJ/cm^2 for fs-pulses and 130 mJ/cm^2 for ns-pulses were used. The size of the laser spot was 2.4 cm $\times$ 0.6 cm.

Cross-sectional specimens for STEM analysis were prepared by focused ion beam technique (Auriga CrossBeam FIB-SEM) [36]. In order to improve the surface quality of the TEM specimens and to reduce the sample thickness further, additional focused low-energy argon ion milling under liquid N_2 cooling (NanoMill system) was applied [36]. Ion energies from 900 eV down to 500 eV were used to obtain a final specimen thickness of approximately 25 ± 5 nm (measured by electron energy loss spectroscopy) as well as to remove Ga ion beam induced surface implantations and amorphous regions caused by the FIB process. Before STEM work, the TEM lamellae were treated in a plasma cleaner (Solarus system) for 10 min with a H_2/O_2 plasma recipe.

The atomic-resolution STEM work was performed on a Titan^3 G2 60–300 microscope (FEI) equipped with a probe Cs-corrector (DCOR), a high-brightness electron gun (X-FEG), a bright-field (BF), two annular dark-field (ADF) and a high-angle ADF (HAADF) STEM detector as well as a post-column Gatan imaging filter (GIF Quantum 963/P with DualEELS and fast shutter). The TEM was operated at 300 kV accelerating voltage. A probe forming aperture of 25 mrad was used in the experiments. Middle-angle ADF (MAADF)-STEM imaging were performed using 40–200 mrad annular ranges of HAADF detector, whereas low-angle ADF (LAADF)-STEM imaging were carried out using 9.3–53.6 mrad annular ranges of the ADF detector. The Cs value was tuned to be smaller than 200 nm. The C5 parameter was adjusted by the manufacturer to be close to 400 μm. These microscope parameters were also used for the image simulations. Beam currents were limited to about 80 pA in all experiments.

The signal to noise ratio of STEM micrographs was improved by the averaging over many STEM image acquisitions. While the TEM uses parallel recording, the serial acquisition of STEM images can encounter problems with specimen drift, which results in image distortions. The specimen drift can be minimised by optimised room design [37] and by developing stable columns or by using multiple rapid exposures and software based drift correction techniques [38–40]. This results in accuracies that are comparable for TEM and STEM [41]. For further details on the compensation of specimen drift and evaluation procedure used in this work see in the Supporting Information section. An examination of the image magnification calibration was carried out using the Si lattice of the substrate material in [110] zone axis (see Fig. S1 in Supporting Information). All images were acquired during the same TEM session and with identical beam settings.

Multislice image simulations were performed with the xHREM/STEM software package [42]. The thermal displacement factors for Te, Sb and Ge were taken from Ref. [19]. The total number of slices was chosen to result in a TEM specimen thickness of 25 nm. The probe size was set to 0.07 nm which corresponds to the specified spatial resolution of the STEM instrument as identified from FFT image calculated from a high-resolution MAADF-STEM micrograph of Si [110].

3. Results and discussion

The chemical composition of the amorphous and laser irradiated GST thin films was verified by EDX measurements recorded at different TEM specimen regions (see Fig. S2 in Supporting Information). EDX spectra were recorded in STEM mode using fast chemical mapping and by averaging the EDX maps. The overall composition of GST films was very close to the desired $Ge_2Sb_2Te_5$ stoichiometry. The laser irradiated GST thin films were entirely crystallized and consisted of either columnar or plate-like shaped grains ranging from 10 to 70 nm in diameters (see Fig. S3 in Supporting Information).

Atomically resolved MAADF-STEM images of metastable GST viewed along the [100], [110] and [112] directions provide direct information on the atomic arrangements present (Fig. 1). Qualitative interpretation of such STEM images is quite straightforward since the image intensities are proportional to the atomic number according to ~$Z^{1.8}$ [43] and thus the atomic columns with higher average Z number in the MAADF images appear brighter than the columns with lower average Z number. Moreover, the information on the local structure and chemical composition can be obtained by evaluation of image intensities. The estimated average lattice parameter of 0.600 ± 0.004 nm matches the GST lattice parameter reported by XRD for metastable crystal structures of non-stoichiometric $Ge_2Sb_2 + xTe_5$ (x = 0, 0.3, 0.5, and 1.0) thin films (0.603 ± 0.001 nm) [44] and by X-ray fluorescence holography (0.604 ± 0.005 nm) reasonably well [25]. In addition, shorter and longer Ge/Sb–Te distances were identified upon extensive image analysis. The average distances of 0.280 ± 0.004 nm and 0.320 ± 0.004 nm were estimated along the [00–1] direction of the