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Investigation of Phase Transformations in $Ge_4Sb_4Te_5$ film using Transmission Electron Microscopy

Manish Singh[1], Chanchal Ghosh[1], Paul Kotula[2], Benjamin Miller[3], John Watt[4], Helena Silva[1] and C. Barry Carter[1]

[1]University of Connecticut, Connecticut, United States, [2]Sandia National Laboratories, Albuquerque, New Mexico, United States, [3]Gatan Inc., California, United States, [4]Los Alamos National Laboratory, Connecticut, United States

Phase-change materials can exhibit a rather unconventional combination of properties. They display a large change in electrical resistivity and optical reflectivity during the phase transformation from amorphous to crystalline state, which suggests a significant change in local atomic configuration. However, transformation from the amorphous to crystalline phase takes place very quickly. This property combination makes these materials suitable for memory applications (Wuttig & Yamada, 2007). Ge-Sb-Te (GST)-based phase-change materials have been studied extensively, in particular the stoichiometric $Ge_2Sb_2Te_5$ (GST-225) alloy lying on the GeTe-Sb_2Te_3 tie line, owing to its optimum thermal stability of amorphous phase at room temperature and crystallization speed. The GST-225 goes from an amorphous state to a crystalline (face-centered cubic) state upon heating with a typical crystallization temperature of ~170 °C (Yamada, 2012). The time scale of the transformation in GST-225 has been observed to be on the order of nanoseconds and this rapid change has been ascribed to unchanged chemistry after phase change. However, uncapped GST-225 films exposed to atmosphere for longer durations show crystallization at ~35 °C along with chemical partitioning in GST-225, which becomes pronounced at higher temperatures (Singh, et al., 2020b; Tripathi, et al., 2020).

The investigation of GST alloys having compositions outside the prototypical $Ge_2Sb_2Te_5$ has also been carried out in quest of improved performance of the GST-based devices. It has been demonstrated that Ge-rich GST is suitable for high temperature applications and high-speed performance can be achieved with Sb-rich GST alloys. One interesting aspect of investigation could be to study GST alloys with both Ge and Sb-rich composition in order to optimize the tradeoff between thermal stability and crystallization speed.

In this investigation a $Ge_4Sb_4Te_5$ (GST-445) film 25 nm thick was directly deposited on a Protochips MEMS heating device using magnetron sputtering and kept uncapped specifically for in-situ TEM study (Ghosh, et al., 2020; Singh, et al., 2020a). In-situ heating experiments were carried out in a C_s-corrected FEI Titan ETEM employing an Aduro 300 Protochips holder. Dynamics of crystallization were followed using a large field of view, high-speed camera (Gatan K3 IS) @ 10 frames per second with a low-dose rate (12.7 e^- $Å^{-2}$ s^{-1}) to minimize the effect of e-beam induced changes in the film. Samples were heated @ 5 °C /s from room temperature to 180 °C. The images and videos have been processed using Python scripting within the Digital Micrograph platform to increase the contrast and visibility. The chemistry of

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the as-deposited and heat-treated $Ge_4Sb_4Te_5$ film was analyzed through STEM-XEDS, employing FEI G2 80-200 chemiSTEM in probe corrected mode.

The bright-field TEM images with embedded selected area electron diffraction (SAD) patterns are shown both for the as-deposited case and after heat treatment at 180 °C in Figure 1. The BF micrograph is essentially featureless and the presence of diffuse rings in the BF-TEM image of as-deposited GST-445 suggests that the film is amorphous in nature (cf. Fig. 1a and inset therein). The presence of nucleated crystals appears darker in the BF image of the heat-treated film due to diffraction contrast (Fig. 1b). The SAD pattern corresponding to the heat-treated film at 180 °C shows the presence of rings which could be indexed to those of FCC phase. The low-dose image of the GST-445 film at room temperature recorded with a large field of view, high-speed K3 IS camera and the corresponding Python-processed image are presented in Figure 2. The recorded image along with an inset giving the FFT from a region of interest is shown in Figure 2(a); the FFT shows spots corresponding to long-range periodicity in the film. This image has been processed with Python scripting and the corresponding color-coded map is presented in Figure 2(b). Colored regions indicate crystalline domains with different orientations (depicted as color wheel as inset in Fig. 2b). These observations indicate the presence of crystals in the as-deposited GST-445 film which can be ascribed to exposure of the film to the atmosphere or quenched in nuclei during deposition. This was made possible by the detection capabilities of the K3 IS camera coupled with Python scripting.

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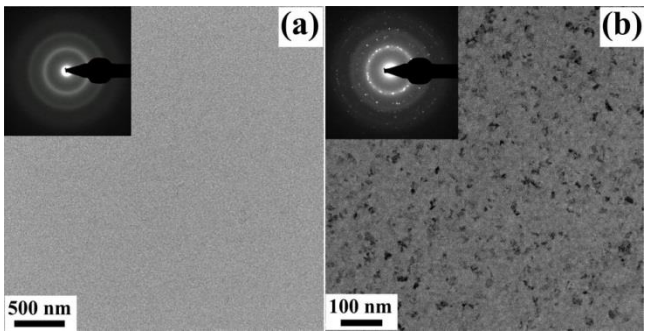

Figure 1. BF-TEM micrographs along with corresponding selected area electron diffraction patterns as insets of GST-445 film (a) in as-deposited condition and (b) heat-treated at 180 °C.

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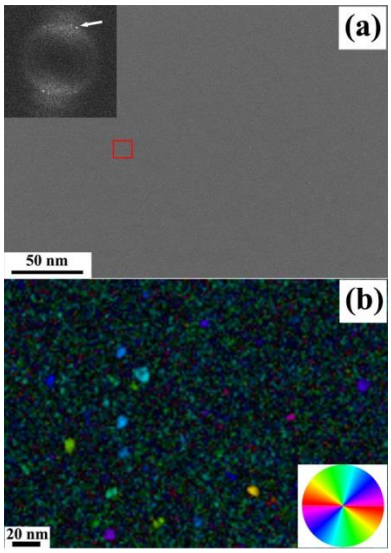

Figure 2. (a) A low electron-dose image of GST-445 film in as-deposited condition acquired by a large-field-of-view and high-speed camera along with embedded FFT from a ROI marked with red square box, (b) corresponding Python processed image with color wheel showing the orientation of the crystalline domains.

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