Investigation of the structural transformation behavior of $Ge_2Sb_2Te_5$ thin films using high resolution electron microscopy

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Structural transformation of the $Ge_2Sb_2Te_5$ was investigated by a high resolution transmission electron microscopy (HRTEM). It was found that Ge atoms undergo umbrella-flip motion from a tetrahedral site into an octahedral site in transforming from the amorphous to the metastable phase of $Ge_2Sb_2Te_5$. The presence of a twin boundary between fcc and hexagonal structured $Ge_2Sb_2Te_5$ was also confirmed through the HRTEM observations. These results support the umbrella-flip model proposed by Kolobov *et al.* [Nat. Mater. **3**, 703 (2004)] and the epitaxial growth model proposed by Park *et al.* [Appl. Surf. Sci. **256**, 8102 (2006)]. © *2007 American Institute of Physics*.
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Ge–Sb–Te based materials are well known as recording materials of phase change memory devices or optical disks.[1–4] The high crystallization speed of Ge–Sb–Te alloys and the stability of the amorphous state have made it possible to commercialize in overwriting devices. Ge–Sb–Te alloys form stoichiometric compounds, such as $Ge_2Sb_2Te_5$, $Ge_1Sb_2Te_4$, and $Ge_1Sb_4Te_7$. It is known that as the percentage of Ge–Te bonds increases, the crystallization activation energy increases which is in turn related to the higher amorphous stability. The crystallization time also decreases with increasing Ge–Te bond fraction. These factors lead to the accepted knowledge that the $Ge_2Sb_2Te_5$ is the best composition among the stoichiometric Ge–Sb–Te compounds.[5]

There are two crystalline phases of $Ge_2Sb_2Te_5$. The first is the stable hexagonal structure and the other is the metastable face centered cubic (fcc) structure. Concerning the metastable structure of $Ge_2Sb_2Te_5$, Yamada-proposed that metastable $Ge_2Sb_2Te_5$ assumed the rocksalt structure with space group *Fm*-3*m*.[6,7] Recently, Kolobov *et al.* proposed that during the phase transformation of $Ge_2Sb_2Te_5$ from an amorphous to the metastable structure, an umbrella flip of Ge atoms from a tetrahedral position into an octahedral position occurs, which leads to the fast crystallization of $Ge_2Sb_2Te_5$.[8] Although there are a few reports on the microstructure of $Ge_2Sb_2Te_5$, it is rare to show the umbrella-flip motion of Ge atoms and the transformation mechanism of $Ge_2Sb_2Te_5$ from the metastable to the stable structure in the atomic level. Therefore, in this work, we have shown details of the umbrella-flip phenomenon and transformation mechanism of $Ge_2Sb_2Te_5$ from the metastable to the stable structure using *in situ* high voltage electron microscope (HVEM).

The amorphous $Ge_2Sb_2Te_5$ thin films were deposited on the SiO_2/Si substrates and the deposition rate was 70 nm/min. A 99.99% $Ge_2Sb_2Te_5$ single target was sputtered in Ar ambient with the 50 W rf power and 1.5 mTorr working pressure. The cross-sectional high resolution transmission electron microscopy (HRTEM) specimen was prepared by mechanical polishing and ion milling with Ar ions. HRTEM studies were performed using JEOL JEM-2000EX operated at 200 kV and HVEM (JEM-ARM1300S, Jeol Ltd.) equipped with *in situ* heating holder. The samples were annealed at 150 °C with the heating rate of 5 °C/min and the TEM images were observed by 5 s interval at 1250 kV acceleration voltage. The point resolution of the instrument was 1.17 Å. The simulated image of an atomic arrangement was also obtained with the National Center for Electron Microscopy Simulation System (NCEMSS) of Lawrence Berkeley National Laboratory.

Figure 1 (a) shows the cross-sectional bright field (BF) TEM image and the selected area electron diffraction (SAED) pattern of the $Ge_2Sb_2Te_5$ thin film annealed at 150 °C for 5 min. The analysis of SAED pattern reveals that the metastable $Ge_2Sb_2Te_5$ phase has a fcc structure. Figure 1(b) shows the HRTEM image of the $Ge_2Sb_2Te_5$ thin film. As shown in the dotted circle, there is an interface between the crystalline and the amorphous phase. Figures 2(a) and 2(b) show the magnified HRTEM images of Fig. 1(b) taken at 1250 kV acceleration energy. The interplanar distance and the angular relationship indicate that this is a metastable fcc structured $Ge_2Sb_2Te_5$ viewed along the [001] direction. Careful inspection of Figs. 2(a) and 2(b) shows that there are some differences in the lattice image. In Fig. 2(a), a sublat-

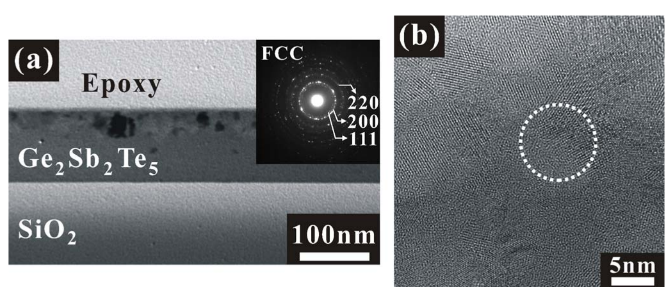

FIG. 1. (a) BF TEM image and SAED pattern of $Ge_2Sb_2Te_5$ thin films annealed at 150 °C for 5 min. (b) The HRTEM image of the same $Ge_2Sb_2Te_5$ thin films.

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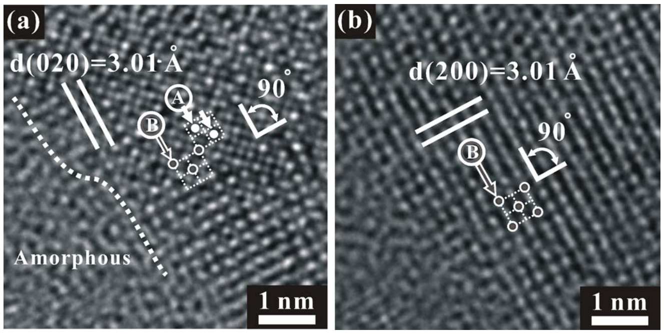

FIG. 2. (a) Magnified HRTEM image of the circled part in Fig. 1(b). A sublattice marked "A" is the tetrahedral site and a sublattice marked "B" is the octahedral site of the fcc structure. (b) The HRTEM image of Fig. 2(a) observed after 5 s.

tice image indicated by "A" is the tetrahedral site and a sublattice indicated by "B" is the octahedral site of the fcc structure, whereas the tetrahedral images are not shown in Fig. 2(b). Generally, contrast of the lattice image is governed by three variables of the HRTEM measurement such as charge density, objective lens defocus, and specimen thickness.[9] Therefore, it is concluded that the tetrahedral lattice images indicated by A in Fig. 2(a) are observed due to the charge density originated by Ge atoms since both figures are obtained at the condition that there is no difference in the specimen thickness and the lens defocus is fixed. Also, the point resolution of HVEM operated at 1250 kV is 1.17 Å, which is enough to resolve the distance between a tetrahedral and an octahedral site in the fcc structured $Ge_2Sb_2Te_5$ since its lattice constant is 6.02 Å. As mentioned before, Kolobov *et al.* suggested that during the phase transformation of $Ge_2Sb_2Te_5$ from an amorphous to the metastable structure, Ge atoms undergo umbrella-flip motion from a tetrahedral site into an octahedral site. Then, Fig. 2(a) reveals that an amorphous region is located beside the region where tetrahedral and octahedral structures coexisted and the amorphous region becomes to be changed into the metastable structure, whereas Fig. 2(b) shows the metastable structured $Ge_2Sb_2Te_5$ where the Ge atoms move from the tetrahedral to the octahedral sites. Figures 3(a) and 3(b) show schematic diagrams of these tetrahedral and octahedral structures based on the Kolobov model viewed along the [001] direction, respectively. If the Ge atoms are in the octahedral sites, the metastable structured $Ge_2Sb_2Te_5$ will be formed and the lattice images caused by the tetrahedral sites are not observed. Therefore, atomic site marked by A in Fig. 2(a) is exactly the same as the schematic image of Fig. 3(a) and the atomic site marked by B in Fig. 2(b) is also the same as the image of Fig. 3(b). Therefore, Fig. 2 is a clear evidence for the Kolobov model. The HRTEM lattice images are simulated

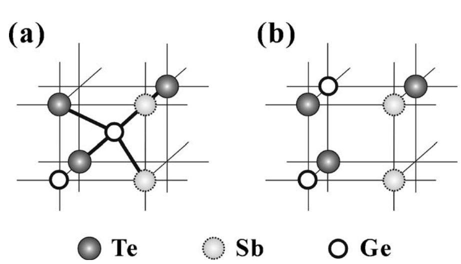

FIG. 3. Schematic diagrams of (a) the amorphous and (b) the metastable $Ge_2Sb_2Te_5$ structures viewed along the [001] direction.

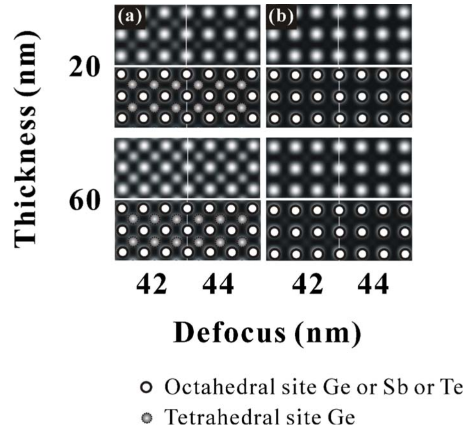

FIG. 4. Series of the simulated HRTEM images of (a) the amorphous and (b) the metastable $Ge_2Sb_2Te_5$ viewed along the [001] direction. The simulated images are changed by three measurement variables such as objective lens defocus, charge density, and film thickness.

depending on the defocus of objective lens and the specimen thickness, and its zone axis is [001]. Figure 4(a) clearly shows the Ge atoms in the tetrahedral sites over all the defocus ranges. However, Fig. 4(b) shows the simulated image of metastable $Ge_2Sb_2Te_5$ structure and in this figure tetrahedral sites are not observed. This means that the simulated images well agreed with the experimental HRTEM results and the umbrella-flip model is experimentally identified. Now, what happens during the phase transformation from the metastable to the stable structure? It can be explained by the epitaxial growth model proposed by Park *et al.*.[10] Figure 5(a) is the epitaxial growth model and in this model the similarity in the atomic arrangement between the fcc and the hexagonal $Ge_2Sb_2Te_5$ structures causes the twin boundary during the growth of the stable hexagonal structure, and the hexagonal grain growth is expanded into the adjacent metastable fcc grain boundary. However, there is still no experimental HRTEM picture to show the twin boundaries between the fcc and the hexagonal structures. Figure 5(b) is the HRTEM image and Fig. 5(c) is the fast Fourier transform images of the fcc and the hexagonal $Ge_2Sb_2Te_5$ thin films. As shown in the HRTEM image, two grains directly meet at the twin plane, and the (0004) plane in the hexagonal structure is parallel with the $(\bar{1}1\bar{1})$ plane in the fcc structure, which is the same as the epitaxial growth model, as shown in Fig. 5(a).

In summary, the phase transformation of $Ge_2Sb_2Te_5$ thin films from the amorphous to the hexagonal structure has been investigated by the HRTEM and NCEMSS simulation

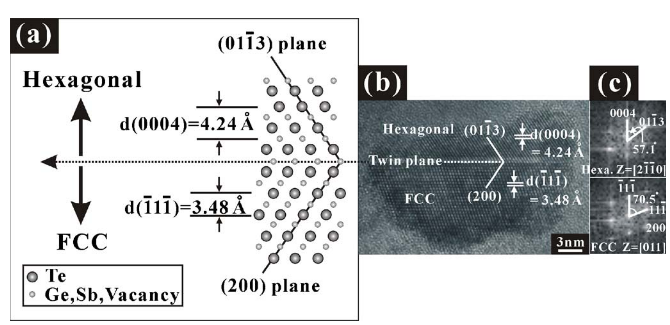

FIG. 5. (a) Epitaxial growth model to show the atomic arrangements of the fcc and the hexagonal structures joined at the twin boundary. (b) The HRTEM image and (c) the SAED patterns of the fcc and the hexagonal structure $Ge_2Sb_2Te_5$ to support the epitaxial growth model.

images. During the phase change from the amorphous to the metastable structure, the Ge atoms occupy the tetrahedral site of fcc structured $Ge_2Sb_2Te_5$ and while changing from the fcc to the hexagonal structure, the HRTEM clearly shows that twin boundary is formed between the fcc and the hexagonal structured $Ge_2Sb_2Te_5$. These experimental results are well consistent with the umbrella-flip model proposed by Kolobov *et al.* and the epitaxial growth model proposed by Park *et al.*

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