Investigation of the structural transformation behavior of Ge$_2$Sb$_2$Te$_5$ thin films using high resolution electron microscopy

Eun Tae Kim and Jeong Yong Lee
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea

Yong Tae Kim
Semiconductor Materials and Devices Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

(Received 12 June 2007; accepted 20 August 2007; published online 6 September 2007)

Structural transformation of the Ge$_2$Sb$_2$Te$_5$ 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$_2$Sb$_2$Te$_5$. The presence of a twin boundary between fcc and hexagonal structured Ge$_2$Sb$_2$Te$_5$ 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.

[DOI: 10.1063/1.2783478]

Ge–Sb–Te based materials are well known as recording materials of phase change memory devices or optical disks. 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$_2$Sb$_2$Te$_5$, Ge$_1$Sb$_2$Te$_4$, and Ge$_2$Sb$_4$Te$_7$. 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$_2$Sb$_2$Te$_5$ is the best composition among the stoichiometric Ge–Sb–Te compounds.

There are two crystalline phases of Ge$_2$Sb$_2$Te$_5$. The first is the stable hexagonal structure and the other is the metastable face centered cubic (fcc) structure. Concerning the metastable structure of Ge$_2$Sb$_2$Te$_5$, Yamada-proposed that metastable Ge$_2$Sb$_2$Te$_5$ assumed the rocksalt structure with space group Fm–3m. Recently, Kolobov et al. proposed that during the phase transformation of Ge$_2$Sb$_2$Te$_5$ 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$_2$Sb$_2$Te$_5$. Although there are a few reports on the microstructure of Ge$_2$Sb$_2$Te$_5$, it is rare to show the umbrella-flip motion of Ge atoms and the transformation mechanism of Ge$_2$Sb$_2$Te$_5$ 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$_2$Sb$_2$Te$_5$ from the metastable to the stable structure using in situ high voltage electron microscopy (HVEM).

The amorphous Ge$_2$Sb$_2$Te$_5$ thin films were deposited on the SiO$_2$/Si substrates and the deposition rate was 70 nm/min. A 99.99% Ge$_2$Sb$_2$Te$_5$ 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$_2$Sb$_2$Te$_5$ thin film annealed at 150 °C for 5 min. The analysis of SAED pattern reveals that the metastable Ge$_2$Sb$_2$Te$_5$ phase has a fcc structure. Figure 1(b) shows the HRTEM image of the Ge$_2$Sb$_2$Te$_5$ 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$_2$Sb$_2$Te$_5$ 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-
sites. Figures 3 suggest that during the phase transformation of Ge$_2$Sb$_2$Te$_5$, Ge atoms move from the tetrahedral to the octahedral site in the fcc structured Ge$_2$Sb$_2$Te$_5$ since its lattice constant is 6.02 Å. As mentioned before, Kolobov et al. suggested that during the phase transformation of Ge$_2$Sb$_2$Te$_5$ 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$_2$Sb$_2$Te$_5$ 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$_2$Sb$_2$Te$_5$ 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 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$_2$Sb$_2$Te$_5$ 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. The HRTEM image of Fig. 2(a) is the fast Fourier transform image of the fcc and the hexagonal Ge$_2$Sb$_2$Te$_5$ thin films. As shown in the HRTEM image, two grains directly meet at the twin plane, 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$_2$Sb$_2$Te$_5$ thin films. As shown in the HRTEM image, two grains directly meet at the twin plane, and the twin plane in the hexagonal structure is parallel with the (0004) 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$_2$Sb$_2$Te$_5$ thin films from the amorphous to the hexagonal structure has been investigated by the HRTEM and NCEMSS simulation.
images. During the phase change from the amorphous to the metastable structure, the Ge atoms occupy the tetrahedral site of fcc structured Ge$_2$Sb$_2$Te$_5$ 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$_2$Sb$_2$Te$_5$. 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.

This work was supported by Samsung Electronics and Korean Ministry of Commerce, Industry, and Energy (MOCIE) under the National Research Project of Phase-Change Random Access Memory Development. Also, the authors greatly appreciate Youn-Joong Kim, Korea Basic Science Institute, for assistance in providing the use of HVEM.