In situ transmission electron microscopy study on the crystallization of GeTe binary alloy

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Microstructural properties of GeTe thin films were investigated by an *in situ* heating method within a high voltage electron microscope (HVEM). The results confirm that the transformation from an amorphous state to a fcc crystalline state yields a GeTe binary alloy with a ring-shaped amorphous structure. The fcc structured GeTe transforms into a GeTe orthorhombic structure during the experiment. The crystallization behavior of the GeTe orthorhombic structure in the HVEM is quite different from thermal crystallization. Our observation of real-time structural change confirms that the relaxed amorphous structure participates in the crystallization process in the electron beam irradiation condition. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2919048]

Binary and ternary chalcogenide materials containing at least one of S, Se, and Te show fast and repeatable transitions from an amorphous state to a crystalline, and vice versa. Of these materials, the GeTe binary is the base material for making $Ge_2Sb_2Te_5$, which is known as the best material for phase change random access memory devices.[1–6] Hence, many researches have focused on the microstructural characteristics of GeTe-based materials. In particular, to find the reason for the fast crystallization, they have focused on the structural relation between the amorphous state and the crystalline state. Even though this type of research is valuable, it does not represent the real space atomic arrangement. Recently, transmission electron microscopy (TEM) studies have investigated the microstructural characteristics of GeTe-based materials.[7,8] However, they do not show the structural changes in real time during the phase transformation. We think that high voltage electron microscopy (HVEM) is an appropriate method because it can be used to analyze, on a local scale, any real-time structural change with a high atomic resolution. Moreover, HVEM enables the crystallization characteristics to be observed under a condition of high electron beam energy. As for the Te-based chalcogenide materials, several attempts have been made to study crystallization characteristics under a condition of electron beam irradiation. However, few high-resolution TEM (HRTEM) studies have investigated the atomic arrangement of Te-based chalcogenide materials on an atomic level. Our focus is on the crystal structure and atomic arrangement of GeTe thin film. In addition, we concentrate on the way the GeTe alloy is transformed from an amorphous structure to a crystal structure under a condition of electron irradiation.

An amorphous GeTe thin film with a thickness of 200 nm was deposited by rf magnetron sputtering method on a SiO_2/Si (001) substrate. The deposition rate was 70 nm/min for the sputtering of a 99.99% GeTe single target in Ar gas with the rf power of 50 W and gas pressure of 1.5 mTorr. A cross-sectional TEM specimen was prepared by mechanical polishing, namely, tripod polishing and dimple grinding, followed by ion milling with Ar ions. The ion milling was performed together with liquid nitrogen cooling to prevent crystallization. The rapid thermal annealing (RTA) process was carried out at 450 °C for 1 min, with a N_2 ambient condition. For the HVEM atomic resolution images, we used a JEM-ARM1300S model microscope (Jeol Ltd.) at 1250 kV and a JEOL JEM-2000EX model microscope at 200 kV. The cross-sectional TEM specimen was heated *in situ* in the HVEM at 450 °C. A fast-Fourier transform (FFT) image of the atomic arrangement was obtained with Gatan Digital Micrograph (Version 3.7.4).

Figures 1(a) and 1(b) show a cross-sectional bright field TEM image and a selected area electron diffraction (SAED) pattern of the GeTe thin film observed with a 200 kV beam after RTA heat treatment at 450 °C for 1 min. The image

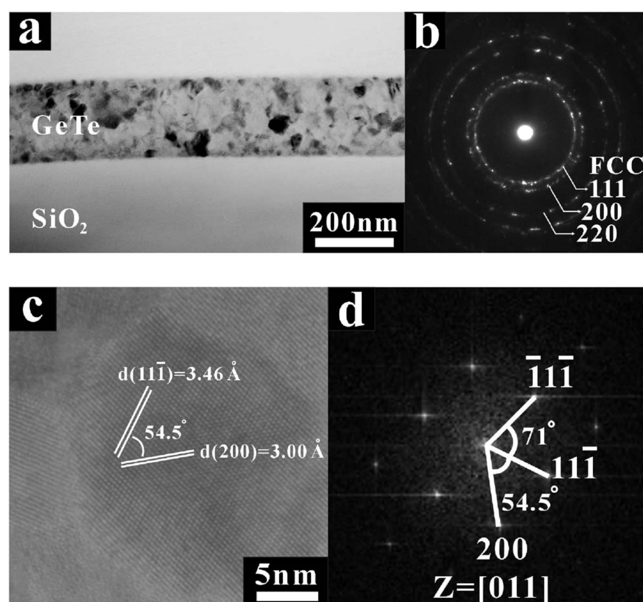

FIG. 1. 200 kV TEM results of the GeTe thin film annealed at 450 °C for 1 min. (a) The cross-sectional bright field TEM image and (b) the SAED pattern. (c) The magnified HRTEM image of GeTe thin film and (d) its FFT image.

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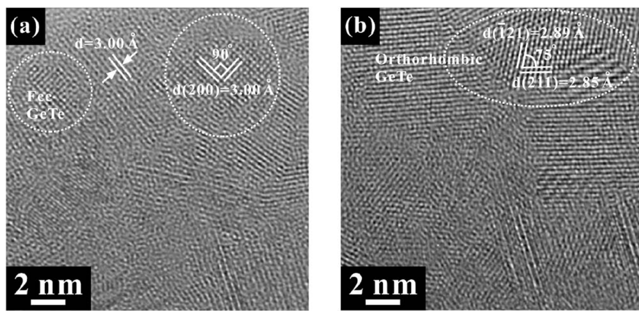


FIG. 2. (a) The magnified HRTEM image of GeTe thin film *in situ* annealed in the HVEM at 450 °C for 1 min. (b) The magnified HRTEM image of GeTe thin film *in situ* annealed in a HVEM at 450 °C for 5 min at the same specimen position in (a).

shows that the GeTe thin film was crystallized with a grain size of approximately 50 nm over the entire film. Note also that the SAED pattern of the polycrystalline GeTe corresponds to a face centered cubic (fcc) lattice with a lattice constant of 6.0 Å.[9] The fcc structured GeTe is confirmed again by the magnified HRTEM and FFT images in Figs. 1(c) and 1(d). To identify the lattice image more precisely, we obtained the HRTEM image and the SAED patterns of the GeTe at 1250 kV, where the resolution is 1.2 Å. This image is shown in Fig. 2(a).

Figure 2(a) shows a magnified HRTEM image of the GeTe thin film annealed *in situ* at 450 °C for 1 min in the HVEM. The interplanar distance and angular relation indicate that this material is fcc structured GeTe viewed along the [001] direction. One noticeable thing is that the amorphous region adjacent to the GeTe fcc structure is ring shaped. In the amorphous region, atoms are arranged along one direction. They are not straight but slightly distorted. Furthermore, the distance between the arranged atoms is nearly the same as that of the (200) or (020) interplanar spacing of the fcc structured GeTe. We therefore think that the fcc structured GeTe originates from the ring-shaped amorphous structure, which has a similar atomic arrangement as the crystalline state.

With regard to the GeTe amorphous structure, Kohara *et al.*[10] proposed a network ring structure of amorphous $Ge_2Sb_2Te_5$ and GeTe by means of a reverse Monte Carlo simulation. They suggested that the ring-shaped amorphous structure of $Ge_2Sb_2Te_5$ and GeTe, which is very similar to the fcc lattice, is the reason for the fast crystallization. Actually, GeTe shows a fast phase change from the amorphous state to the crystalline state, which indicates that the local amorphous structure is similar to the crystal structure. The HRTEM image in Fig. 2(a) confirms the structural similarity between the amorphous and the crystalline GeTe structure. Unfortunately, the exact atomic position in the amorphous phase is difficult to see because it is not a crystalline state.

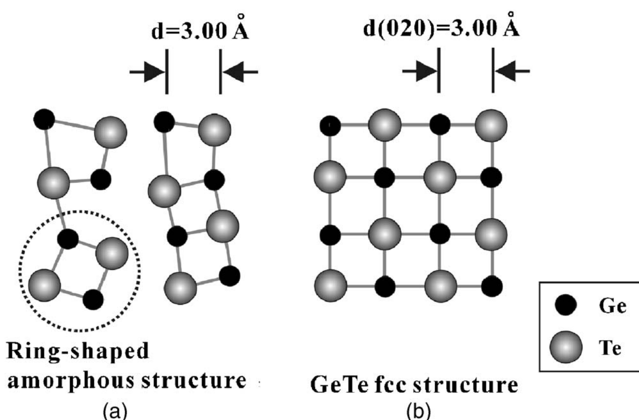
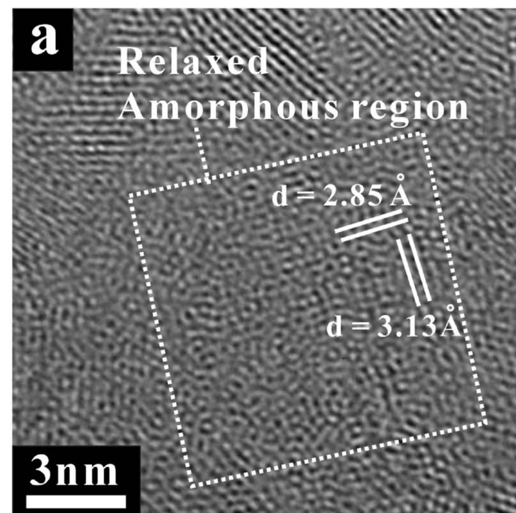
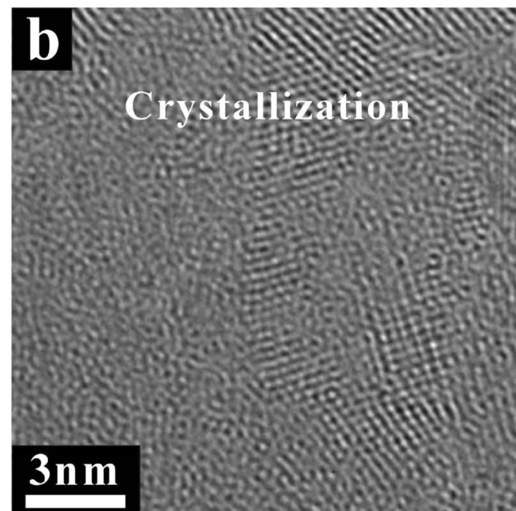


FIG. 3. Schematic presentation for the atomic arrangement of the amorphous and fcc structured GeTe based on Fig. 2(a).





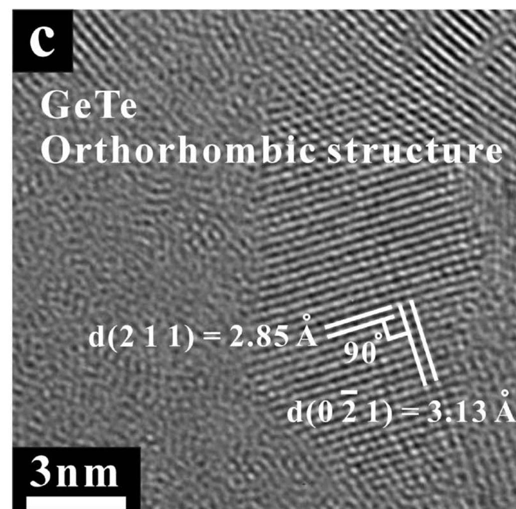


FIG. 4. HRTEM images of the GeTe thin film in the HVEM. Each image is successively observed at 10 s intervals in the same specimen position.

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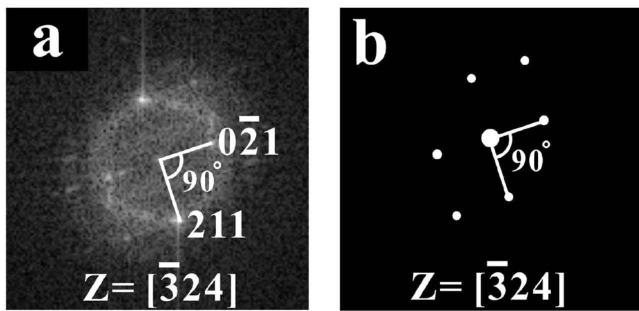

FIG. 5. (a) FFT image of GeTe orthorhombic structure in Fig. 4(c). (b) Simulated diffraction pattern of GeTe orthorhombic structure viewed along the [$\bar{3}$ 2 4] direction.

However, from the results of Fig. 2(a), we can infer that the atomic arrangement in the amorphous structure is the same as that shown in Fig. 3. Figures 3(a) and 3(b) show schematic diagrams of the ring-shaped amorphous structure and fcc structured GeTe based on the HRTEM image in Fig. 2(a) as well as the model of Kohara *et al.*

Figure 2(b) shows a HRTEM image of the GeTe thin film. The image was obtained at the same position as that of Fig. 2(a). The film was annealed at 450 °C for 5 min in the HVEM. As shown in Fig. 2(b), the fcc structured GeTe region transforms into a GeTe orthorhombic crystal structure. The crystalline GeTe is known to undergo a pressure-induced phase transformation. It is known that as the pressure increases in the solid pressure transmitting medium, anisotropic stress components lead to the following sequence of structural transformations: rhombohedral→cubic NaCl →orthorhombic.[11] From the HRTEM results, we can deduce that the formation of the orthorhombic structure is due to the high energy electron beam irradiation in the HVEM.

As shown in Fig. 4, we successively took the HRTEM images at 10 s intervals in the same specimen position to investigate the real-time structural changes. First, we used the FFT method to analyze the crystal structure shown in Fig. 4(c). Our analysis of the FFT image, which is shown in Fig. 5(a), reveals that the crystalline phase is in the form of orthorhombic structured GeTe viewed along the [$\bar{3}$ 2 4] direction. The same structure is confirmed by the simulated FFT image in Fig. 5(b). Interestingly, as shown in Fig. 4, we can see that the amorphous structure suddenly transforms into the GeTe orthorhombic crystalline phase almost independently of the temperature. From the HRTEM images in Fig. 4, we can understand why the GeTe-based chalcogenide materials quickly crystallize under the condition of electron beam irradiation. In a comparison of the HRTEM images in Figs. 4(a) and 4(c), the amorphous structure is very similar to the GeTe orthorhombic structure. Hence, there is no long-range atomic diffusion in the crystallization process, which means that the transformation is diffusionless. We think that the atomic arrangement in Fig. 4(a) represents a relaxed amorphous structure of the GeTe alloy. Actually, there are several studies on the relaxed amorphous structure of chalcogenide materials. With regard to the phase transformation mechanism in the Sb_xTe alloy, Pandian *et al.*[12] revealed that the relaxed amorphous phase induced by the electron beam irradiation increases the crystal growth rate of Sb_xTe due to a better structural matching at the amorphous-crystalline interface. Furthermore, Situ *et al.*[13] suggested that several chalcogenide materials have a relaxed amorphous state in a process of laser-pulsed crystallization. Note also that the times required for the crystallization in laser-pulsed condition is much less than that of thermal crystallization. According to Pandian *et al.*,[14,15] the phase change behavior of Sb_xTe and $Ge_2Sb_{2+x}Te_5$ is changed with and without capping layers since interface may influence the transformation from the amorphous state into the crystalline state. It is also observed that the amorphous structure in a very thin HRTEM sample without a capping layer enhances the crystal growth rate of Sb_xTe.

In summary, we confirmed that the GeTe binary alloy has a ring-shaped amorphous structure during the transformation from an amorphous state to a fcc crystalline state. We also confirmed the existence of a relaxed amorphous structure under the condition of electron beam irradiation. We think that the fast crystallization under a condition of electron beam irradiation is due to the structural matching between the amorphous phase and the crystalline phase. The results of these HRTEM experiments agree well with the results of previous microstructural research on the GeTe binary alloy.

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[1]N. Yamada, E. Ohno, K. Nishiuchi, and N. Akahira, J. Appl. Phys. **69**, 2849 (1991).
[2]M. Wuttig, R. Detemple, I. Friedrich, W. Njoroge, I. Thomas, V. Weidnhof, H.-W. Wöltgens, and S. Ziegler, J. Magn. Magn. Mater. **249**, 492 (2002).
[3]J. K. Olson, H. Li, T. Ju, J. M. Viner, and P. C. Taylor, J. Appl. Phys. **99**, 103508 (2006).
[4]A. Pirovano, A. L. Lacaita, A. Benvenuti, F. Pellizzer, and R. Bez, IEEE Trans. Electron Devices **51**, 452 (2004).
[5]T. Nonaka, G. Ohbayashi, Y. Toriumi, Y. Mori, and H. Hashimoto, Thin Solid Films **370**, 258 (2000).
[6]C. J. Kim, S. G. Yoon, K. J. Choi, S. O. Ryu, S. M. Yoon, N. Y. Lee, and B. G. Yu, J. Vac. Sci. Technol. B **24**, 721 (2006).
[7]Y. J. Park, J. Y. Lee, M. S. Youm, Y. T. Kim, and H. S. Lee, J. Appl. Phys. **97**, 093506 (2005).
[8]B. J. Kooi and J. Th. M. De Hosson, J. Appl. Phys. **92**, 3584 (2002).
[9]JCPDS Card No. 65-0415.
[10]S. Kohara, K. Kato, S. Kimura, H. Tanaka, T. Usuki, K. Suzuya, H. Tanaka, Y. Moritomo, T. Matsunaga, N. Yamada, Y. Tanaka, H. Suematsu, and M. Takata, Appl. Phys. Lett. **89**, 201910 (2006).
[11]J. M. Leger and A. M. Redon, J. Phys.: Condens. Matter **2**, 5655 (1990).
[12]R. Pandian, B. J. Kooi, J. Th. M. De Hosson, and A. Pauza, J. Appl. Phys. **101**, 053529 (2007).
[13]H. Situ, Z. T. Wang, and A. L. Jung, J. Non-Cryst. Solids **113**, 88 (1989).
[14]R. Pandian, B. J. Kooi, and J. Th. M. De Hosson, J. Appl. Phys. **100**, 123511 (2006).
[15]R. Pandian, B. J. Kooi, G. Palasantzas, J. Th. M. De Hosson, and A. Pauza, Appl. Phys. Lett. **91**, 152103 (2007).

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