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Surface energy and the equilibrium shape of hexagonal structured $Ge_2Sb_2Te_5$ grain

Yu Jin Park and Jeong Yong Lee[a)]
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

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Surface energy and the equilibrium shape of hexagonal structured grain in $Ge_2Sb_2Te_5$ were investigated by a transmission electron microscopy (TEM) study. As a result, we have found that the equilibrium shape of hexagonal structured $Ge_2Sb_2Te_5$ is a lengthened shape with (0001) plane at the major axis, which was experimentally revealed by TEM images. The hexagonal structured $Ge_2Sb_2Te_5$ grain has low surface energy in $\{0001\}$, $\{1\bar{1}03\}$, and $\{\bar{1}106\}$ planes which have no additional broken bonds from the atoms on the steps. Therefore, it is strongly facetted by the plane having low surface energy, thus, becoming an equilibrium shape. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2204837]

The $Ge_2Sb_2Te_5$ pseudobinary alloy has been widely investigated as programming material of phase-change random access memory (PRAM) cell because the electrical resistance of $Ge_2Sb_2Te_5$ is drastically changed due to the ultimately fast phase transition from amorphous to polycrystalline state.[1–8] Recently, the PRAM is spotlighted as a next generation nonvolatile memory device. With respect to the crystal structure of $Ge_2Sb_2Te_5$, which is one of the most important materials for PRAM cell, it is known to have a stable hexagonal structure and a metastable rocksalt structure having a face centered cubic (fcc) lattice. The rocksalt structure model of the metastable $Ge_2Sb_2Te_5$ was proposed by Yamada and Matsunaga,[9] and their model has been influentially accepted up to now for the reason of the short range diffusion and ordering of the different atoms.[10] As for the crystal structure of the stable hexagonal $Ge_2Sb_2Te_5$, Petrov *et al.*[11] have suggested the atomic arrangement of the nine cyclic layers, and recently, a revised model of atomic arrangement on the hexagonal structured $Ge_2Sb_2Te_5$ has been proposed by Kooi and De Hosson[12] and Matsunaga *et al.*[13] In spite of the numerous researches conducted on the microstructure of the $Ge_2Sb_2Te_5$, a high-resolution transmission electron microscopy (HRTEM) study on an atomic level for the investigation of the crystal structure and atomic arrangement of the $Ge_2Sb_2Te_5$ was somewhat uncommon. This letter reports the data for surface energy and the equilibrium shape of hexagonal structured grain in $Ge_2Sb_2Te_5$ thin films deposited on SiO_2/Si (001) substrates by sputtering method. A TEM study was performed on the $Ge_2Sb_2Te_5$ thin films and was investigated by analyzing the HRTEM image in order to precisely reveal the equilibrium shape of hexagonal structured $Ge_2Sb_2Te_5$ on an atomic level.

The amorphous $Ge_2Sb_2Te_5$ thin films with a thickness of 200 nm were deposited on SiO_2/Si (001) substrates in order to prevent the substrate effects of Si single crystal on the crystallization of $Ge_2Sb_2Te_5$ thin films. The deposition rate was 70 nm/min by sputtering a single composite $Ge_2Sb_2Te_5$ target in Ar ambient where the rf power and the gas pressure were set to 50 W and 0.20 Pa, respectively. A rapid thermal annealing (RTA) process was carried out under a N_2 ambient condition at 300 °C for 1 and 5 min, respectively. Cross-sectional TEM specimens were prepared by mechanical polishing, such as a tripod polishing and a dimple grinding, followed by an ion milling with Ar ions. The mechanical polishing was mainly done through out the specimen preparation, and the ion milling was conducted using the liquid nitrogen cooled stage of Gatan dual ion miller with the condition of 4 kV and 0.4 mA to avoid the sample heating, because the undesirable and additional crystallization of the $Ge_2Sb_2Te_5$ may occur during the conventional Ar ion milling. A bright field (BF) TEM image, selected area electron diffraction (SAED) patterns, and HRTEM images were obtained with JEOL JEM-3010 operated at 300 kV with a high-resolution pole piece.

Unlike the isotropic crystallization in the fcc structure, in general, the grain, having the anisotropic hexagonal structure, undergoes a preferably oriented grain growth. The origin of anisotropic growth is expected to the difference of surface energy for each direction. The surface energy of crystal is well explained in the previously published textbook. A crystal plane at an angle θ to the close-packed plane will contain broken bonds in excess of the close-packed plane due to the atoms at the steps as shown in Fig. 1(a). Therefore, the close-packed orientation ($\theta=0$) lies at a cusped minimum in the energy plot. Referring to the previously reported literature, the polar representation of γ known as a γ plot has the useful property of being able to predict the equilibrium shape of an isolated single crystal.[14]

The theory for the equilibrium shape of crystal determined by the difference of surface energy based on broken bonds model is still persuasive in the growth of hexagonal structured $Ge_2Sb_2Te_5$. Figure 1(b) shows the atomic arrangement of hexagonal structured $Ge_2Sb_2Te_5$ viewed along $\langle 11\bar{2}0\rangle$ where each close-packed plane can directly be observed. In addition to the $\langle 11\bar{2}0\rangle$ zone axis, the identical

[a)]Electronic mail: j.y.lee@kaist.ac.kr

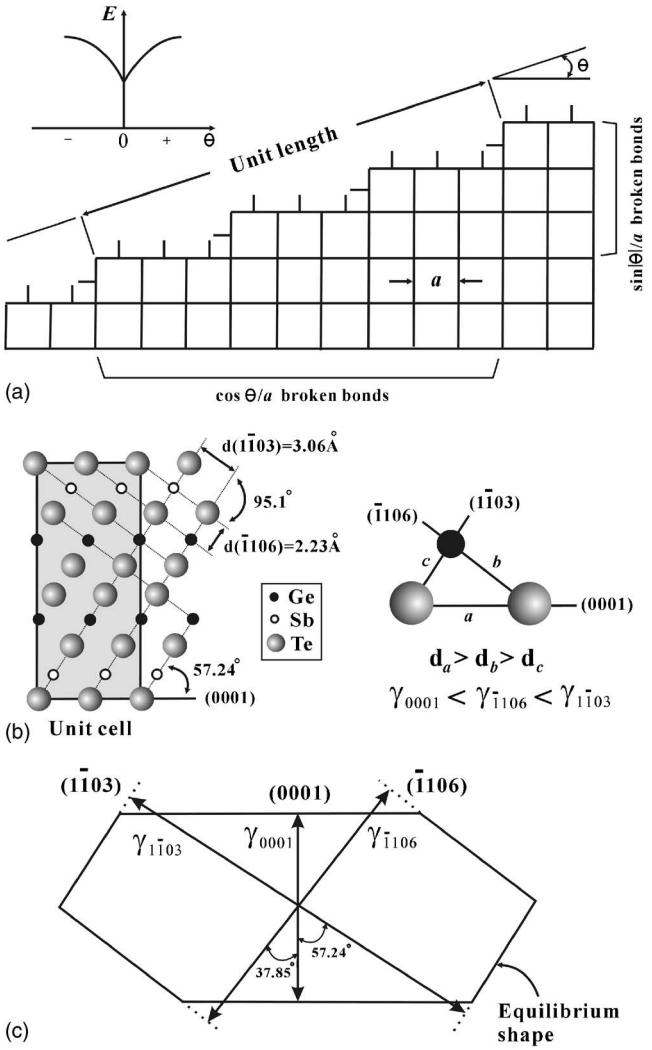

FIG. 1. (a) The "broken bond" model for surface energy and the variation of surface energy as a function of θ. (b) The atomic arrangement of hexagonal structured $Ge_2Sb_2Te_5$ viewed along $\langle 11\bar{2}0\rangle$, and comparison of surface energy among the low index planes. (c) A possible $(11\bar{2}0)$ section through the γ plot of a hexagonal structured $Ge_2Sb_2Te_5$.

family plane can be observed also on the direction of $\langle 01\bar{1}0\rangle$. The planes which are {0001}, $\{1\bar{1}03\}$, and $\{\bar{1}106\}$ have low surface energy, and the comparison of surface energy among those low index planes is indicated in the figure. Excluding the high indexes having atomic steps because they have additional broken bonds, and comparing the number of broken bonds per unit length of {0001}, $\{1\bar{1}03\}$, and $\{\bar{1}106\}$ which have no atomic steps, the relative amount of surface energy is determined as follows:

$$\gamma_{0001} < \gamma_{\bar{1}106} < \gamma_{1\bar{1}03}.$$

If we draw the γ plot on the basis of relative surface energy and construct an equilibrium shape, that of hexagonal structured $Ge_2Sb_2Te_5$ is a lengthened shape with (0001) plane at the major axis as shown in Fig. 1(c). Actually, the shape of hexagonal structured grain experimentally observed in the direction of $\langle 11\bar{2}0\rangle$ is similar to the equilibrium shape.

Figure 2(a) shows the BF TEM image and SAED patterns of $Ge_2Sb_2Te_5$ thin films annealed at 300 °C for 1 min. They show that the observed grain has the hexagonal structure and grow parallel to (0001) plane. When the amorphous

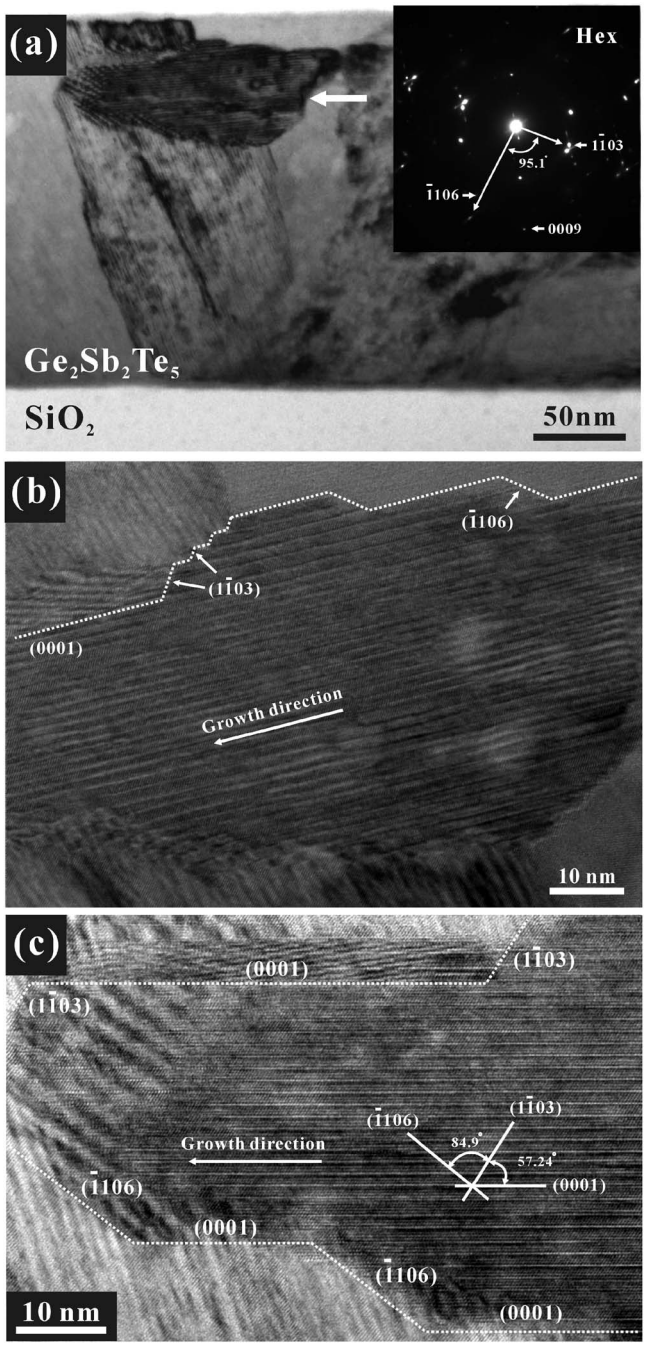

FIG. 2. (a) BF TEM image and SAED patterns of $Ge_2Sb_2Te_5$ thin films annealed at 300 °C for 1 min. They show that the observed grain has the hexagonal structure and grows parallel to (0001) plane. (b) HRTEM image of hexagonal structured $Ge_2Sb_2Te_5$. It shows {0001}, $\{1\bar{1}03\}$, and $\{\bar{1}106\}$ facets. (b) The magnified HRTEM image which is a part of Fig. 2(a).

$Ge_2Sb_2Te_5$ thin films are crystallized, generally, the metastable fcc structured crystalline phase, having low activation energy, appears first, then this metastable phase is transformed to the stable hexagonal structured crystalline phase if the sufficient energy, capable of phase transforming, are supplied to $Ge_2Sb_2Te_5$ thin films. As shown in the figure, the metastable fcc structured phase was not observed in our work. This means that the annealing energy of our experimental condition is sufficient for transformation from the metastable phase to stable one. Therefore, discussions on the equilibrium shape of hexagonal structured $Ge_2Sb_2Te_5$ grain can be stated.

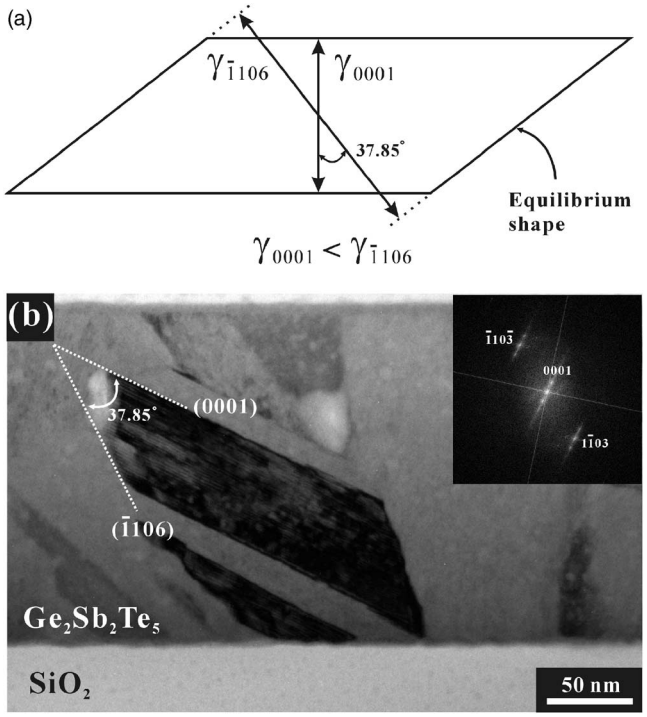

FIG. 3. (a) A possible $(11\bar{2}0)$ section forming {0001} and $\{\bar{1}106\}$ facets only. (b) BF TEM image of $Ge_2Sb_2Te_5$ thin film annealed at 300 °C for 5 min. Note that hexagonal structured grain is strongly facetted.

Focusing on the objective of this work, more detail investigation on HRTEM image of Fig. 2(b) indicates that the hexagonal structured $Ge_2Sb_2Te_5$ grain is facetted by {0001}, $\{1\bar{1}03\}$, and $\{\bar{1}106\}$ planes. In addition, the hexagonal structured grain grows parallel to (0001) plane like an equilibrium shape shown in Fig. 1(c). Figure 2(c) shows the magnified HRTEM image, which is a part of Fig. 2(a). It shows well the crystallographic relationship of hexagonal structured $Ge_2Sb_2Te_5$ as well as {0001}, $\{1\bar{1}03\}$, and $\{\bar{1}106\}$ facets.

A square can be drawn by two different directions only, therefore, the equilibrium shape of hexagonal structured grain can be constructed by {0001} and $\{\bar{1}106\}$ facets which only have the first and second lowest surface energies, as shown in Fig. 3(a). Figure 3(b) shows the BF TEM image of $Ge_2Sb_2Te_5$ thin film annealed at 300 °C for 5 min. Though it is not exactly satisfying, the $\langle 11\bar{2}0\rangle$ zone axis, however, it shows that the hexagonal structured grain is grown parallel to (0001) plane and strongly facetted by {0001} and $\{\bar{1}106\}$ planes only. This result indicates that the only two planes having the lowest surface energy can be sustained, and the $\{1\bar{1}03\}$ plane having third lowest plane can be vanished as the crystallization goes on. Considering the grain is formed in three dimension, $\{11\bar{2}0\}$ planes corresponding to the upper and lower surfaces of the crystalline are also important. Even though the surface energy of $\{11\bar{2}0\}$ planes is hard to compare with all the facets because these planes cannot be directly observed on the direction of $\langle 11\bar{2}0\rangle$ zone axis, it is expected that the surface energy of $\{11\bar{2}0\}$ plane is lower than that of $\{1\bar{1}03\}$ which was disappeared in Fig. 3(b).

Summarizing the above results, the hexagonal structured $Ge_2Sb_2Te_5$ grain has low surface energy in {0001}, $\{1\bar{1}03\}$, and $\{\bar{1}106\}$ planes which have no additional broken bonds from the atoms on the steps, therefore, it is strongly facetted by these plane, thus, becoming an equilibrium shape.

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