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Irradiation Induced Modifications of Amorphous Phase in GeTe Film

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The modified amorphous GeTe formed by pulsed laser irradiation in as-grown GeTe has been analyzed in terms of variations of local bonding structure using extended x-ray absorption fine structure (EXAFS). The modified GeTe film has octahedral-like Ge-Te bonding structure that can be effectively induced by irradiation process. The EXAFS data clearly shows that the irradiation can lead to reduction of the average coordination number. Variations in the transition temperature for the irradiated film during crystallization can be described by the presence of octahedral-like local structure.

Keywords : Chalcogenide, Phase change, GeTe, EXAFS

I. Introduction

Chalcogenide materials, S-, Se- and Te-based alloys, have been investigated for the phase change phenomena with correlated changes of electrical resistivity and optical reflectivity [1,2]. The applications based on the characteristics of reversible phase change have been attractive such as DVD optical disk and phase change random access memory (PCRAM) [1,2]. In particular, pseudo binary GeTe-Sb_2Te_3 alloys along a tie-line have phase change characteristics that show reversible phase transitions between the amorphous and crystalline phases on a time scale of a few nanoseconds. To date, pseudo binary alloys, particularly $Ge_2Sb_2Te_5$, have been utilized in non-volatile memory devices and optical disks [3]. Alloys such as $GeSb_2Te_4$, $Ge_2Sb_2Te_5$ and $GeSb_4Te_7$ along the same tie-line show similar crystallographic characteristics indicating metastable and stable crystal structures that are characterized by their cubic and hexagonal lattices [4,5].

Understanding of the local structure of Ge atoms in GeTe-Sb_2Te_3 phase change materials provides the insight for explaining the phase change between amorphous and crystalline phases. This is due to the fact that the local structure of the Ge atom is characterized by its tetrahedral and octahedral local structures in the amorphous and crystalline phases, respectively. However, several studies on the local structure of the as-grown amorphous phase have caused difficulties in defining the crystallization mechanism, including symmetry changes, due to deviations between the as-grown and amorphized phases. Previous studies on the amorphization induced by pulsed laser irradiation show that the local structure of Ge atoms is similar to that of the

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crystalline phase. If the Ge-centered local structure of the as-grown amorphous phase can be modified, these modifications could allow the crystallization characteristics to deviate from those of the as-grown amorphous phase. There have been several studies looking into the permanent modification of the amorphous phase using energetic ion and photo irradiation. These techniques could indicate the presence of local minima in the amorphous structures that have a sufficient energy barrier above the thermal energy.

De Bastiani *et al.* carried out modifications of GeTe amorphous structure using Ge^+ ion irradiation, and showed that the modified amorphous GeTe is dominantly composed of octahedral-like Ge local structure with reduction of tetrahedral Ge atoms [6]. However, in the modification process based on the ion irradiation, the role of the implanted ion should be considered. The pulsed laser irradiation effectively modifies the local structure of as-grown amorphous phase without arising long-range ordering and considering additive elements. In this paper, the modified amorphous GeTe was compared with the as-grown amorphous GeTe, which shows the similarity and discrepancy for the local structural characteristics by the comparison. In the crystallization mechanism, variations of coordination number of the Ge-centered local structure are important contribution, and lead to reduce the crystallization energy barrier.

II. Experimental

80 nm-thick GeTe film was deposited on a thermally-grown SiO_2 300 nm/Si (100) substrate at room temperature by an ion beam sputtering deposition (IBSD) with a base pressure of 3.0×10^{-8} torr. The atomic concentrations and contaminant elements of the as-grown amorphous GeTe were analyzed by the Rutherford backscattering spectrometry (RBS) and *in-situ* photoemission spectroscopy (XPS), which shows well matched target composition without any contaminant elements. The amorphous phase was investigated by X-ray diffraction (XRD) with a wavelength of 0.154 nm at the 8C1 beamline of Pohang Accelerator Laboratory, Korea. The measurement of the x-ray diffraction was conducted based on symmetry technique, indicating out of plane. To modify the local structure of the as-grown amorphous phase, the KrF pulsed laser (wavelength=248 nm, duration=25 ns) was irradiated along normal direction on the sample surface via sapphire view port without breaking the vacuum. The beam size was retained as a 10 mm×10 mm using the optical aperture. The change in resistance as a function of the annealing temperature was measured with a constant heating rate of 8 K/min using a two-point contact method, and the temperature was recorded using a thermocouple in contact with the sample surface. The local structural variations with the pulsed laser irradiation were investigated by extended x-ray absorption fine structure (EXAFS) at the 8C beamline of the Pohang Accelerator Laboratory (PAL), Korea. The beam diameter of the incident X-ray is about 1 mm and centered to the sample. Ge *K*-edge X-ray absorption spectra were acquired in the range of 0~15 k using fluorescence mode with a 7-channel Ge detector, which provide the EXAFS spectra with good signal to noise ratio.

III. Results and Discussion

Fig. 1(a) shows schematic representation for modification process of as-grown GeTe film, where the film is irradiated by pulsed laser without breaking the vacuum. The approximately 80% of the surface area on the films was irradiated by pulsed laser. The *in-situ* process for modifications of the

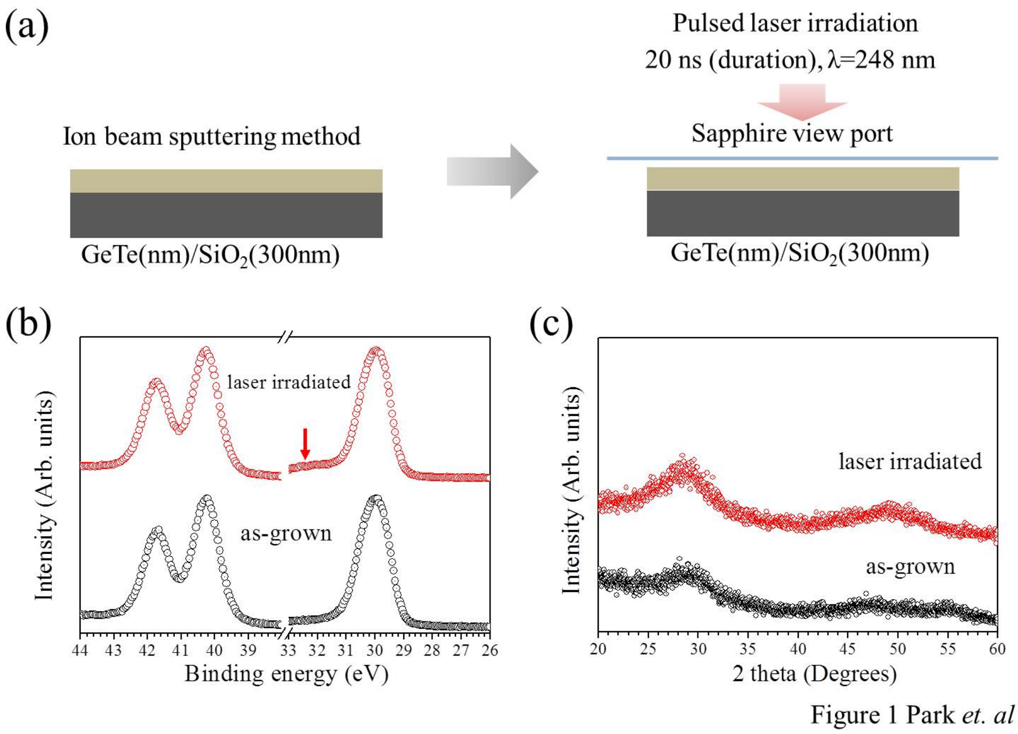

Figure 1. (a) Modification process of as-grown GeTe film by the pulsed laser irradiation, where the deposition and irradiation processes are conducted in 3×10^{-8} torr. (b) Spectra of Ge 3*d* and Te 4*d* orbitals in as-grown and irradiated GeTe films. (c) X-ray diffraction results of as-grown and irradiated films. The hollow patterns clearly indicate that the films are amorphous phase under deposition and irradiation processes.

as-grown amorphous phase is effective in the aspect of the surface contamination, because the irradiation energy is enough to induce the surface reaction in the atmospheric condition. For investigating the chemical states of the film surface, the irradiated GeTe film was transferred to XPS analysis chamber by the isolated transfer cell. Fig. 1(b) shows Ge 3*d* and Te 4*d* orbitals of as-grown and irradiated GeTe films. The spectral shape and binding energy of the irradiated film indicate that chemical states remain well despite the irradiation process. Although the small shoulder peak above Ge 3*d* shows the formation of non-stoichiometric Ge-O bonding due to residual oxygen atoms under the irradiation process, the portion of the Ge-O bonding is about 6%. As a result, the modification of the as-grown amorphous phase by the laser irradiation is well induced without the severe contamination. Moreover, spectral features of the irradiated film are approximately equal to the as-grown film without any distortion of spectra, indicating that no phase transition (i.e., crystallization) occurs. Likewise the XPS results, the x-ray diffraction of as-grown and irradiated GeTe film indicates the typical hollow pattern of the amorphous phase as shown in the Fig. 1(c). However, the irradiation can effectively modify the local structure such as the bond angle and the coordination number, although the distinctive features after the irradiation process can be not observed. The variation of the transition temperature between the as-grown and the irradiated films can provide the difference in the fine structure of both amorphous phases because the crystallization activation energy is significantly affected by the local structural environment.

Fig. 2 shows the sheet resistance changes of as-grown and irradiated GeTe films under same ramping rate of 8 K/min. The resistance of as-grown GeTe film suddenly decreases, indicating that the amorphous phase is transformed to crystalline phase. The resistance change in irradiated film with increasing temperature shows the behavior similar to that of as-grown film. Moreover, the overall behavior of the resistance changes is not distorted by irradiation excluding the change in transition temperature. In the context, the important finding is that the transition temperature (T_c) becomes lower in the case of as-grown film. The level of the T_c from the amorphous to the crystalline is proportional to the energy required for activating structural changes between short and long range ordering. Therefore, the T_c can be affected by atomic nature of the local structure depending on the amorphous and crystalline phases. In particular, the shift of the T_c obviously indicates that the local atomic arrangement of the irradiated film is deviated from that of the as-grown film. It is valuable to understand the structural origin for the shift of the transition temperature.

The EXAFS can provide more detailed information on the atomic configuration in tetrahedral local structure of Ge atoms. In particular, it shows the detailed atomic arrangement such as bond length of nearly 1-D from modulation between the photoelectron of absorbed atom and the photoelectron scattered at neighboring atoms. Fig. 3 shows the Fourier transformed (FT) magnitude of EXAFS signal for Ge *K*-edge in as-grown and irradiated amorphous GeTe films. The main bonding environment of Ge atoms is composed by the Ge-Ge and Ge-Te bonding structure, which is well agreement with previous reports [7,8]. The average number of coordination is lower than 4, indicating existence of 3-fold geometry. However, the bond length along the radial direction (single scattering) of Ge-Te cannot provide any information for the bonding geometry, because the value simply remains same as that of the tetrahedral Ge-Te bonding geometry. In the previous EXAFS studies on the amorphous GeTe and $Ge_2Sb_2Te_5$ systems, Ge-Te bond length shows a single value (2.63±0.02 Å), and the mean-square relative displacement (MSRD) indicating distribution of correlated bond length typically shows the lower value than that of crystalline phase. In the case of modified (irradiated) amorphous GeTe, the bond length of central Ge atoms (without phase correction)

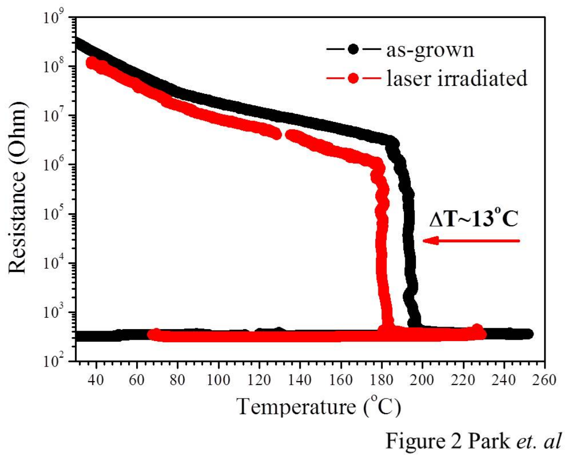

Figure 2. Plot of sheet resistance as a function of annealing temperature in the irradiated amorphous phases, compared to the as-grown amorphous phase.

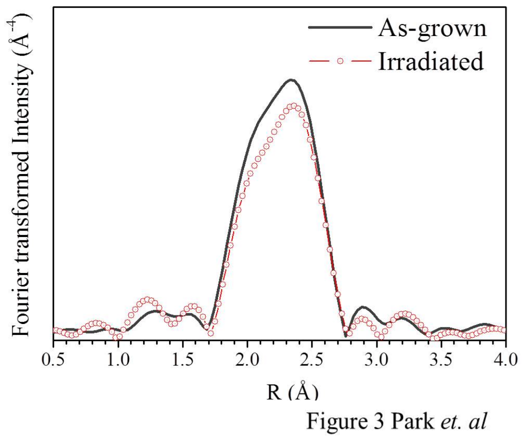

Figure 3. Fourier-transform magnitude of Ge *k*-edge EXAFS for as-grown and irradiated amorphous GeTe films.

still remains after irradiation. The reduction of FT magnitude is mainly correlated with the variations of coordination number and MSRD along each bonding pair. Moreover, we considered the possibility that the irradiation leads to variations of the interatomic distribution for Ge-Te bonding as well as the bonding symmetry of Ge atom.

The EXAFS fitting process for the Ge k-edge was conducted based on the single scattering path using

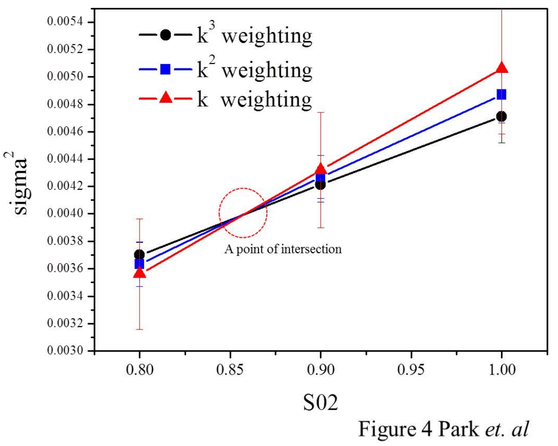

Figure 4. Determination of the reduction factor for the Ge K-edge from reference Ge foil. The correlation between S02 and σ2 for the Ge-Ge bond is mostly broken by sequentially fixing S02 and performing the fits using different k weights.

Feff8.4 code. Since the coordination information originating from fitting process is considerably sensitive to the reduction factor, S_0^2, its value carefully was acquired from the reference Ge foil. Fig. 4 shows the correlations between S_0^2 and the σ^2 with differing k weighting. The correlation of both parameters with differing k obviously shows a point of intersection, which means the amplitude of EXAFS signal does not depend on the k weighting around ~ 0.85 (S_0^2). The value of S_0^2 is also acceptable for applying to Ge-centered bonding structures. In the fitting process, we considered the two local symmetry of the Ge-Te bonding such as the tetrahedral (T_d) and pyramidal (P_y) symmetry as shown in the Fig. 5(a). The bond length and bond angle in each symmetry were adjusted to find the minimum value of the reduced Chi-square error. The Ge-Ge and Ge-Te bonding based on the tetrahedral and octahedral structures clearly describe the Fourier-filtered signal of first shell as shown in Fig. 5(b). In addition, the third cumulant C_3 was included for considering the possibility of arising anharmonicity in the irradiated amorphous GeTe. The effective distance distribution can be represented by cumulant expansion as introduced in the previous study [9]. The C_3 cumulant is related with anharmonicity, compared to a Gaussian

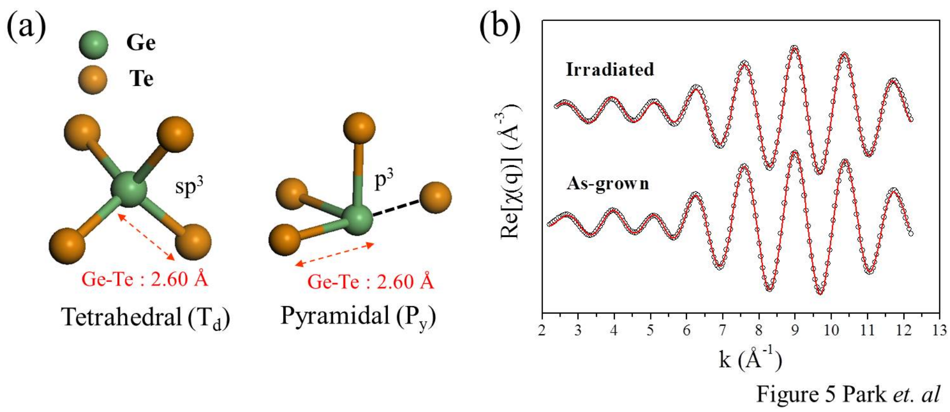

Figure 5. (a) Tetrahedral and octahedral local structures of the Ge-Te bonding in both amorphous phases. (b) Fourier-filtered Ge *K*-edge EXAFS data (open circle) and fitting results (solid line) for as-grown and irradiated GeTe films.

Table 1. The fitting parameter of as-grown and irradiated GeTe films.

	Bond	R (Å)	N	σ^2
As-grown	Ge-Te	2.64 (2)	1.75 (35)	0.0087 (20)
	Ge-Ge	2.48 (1)	1.81 (34)	0.0044 (14)
Irradiated	Ge-Te	2.62 (1)	1.67 (38)	0.0066 (21)
	Ge-Ge	2.49 (1)	1.72 (58)	0.0065 (31)

distribution of the interatomic distance. The EXAFS fitting parameter of Ge-Ge and Ge-Te bonding pairs was summarized in Table 1. Although the irradiation leads to changes of Ge-centered bonding geometry, the bond length of Ge-Te (2.62±0.01 Å) and Ge-Ge (2.49±0.01 Å) is nearly similar to that of as-grown film. However, non-zero value of the C_3 cumulant (0.00064±0.00037 $Å^3$) for Ge-Te bonding indicates the presence of asymmetric anharmonicity for bonding distribution. Moreover, MSRD or C_2 cumulant (0.0066±0.0021 $Å^2$) of Ge-Te bonding in modified amorphous phase has been defined as a lower value than that (0.0087±0.0044 $Å^2$) in as-grown amorphous phase. Such changes induced by irradiation are simultaneously accompanied by the decreasing coordination number (decreased from 3.56 to 3.39), which can be connected with enhanced octahedral-like geometry. In other words, the laser irradiation is able to transform from the sp^3 hybridized bonding orbital to non-hybridized p^3 bonding orbital in amorphous phase.

Following the umbrella flip model of the crystallization mechanism, the Ge motion within atomic scale between tetrahedral and octahedral sites significantly facilitates the crystallization [10], which can be also understood as the transition between the non-hybridized p^3 bonding and hybridized sp^3 bonding in respect of the formation of the bonding orbital. The crystal structure with rhombohedral lattice (or distorted rocksalt) has the long Ge-Te bonding of 3.15 Å for maintaining the attraction of interlayers along C_3 axis. The formation of the octahedral-like structure in the irradiated film can effectively play a role of seed for the crystallization, although the interatomic distance still remains as that of tetrahedral structure. Therefore, the shift of the transition temperature between the as-grown and the irradiated films can be described by the presence of octahedral-like local structure.

IV. Conclusions

The pulsed laser irradiation effectively modify the as-grown amorphous phase, which can be characterized by transition between the octahedral-like local structure (or pyramidal structure) and tetrahedral structure. In this study, the modified amorphous phase comparing with as-grown phase shows raised octahedral-like Ge-Te bonding. The presence of the octahedral-like Ge-Te bonding enables the amorphous GeTe film to have the structural similarity between the irradiated and crystalline GeTe films. The similarity can lead to reduction of the activation energy for the crystallization process in GeTe phase change material.

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