Crystallization behavior of GeSbTe nonthermally amorphized by femtosecond laser pulse irradiation

Kazuyuki Tajima, Nariaki Kitamura, and Toshiharu Saiki
Graduate School of Science and Technology, Keio University
3-14-1 Hiyoshi, Kohoku, Yokoham, Kanagawa 223-8522, Japan
tajima@saiki.elec.keio.ac.jp

Abstract
By means of femtosecond laser pulse irradiation we investigated crystallization process of GeSbTe (GST) in various amorphous states. We compared the number of pulses required for crystallization of amorphous GST samples prepared by three different ways: as-deposited, amorphized by single-femtosecond (higher-fluence) pulse irradiation, and amorphized by multi-femtosecond (lower-fluence) pulse irradiation. We found that the amorphous GST nonthermally amorphized by lower fluence pulses was recrystallized most efficiently in terms of the number of irradiation pulse. Through TEM and NSOM observation we also discussed the mechanism of amorphization and crystallization process with multi-pulse excitation.

1. Introduction

High speed crystallization in GeSbTe phase change materials is one of the most critical factors to be addressed for rewritable optical and electronic memory applications. Recently we have found that a single femtosecond laser pulse gives rise to nonthermal amorphization, which takes place below the melting point [1]. In a pump-probe transient reflectivity measurement, the reflectance dropped steeply within 500 fs after the pulse excitation. This ultrafast amorphization indicates that switching of Ge atoms can be initiated by photoexcitation of electrons to break the weaker Ge−Te bond, and that it is completed within a subpicosecond time scale. Based on the scenario of Ge switching model we would also expect that photoexcitation makes a significant contribution to the switch-back of Ge atom: recovery to the crystalline phase.

In this study we performed crystallization of amorphous states by multi-pulse irradiation of femtosecond pulse. We found that the amorphous state induced by femtosecond pulse irradiation can be much more easily crystallized compared with as-deposited amorphous phases. By means of TEM and NSOM observation, the mechanism of multi-pulse amorphization and crystallization processes were also discussed.

2. Experiments

The sample investigated was a $Ge_2Sb_2Te_5$ (GST) thin film with a thickness of 20 nm sputtered on a glass substrate. The GST film was covered with a 10-nm SiO_2 protection layer. The main excitation source was a Ti:Sapphire laser system operating at 800 nm central wavelength with a pulse duration of 170fs. In order to compare crystallization behavior depending on initial amorphous states, we amorphized the GST film with three different ways (Fig. 1): (i) as-deposited, (ii) amorphized by single-femtosecond (higher-fluence) pulse irradiation, and (iii) amorphized by multi-femtosecond (lower-fluence) pulse irradiation.

For crystallization of the individual amorphous states, a train of weak femtosecond pulse with fluence of 6.5 mJ/cm^2 was focused onto the amorphous area of the sample. A He-Ne laser was used as a probe beam to measure the change of transmission upon crystallization after each femtosecond pulse excitation.

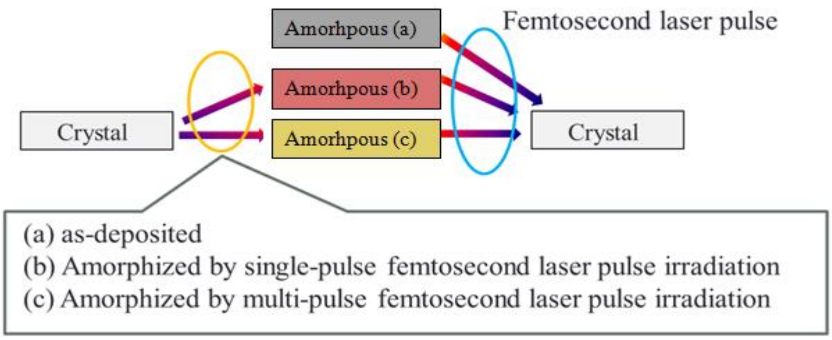

Figure 1: Summary of amorphization and crystallization processes.

3. Results and discussion

Figures 2(a)-(c) show normalized transmissions of probe beam as a function of the number of femtosecond pulses irradiated for different initial amorphous states. In the case of amorphous state induced by multi-femtosecond pulse irradiation, only 10 pulses are sufficient to reach 10% decrease in transmission whereas 150 pulses are required for the as-deposited amorphous state. The difference mainly comes from the fact that, in the case of as-deposited, the first 70 pulses serve to create nucleation centers for crystallization.

It is also important to note that 30 pulses are needed to crystallize the amorphous state induced by single-femtosecond pulse irradiation, where a higher fluence pulse is applied compared to the case of multi-femtosecond pulse irradiation. To understand the difference, we compare electron diffraction patterns obtained from TEM measurements. Figures 3(a) and 3(b) show diffraction patterns of the amorphous phase induced by single-pulse and multi-pulse excitation, respectively. In the case of multi-pulse amorphization with lower fluence, diffraction spots were superimposed to amorphous halo, demonstrating the presence of crystalline phase. The amorphous state induced by multi-pulse can be efficiently crystallized because the amorphized GST is partially left in the crystalline phase.

Figure 4 is a plot of the number of femtosecond pulse irradiation required for 10% decrease in transmission as a function of laser pulse fluence for amorphous phases prepared by single-pulse (red) and multi-pulse excitation (blue). In both cases, a larger number of pulses are spent for crystallization with a

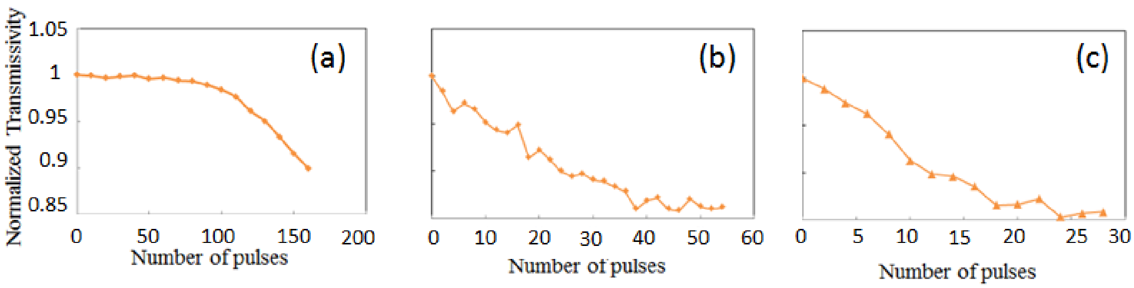

Figure 2: Normalized transmissions of probe beam as a function of the number of femtosecond pulses irradiated for three different initial amorphous states: (a) as-deposited, (b) amorphized by single-femtosecond pulse irradiation, and (c) amorphized by multi-femtosecond pulse irradiation.

Figure 3: TEM electron diffraction patterns of two different amorphous states: (a) amorphized by single-femtosecond pulse irradiation and (b) amorphized by multi-femtosecond pulse irradiation.

reduction of pulse fluence. Over the entire fluence range, amorphous phase created by single-pulse irradiation needs more pulses to be crystallized. The difference is most pronounced around the fluence of 8 mJ/cm^2. More importantly, in high fluence region (>12 mJ/cm^2), further reduction in the number of pulse was not observed. To clarify the reason we performed NSOM imaging of crystallized area after irradiation of 200 pulses with a fluence of 13 mJ/cm^2. As shown in Fig. 5, we see a bright spot, which indicates that amorphous phase remains in the crystallized area. This means that, at the center of beam spot, the fluence exceeds the nonthermal amorphization threshold, which impedes the crystallization of whole irradiated area.

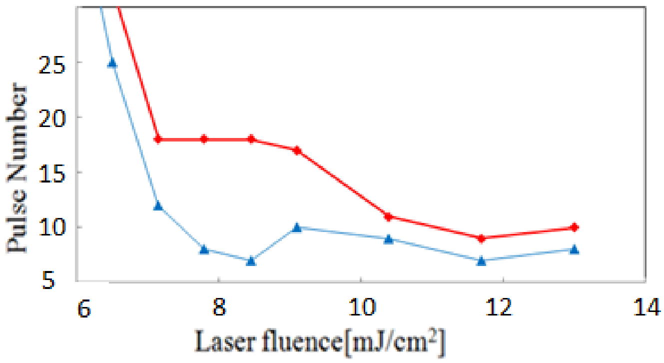

Figure 4: Plot of the number of femtosecond pulse irradiation required for 10% decrease in transmission as a function of laser pulse fluence for amorphous phases prepared by single-pulse (red) and multi-pulse excitation (blue).

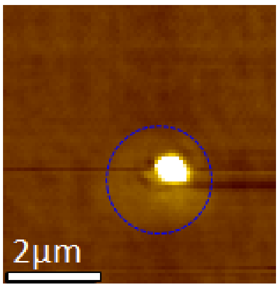

Figure 5: NSOM images of crystallized area after irradiation of 200 pulses with a fluence of 13 mJ/cm^2.

4. Conclusion

Under multi-femtosecond pulse irradiation we compared crystallization behavior of GeSbTe thin films with different amorphous phases. We found that crystallization of the amorphous state nonthermally created by low-fluence femtosecond pulse irradiation is the most efficient in terms of the number of irradiation pulse. The result suggests that the photoexcitation of high density electron can be a trigger for fast and efficient crystallization.

Acknowledgement

We are grateful to K. Yusu (Toshiba) and T. Shintani (Hitachi) for providing us with GST thin film samples, and to T. Yamamoto (The University of Tokyo) for supporting measurement of TEM. This work was supported by the Strategic Information and Communications R&D Promotion Program from the Ministry of Internal Affairs and Communications.

References

[1] M. Konishi, H. Santo, Y. Hongo, K. Tajima, M. Hosoi, and T. Saiki, "Ultrafast amorphization in $Ge_{10}Sb_2Te_{13}$ thin film induced by single femtosecond laser pulse", Appl. Opt. **49**, pp. 3470-3473 (2010).