Sub-picosecond non-melting structure change in a GeSbTe film induced by femtosecond pulse excitation

H. Santo, Y. Hongo, K. Tajima, M. Konishi, and T. Saiki
Department of Electronics and Electrical Engineering, Keio University
3-14-1 Hiyoshi, Kohoku, Yokohama, Kanagawa 223-8522, Japan

Abstract

A recent study has clarified that the phase change of the crystalline GeSbTe (GST) into amorphous is due to a slight displacement of Ge atoms from their position in the crystalline lattice. It suggests that ultrafast phase change may occur under irradiation of a single femtosecond laser pulse, which excites a large fraction of valence electrons to the conduction band. We performed femtosecond pump-probe measurements to discuss amorphization dynamics in a GST thin film and found that the reflectivity dropped abruptly within 500 fs after the pump pulse excitation and it was followed by a small change in reflectivity within 10 ps.

Keywords: GeSbTe, amorphization, femtosecond laser pulse, non-melting

1. Introduction

Multicomponent chalcogenide, GeSbTe (GST) in particular, has been used for re-writable optical recording media such as DVD-RAM. In the optical recording system, reversible phase changes between crystalline and amorphous phases are induced by short laser pulses with duration of tens of nanoseconds. While the atomic structure of the crystalline phase is well-understood to possess an octahedral-like arrangement (rocksalt structure), the bonding structure in the amorphous phase still remains open for discussion. Among many theoretical and experimental studies, the investigation of local structure with the extended X-ray absorption fine structure (EXAFS) spectroscopy by Kolobov *et. al.* has significantly contributed to understand the mechanism of the fast and repeatable switching as well as large changes in reflectivity [1]. Their study has clarified that the crystalline phase has a distorted rocksalt structure and amorphization takes place due to a displacement of Ge atom from octahedral to tetrahedral arrangement. The result indicates that the switching of Ge atom can be initiated by photoexcitation of electrons to break the weaker Ge-Te bond and will be completed within subpicosecond time scale (the inverse of the phonon frequency). A femtosecond laser pulse will enable to induce such an ultrafast phase change due to the local displacement of individual Ge atom.

In this paper we performed femtosecond pump-probe measurements to investigate amorphization dynamics in a crystalline GST thin film. It was found that the reflectivity of the probe pulse decreased rapidly within a time of 500 fs after the pump pulse irradiation, and it was followed by a small change in reflectivity within 10 ps depending on the pump pulse fluence. In order to discuss the phase change mechanism more clearly, a double pump pulse measurement was also carried out.

2. Experimental

The sample investigated was a crystalline $Ge_{12}Sb_2Te_{13}$ film with a thickness of 20 nm on a glass substrate. To investigate ultrafast phase-change dynamics after irradiation of a single femtosecond laser pulse, we measured a temporal reflectivity evolution of the GST film using a pump-probe technique. We described the pump-probe setup schematically in Fig. 1. The light source was a mode-locked Ti:sapphire laser. The laser pulse width and the center wavelength were 90 fs and 800 nm, respectively. We used a Pockels cell (electro-optic modulator) to extract a single pulse from the train with a repetition rate of 82MHz. The extracted pulse was divided into a pump and a probe pulse at the first polarizing beam splitter (PBS). The fluence of the probe pulse was one tenth of that of the pump to avoid inducing amorphization by the probe pulse itself. The delay time τ between pump and probe pulses was scanned with an optical delay line. Finally, the pump and probe pulses were recombined collinearly at the second PBS and focused onto the samples by a microscope objective with a numerical aperture of 0.35. The sample was translated at a speed of 50 μm/s in order to ensure each pump-probe irradiation on a fresh area of the sample. The reflected probe beam and a reference beam were detected by a balance detector so that the laser fluctuation was canceled.

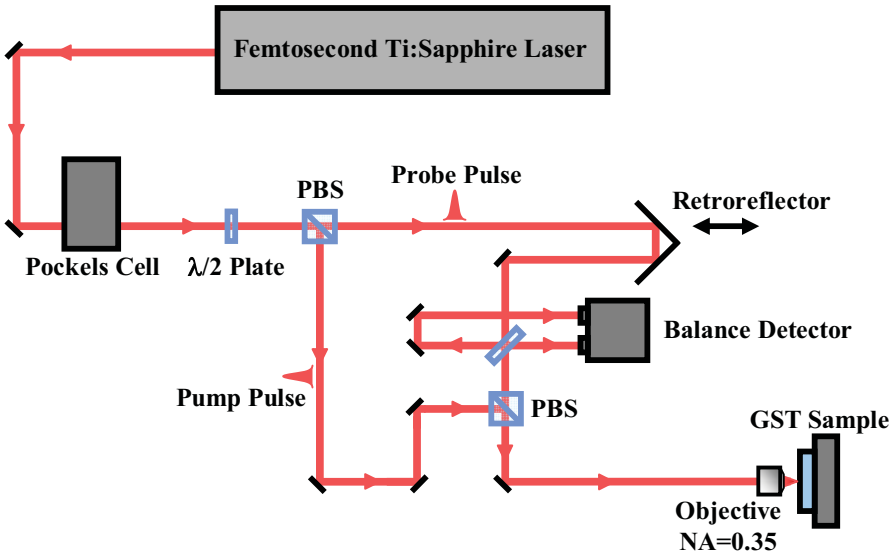

Fig. 1. Schematic of a femtosecond pump-probe measurement system.

At each delay time, the reflected probe signal was averaged over 10 times.

3. Results and Discussion

Figure 2 shows temporal reflectivity evolutions of the probe pulse for various pump pulse fluences. For all fluences, the reflectivity dropped abruptly within 500 fs after a single pulse excitation. After that, the reflectivity continued to slowly decrease or recovered within 10 ps, depending on the pump fluence. Except for the lowest fluence of 12.8 mJ/cm^2, where the reflectivity recovered to its initial value at a sufficient delay (not shown), the amorphization (or some kind of structure change) occurred partially or totally in the irradiated area. We confirmed that the amorphized area can be recrystallized with an irradiation of continuous-wave He-Ne laser. For the fluences of 12.8, 16.6, and 18.1 mJ/cm^2 surface observation using a scanning electron microscope revealed that the transition occurred without melting.

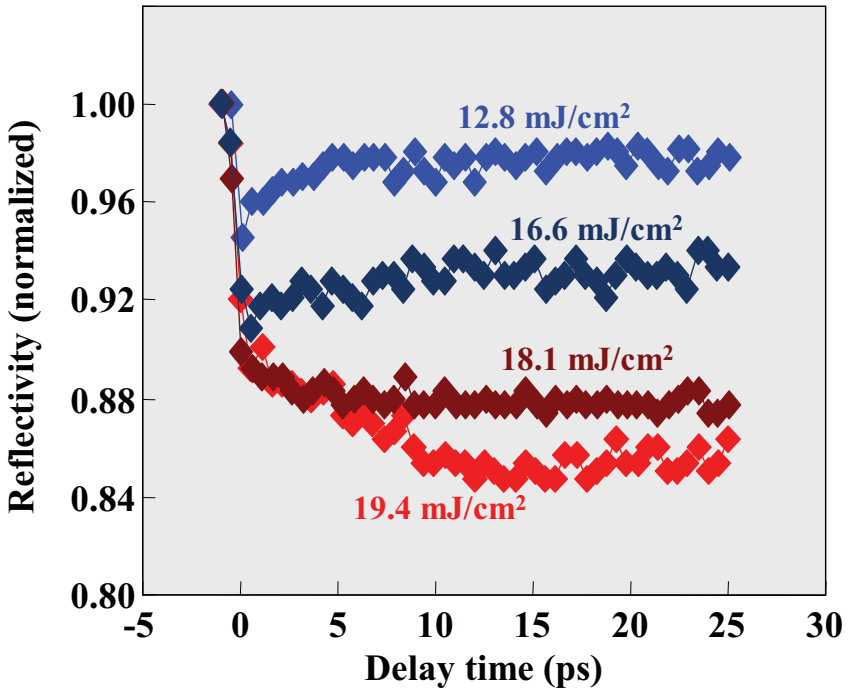

Fig. 2. Temporal evolutions of the reflectivity change in a crystalline GST film upon irradiation of single femtosecond laser pulses.

According to the amorphization model proposed by Kolobov *et al.*, the following scenario might explain the temporal evolutions [2]: 1) The initial drop of reflectivity is attributed to break-up of relatively weak Ge-Te bonds and displacement of Ge atoms due to the high-density electron excitation. 2) The additional change is governed by the occupancy of

the complex defects related to the Ge displacement. If the excitation density is sufficient to occupy the complex defects and to maintain the Ge atoms at the displaced position, the reflectivity remains constant or exhibits an additional reduction. If the excitation density is insufficient, the GST recovers to the crystalline structure and the reflectivity regains its original value.

To make clear whether ultrafast photoexcitation plays an essential role in the phase change mechanism, or not, we performed double-pulse excitation measurements, where we control the temporal photoexcited carrier density by tuning the delay of two pump pulses of equal fluence. Figure 3 shows an optical microscope image of amorphous marks with double pulse excitation for a delay of 0 fs (actually a single pulse excitation with a duration of 140 fs) and 300 fs. The total pulse fluence irradiated on the sample is same in both cases, however, the amorphization threshold increased for the delay of 300 fs. The result indicates that high density carrier excitation at a time, within a femtosecond time scale, makes an important contribution to the amorphization. To occupy the complex defects and maintain the Ge atoms at the displaced position, excitation of more than two electrons (one for the break-up of Ge-Te bond and the other for the occupancy of defect) per unit cell should be required. Moreover it is also likely that to stabilize the Ge atom displacement several unit cells are expected to participate in the phase change. If such amorphization mechanism is valid, the photoexcitation by a femtosecond pulse is crucially advantageous.

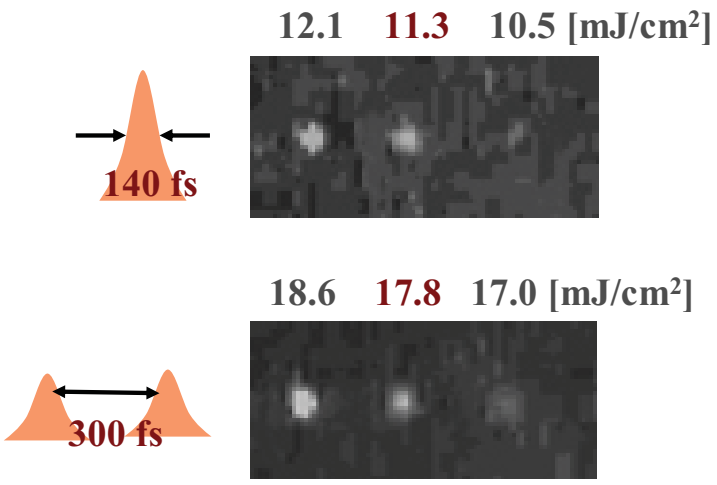

Fig. 3. Optical microscope images of the amorphous marks formed by single and double excitation femtosecond laser pulses for different pump fluences.

Acknowledgement

We are grateful to Dr. K. Yusu (Toshiba Corporation) for providing us with a GeSbTe thin film sample.

References

[1] A. V. Kolobov, P. Fons, A. I. Frenkel, A. L. Ankudinov, J. Tominaga, and T. Uruga, Nature Materials **3**, 703 (2004).

[2] A. V. Kolobov, A. S. Mishchenko, P. Fons, S. M. Yabubenya, and J. Tominaga, J. Phys. Condens. Matter **19**, 455209 (2007).