Optical anisotropy in amorphous GeSbTe thin films induced by nonthermal phase change with femtosecond pulse excitation

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ABSTRACT

So far we have experimentally demonstrated ultrafast and nonthermal amorphization of GeSbTe thin films by femtosecond optical pulse excitation. We have also found that the nonthermally amorphized phase can be more efficiently crystallized than the melt-quenched amorphous phase. These results suggest that switching of Ge atoms can be initiated by photoexcitation of electrons to break the weaker Ge-Te bond, and that the initial crystalline structure is memorized by preserving the covalent backbone. In this study, based on this context, we demonstrate that the nonthermal amorphization can lead to optical anisotropy by effectively breaking the Ge-Te bonds, running parallel to the polarization of the excitation light. We obtained significantly giant optical anisotropy characterized by the polarization rotation angle of the probe beam as large as 1.5°.

Key words: optical anisotropy, femtosecond laser, nonthermal phase change, polarization spectroscopy

1. INTRODUCTION

Chalcogenide phase change materials, such as GeSbTe, have been extensively investigated for switching and data storage applications. The operating principle of switching devices and rewritable memory devices is based on the reversible change between crystalline and amorphous phases in a material. In the case of optical data storage an amorphous recording mark is formed by melting and quickly quenching under intense nanosecond laser pulse irradiation. The recording mark can be erased by annealing near the glass transition temperature under less intense and longer pulse heating. In many Te-based chalcogenides this phase change of state takes place in nanoseconds.

Regarding GeSbTe the atomic structure of amorphous state is not fully determined while the crystalline state is well known to possess a distorted rock salt-like structure. Among relevant fundamental studies the investigation of the local structure by extended x-ray absorption fine-structure spectroscopy by Kolobov *et al*. has provided a major step to clarify the fast and repeatable switching mechanism [1]. Their study revealed that amorphization occurs due to displacement of the Ge atoms from an octahedral to a tetrahedral arrangement.

The amorphization mechanism suggests that switching of Ge atoms can be triggered by photoexcitation of electrons (transition from bonding to antibonding states) to break the weaker Ge-Te bond, and that it is completed in a subpico- to picosecond time scale (the inverse of the phonon frequency). A femtosecond laser pulse can induce such an ultrafast phase change due to the local displacement of individual Ge atoms. Moreover, because the femtosecond-pulse amorphization probably requires a lower energy deposition than that of a nanosecond pulse, the process is anticipated to be complete without the formation of a liquid phase.

So far we demonstrated nonthermal amorphization of a GeSbTe thin film with femtosecond laser pulse excitation [2]. A pump-probe measurement revealed two-step reflectivity change: sub-picosecond dominant drop followed by a few picosecond additional change. It is considered that the initial reflectivity drop corresponds to a period when resonant bonding is broken while the atomic structure still preserves the average long-range order of the crystalline phase. The second slow change is attributed to the transformation to the amorphous state, which is obtained by relaxation and loss of the long-range order [3].

These experimental results can be consistently understood within nonthermal Ge-switching model. By extending the

context we expect that a structural anisotropy can be introduced even in the amorphous state initiated by selective breaking of Ge-Te bond with linearly-polarized pulsed laser excitation. The resonance bonding running along the excitation light polarization will be preferentially excited [4] and broken. In Te-based chalcogenides since the optical contrast is primarily provided by the nature of the bonding, rather than by the spatial location of the atoms [3], the anisotropy in resonance bonding will cause significant optical anisotropy. In this study, to demonstrate this scenario, we conducted polarization microscopic measurements to evaluate the optical anisotropy of amorphous recording marks formed by femtosecond pulse excitation.

2. EXPERIMENTS

The sample investigated was a 20 nm thick $Ge_2Sb_2Te_5$ film sputter deposited on a glass substrate. The GeSbTe film was covered with 10 nm thick SiO_2 layer and was annealed at 280 °C to obtain the crystalline phase. The excitation source was a Ti:Sapphire laser system operating at 800 nm central wavelength with a pulse duration of 170 fs. A set of amorphous recording marks was obtained by femtosecond pulse excitation with different polarization directions (from θ=0° to 180° for every 10° interval). The excitation pulse was focused onto the sample surface by a microscope objective with a numerical aperture of 0.6. As a probe beam to evaluate the optical anisotropy of individual recording marks, we used He-Ne laser light with reflection configuration. The polarization direction of the incident beam was set to be θ=0°. The polarization state of the reflected light from the recording mark was analyzed by differential detection of two orthogonal polarization components (I_x-I_y).

We prepared two amorphous states with different fluence irradiation: (i) amorphized by single-femtosecond (higher-fluence) pulse irradiation, and (ii) amorphized by multi-femtosecond (lower-fluence) pulse irradiation. To make clear the difference in the nature of amorphous states, we observed gradual crystallization process by a train of weak femtosecond pulse with an energy of 0.38 nJ. Again He-Ne laser was used as a probe beam to measure the change of transmission upon crystallization after each femtosecond pulse excitation.

3. RESULTS & DISCUSSION

In Fig. 1 we compare crystallization behavior of two different amorphous phases. The transmission of the probe beam is plotted as a function of the number of femtosecond pulse for crystallization. The value 1.0 corresponds to the transmission of the initial crystalline state prior to amorphization. In the case of amorphous state induced by multi-femtosecond pulse irradiation, only 15 pulses are sufficient to reach 10% decrease in transmission whereas 70 pulses are required for the amorphous state induced by single-femtosecond pulse irradiation. In the latter case at the center of irradiated area the temperature reaches above the melting point and melt-quenched amorphization takes place. Similar

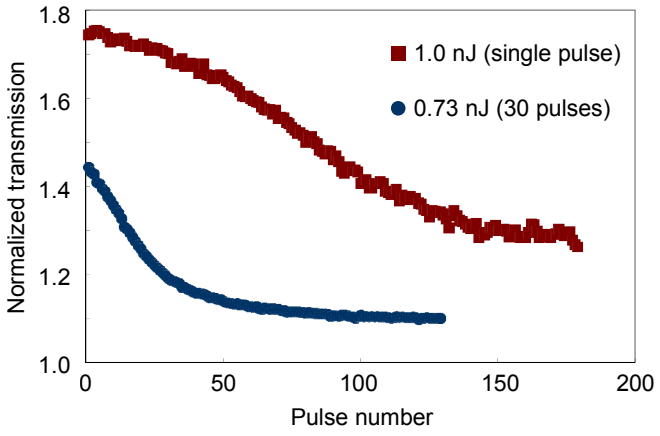

FIG. 1: Reflection of the probe beam as a function of the number of femtosecond pulses irradiated for two different initial amorphous states: (a) amorphized by single-femtosecond pulse, and (b) amorphized by multi-femtosecond pulses.

to the as-deposited amorphous state, in the case of melt-quenched state, a few tens of pulses are needed for the creation of nuclei and crystallization proceeds more slowly.

Figure 2(a) shows a reflection intensity image of amorphous recording marks prepared by multi-pulse excitation (15 pulses) with a pulse energy of 0.64 nJ. The polarization direction was changed from θ=0° to 180° for every 10° interval as indicated by the arrows. As far as the reflection intensity is measured we do not see any dependence on the polarization of excitation pulse.

In Fig. 2(b) the polarization state of reflected light is mapped in the same scanning area as Fig. 2(a). We obtained significantly large differential signal, which demonstrates the optical anisotropy induced in amorphous marks. The sign of the signal (I_x-I_y) corresponds to the direction of rotation of reflected probe beam. When the polarization of the femtosecond recording pulse is parallel (θ=0°) and orthogonal (θ=90°) to the probe beam, the signal intensity is nearly zero, while when θ=40-50° and 140-150°, the signal takes the maximum value with opposite signs. The maximum rotation angle of the probe beam polarization is estimated to be 1.5°, which is comparable to that can be obtained in magneto-optical recording media.

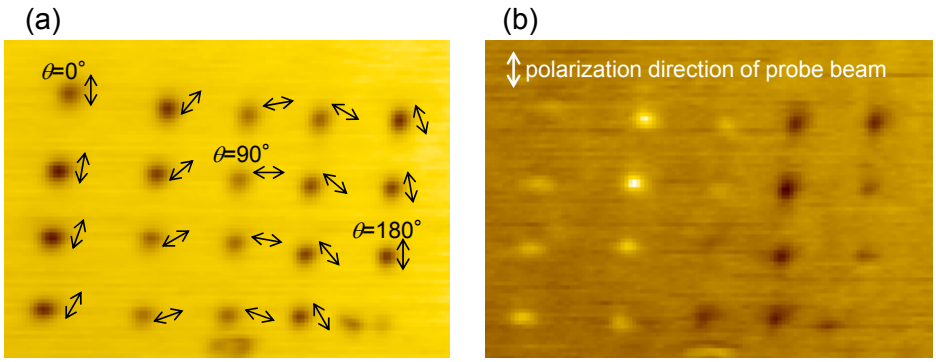

FIG. 2: Two-dimensional mapping of (a) the intensity and (b) the polarization rotational angle (differential signal of two orthogonal polarization components) of the reflected probe beam for a set of amorphous recording marks generated by multi-femtosecond pulse excitation with different polarization directions, which are indicated by the arrows.

It should be noted that we did not obtain any optical anisotropy signal in the amorphous marks created by single femtosecond pulse excitation with an energy of 0.9 nJ. We believe that this is closely related to the result of comparison of crystallization rate between single-pulse and multi-pulse excitation in Fig. 1. For the amorphous state by thermal (melt-quenching) process, the spatial location of atoms is too much randomized to preserve the bonding

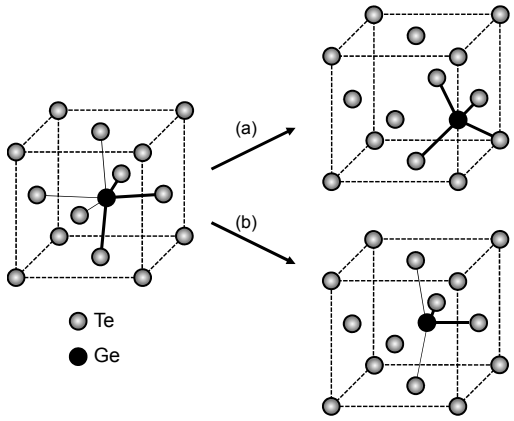

FIG. 3: Ge switching models proposed by (a) Kolobov *et al*. and (b) Robertson *et al*.

anisotropy.

A possible explanation would be given by Ge-switching model. As illustrated in Fig. 3(a), Kolobov's model unveiled amorphization mechanism as Ge atom displacement along the (111) direction, from octahedral to tetrahedral [1]. In this model, however, resonance bonding of all three *p*-orbitals (p_x, p_y and p_z) is assumed to be broken upon amorphization and therefore large anisotropy effects are not expected. Recently Robertson *et al*. have suggested another switching model, where the Ge atom is displaced along (110) rather than (111) as shown in Fig. 3(b) [5]. If the excitation pulse is linearly polarized in *x* direction, resonance bonding of p_x and one of the other two orbitals (p_y or p_z) are broken and anisotropic distribution in the orbital alignment will be created. This model is more consistent with the experimental result.

4. CONCLUSION

We experimentally demonstrated unprecedented optical anisotropy in amorphous phase GeSbTe which was induced by femtosecond pulse excitation with rather low fluence. The magnitude of optical anisotropy was evaluated by measuring the rotation angle of probe beam polarization and the maximum rotation angle found to be as large as 1.5°. The result implies that the storage capacity is expected to be enhanced by a factor of m×n for m-valued multilevel intensity detection and n-valued multilevel polarization detection. Also we have gained deeper insight into the mechanism of nonthermal amorphization with femtosecond optical pulse excitation. At moderate fluence atomic arrangement in the amorphous state is not completely random but involves a certain degree of order and bonding anisotropy is preserved.

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Biography

Toshiharu Saiki was born in Tokyo, Japan in 1965. He received the B.S. and M.S. degrees in physics, and the Ph.D degree in applied physics from the University of Tokyo. In 1993, he joined the Kanagawa Academy of Science and Technology (KAST), where he later became a project leader. He had been an Associate Professor in the Department of Electronics and Electrical Engineering at Keio University since 2002 and Professor since 2009.
His current research interests include near-field optical microscopy and spectroscopy in semiconductor quantum-confined systems and nanoparticles and biomolecules in solution, and ultrafast spectroscopy of phase change materials. He has developed a highly sensitive near-field scanning optical microscope (NSOM) with a spatial resolution of 10 nm and has demonstrated real-space mapping of exciton wavefunctions confined in a quantum dot.