# Possibility of nanoscale amorphization of GeSbTe by femtosecond pulse excitation

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We have experimentally demonstrated that a femtosecond optical pulse induces ultrafast amorphization of crystalline GeSbTe without melting. If the amorphization process is non-thermal and is purely due to high-density excitation of electrons at a time, local amorphization in a nanoscale volume is anticipated by carefully adjusting the laser fluence. In this study, we discuss the mechanism of local amorphization evaluating the number of photoexcited electrons required for minimum unit that forms amorphous state.

## 1. INTRODUCTION

GeSbTe(GST) has been used for re-writable optical media such as DVD-RAM. In optical recording system, reversible phase changes between crystalline and amorphous phases are induced by short laser pulses with a few tens-of-nanoseconds duration. [1]

A recent study has clarified that the phase change of crystalline GST into amorphous state is due to a slight displacement of Germanium (Ge) atoms from their position in the crystalline lattice[2] [3]. In this model, amorphization can be achieved by selectively breaking the weak Germanium-Tellurium (Ge-Te) bond without melting. It was stated that ultrafast phase change may occur under irradiation of a single femtosecond laser pulse.

In a semiconductor, an ultra short laser pulse such as a femtosecond pulse excites a large fraction of valence electrons from the valence band into the conduction band. Meanwhile, approximately 10% of carriers in valence band are excited. When the carriers are excited, atomic forces are strongly modified due to the shift of equilibrium position, which means that atoms get rapidly sufficient energy to immediately start to move. This phenomenon (occurred within a few hundreds of femtoseconds) is much faster than the time scale for the conversion of excited electron energy into thermal energy (a few picoseconds), therefore, these structural change are called "*non-thermal structural change*". This phenomenon has been reported previously in several semiconductors such as Si or GaAs[4-10].

Our previous experiments demonstrated the potential of ultrafast transformation of GST. Experimentally, we found that a single femtosecond laser pulse (~100 fs) induces local amorphization in GST crystalline film. The reflectivity decreases drastically at the scale of (500 fs) after the irradiation. Also, we achieved an ideal switching response where the initial reflectivity last until final state.

In this work, we demonstrate an experimental study on the mechanism of local amorphization in GST films upon irradiation with several femtosecond laser pulses. Above a fluence of 18.7 mJ/cm$^2$, a single pulse induces amorphization with a sufficient optical contrast. Even below the threshold, however, we found that multi-pulse excitation gives rise to amorphization. Also, we pointed out the mechanism of local amorphization by evaluation the number of photoexcited electrons required for minimum unit that forms amorphous state.

## 2. MATERIALS AND METHODS

The sample used in this study consisted of crystalline $Ge_{10}Sb_2Te_{13}$ films (thickness=20nm,) deposited on a glass substrate (thickness=0.6 mm). Optical excitation was performed using Ti:sapphire laser system operating at 800 nm central wavelength with a pulse duration of 140 fs and a repetition rate of 82 MHz. A femtosecond laser pulse was focused onto the sample surface through a microscope objective (Numerical aperture = 0.35).

Our experiment consists of two parts: first, we induced amorphization with multi-pulse excitation. Above a fluence threshold of 18.7 mJ/cm$^2$, a single pulse induces amorphization with a sufficient optical contrast. Even below this threshold, by adjusting the number of pulses and considering the fluence value, we can generate an amorphous state as that generated by a single pulse excitation in terms of the optical contrast and surface features, as was observed by a scanning electron microscope (SEM). We estimated the number of excited electrons engaged in achieving sufficient amorphous contrast in order to examine the relative excitation intensity that is necessary to achieve sufficient amorphous contrast. In order to prevent thermal deposits, we reduced the pulse repetition rate down to 10-300 Hz.

Second, while irradiation of femtosecond laser pulses, we irradiated the sample surface with (He-Ne) laser beam at the same time, and we measured the transmission efficiency of the sample by utilizing a fast photodiode after considering the desired time window and temporal resolution. These in situ measurements

were intended to observe the accumulation of the slight structural transition of the sample while the pulses are being irradiated.

Based on the Ge switching model which was proposed in Ref. 3, we estimated the minimum units number where structural change occur by using the number of excited electrons.(i.e. how Te units relate to the local structural change where Ge atom switched).

## 3. RESULTS and DISCUSSION

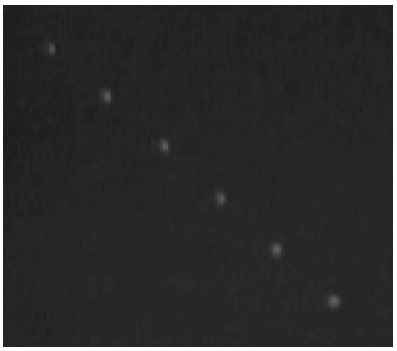

Figure 1. CCD image of amorphization marks with both single pulse and multi-pulse excitation. (from top left to bottom right, a single pulse of 18.7 mJ/cm$^2$, 4 pulses of 17.4 mJ/cm$^2$, 24 pulses of 16.2 mJ/cm$^2$, 230 pulses of 14.9 mJ/cm$^2$, 2300pulses of 13.9 mJ/cm$^2$, 51120 pulses of 12.5 mJ/cm$^2$)

A slight structural change is accumulated by a multi-pulse Ti:sapphire irradiation that made it possible to observe an amorphous mark of crystalline substrate with a sufficient contrast by a optical microscope. Figure 1 shows an image of amorphous marks induced with both a single excitation pulse and several weaker multi-pulses. In order to make the contrast of amorphous marks being the same, we continued irradiating the sample by He-Ne laser at the center of the Ti:sapphire laser spot and measuring the transmission at 633nm. When the transmission increased by 9 %, we terminated the irradiation of Ti:sapphire pulses. Then we calculated the number of pulses ($N_p$) at each fluence and illumination time. Results show that 51120 pulses with 67 % pulse intensity compared to a single excitation pulse can induce amorphization.

The transmission measurement is useful for detecting how the slight changes accumulate. As stated earlier, we illuminated the sample with He-Ne laser while being irradiated by a multi-pulse of Ti:sapphire laser. Figure 2 shows the transmission as a function of pulse number for difference fluencies.

We related these results to the developing process of the structural transition area (i.e. Te lattice where Ge switching occurred). We proposed a phase transition model where the contrast of the amorphous mark becomes observable due to the increase in the volume where Ge switching occurred. The local structural change with single pulse excitation cannot be observed

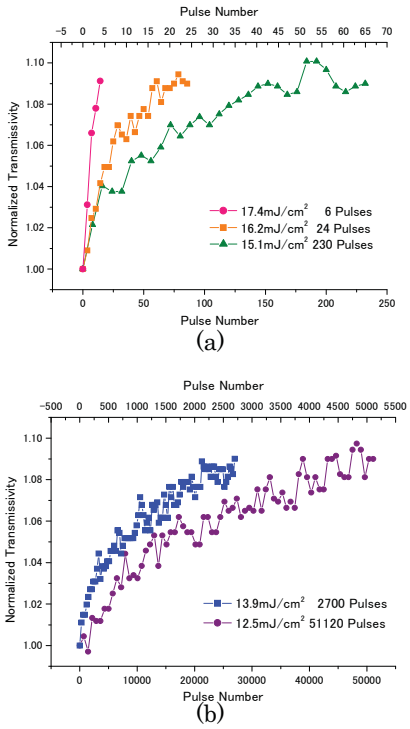


Figure 2. Transmission efficiency as a function of pulse number for difference fluencies (a) fluencies = 17.4, 16.2 and 15.1 mJ/cm$^2$. The above horizontal axis corresponds to the red and orange curves, while the bottom horizontal axis corresponds to the green curve. (b) fluencies =13.9 and 12.5 mJ/cm$^2$ . The above horizontal axis corresponds to the blue curve while the bottom horizontal axis corresponds to the purple curve.

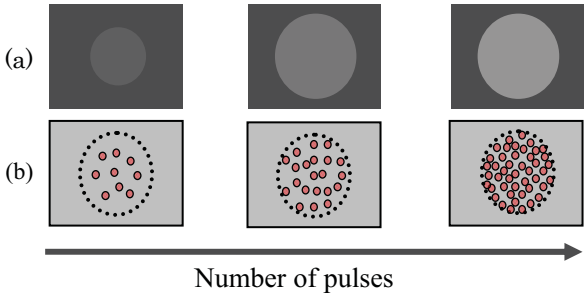


Figure 3. (a) (from left to right) Demonstration of amorphous mark contrast enhancement while increasing the number of excitation pulses.(b) Corresponding illustration of Ge switching area increment as the number of excitation pulses increase.

while it become detectable with multipulse excitation as illustrated in Figure 3 (a) and 3(b). This local structural change, which occurred without melting, can be referred to the slight displacement of Ge atoms.

We consider that the structural transition is not induced by thermal melting but by the electron excitation. Figure 4 shows Relation between the excitation intensity and the amorphized volume fraction per pulse which is proportional to 1 / $N_p$. From this figure, the relation between 1 / $N_p$ and the fluence $F$ is given by $1/N_p \propto F^{28}$ where the exponent (~30) corresponds to the number of excited electrons engaged in achieving sufficient amorphous contrast.

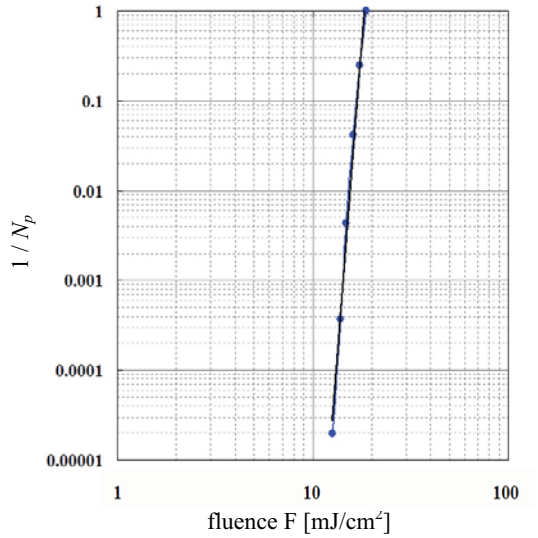


Figure 4. Relation between the excitation intensity and the amorphized volume fraction per pulse which is propotional to $1 / N_p$.

From our experimental results of relative excitation intensity and based on the Ge switching model, we could estimate the number of minimum units where structural changes occur (i.e. number of minimum Te units where Ge atom switched). From Figure 1, we deduced the density of the excited carriers by the fluence of a single pulse excitation. By multiplying this value by the bulk volume of a Te lattice (shown in Figure 5) gives a carrier number 1.5. Based on the assumption that approximately 30 electrons are engaged in phase transition at a time, we can consider that phase transition is induced in an area of about 20 neighboring Te lattices where Ge atom was switched.

As was stated in Figure 2, during the initial multi-pulse irradiation, the structural changes occur at about 20 neighboring Te lattices simultaneously, thus, there was a pronounced increase in the transmission efficiency. As the pulsing continues, excitation pulses are likely to hit the where local structural changes were already occurred, so we couldn't observe an apparent transmission efficiency change. Therefore, as the pulsing continues, the gradient of the curve saturates.

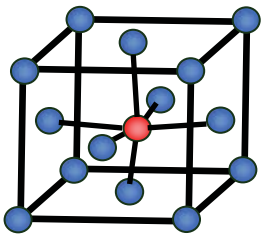

Figure 5. A Te lattice with Ge atom being displaced from the center of the cell

## CONCLUSION

We have shown that sufficient phase transition can be induced by a multi-pulse laser excitation even below the threshold fluence for single pulse amorphization. We believe that Ge switching induced by a femtosecond laser pulse when carriers excited at a time in neighboring Te lattice units creates potential for nanoscale phase transition.

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