Ultrafast sub-threshold photo-induced response in crystalline and amorphous GeSbTe thin films

M. J. Shu,1 I. Chatzakis,2 Y. Kuo,3 P. Zalden,4 and A. M. Lindenberg2,5,6
1Department of Applied Physics, Stanford University, Stanford, California 94305, USA
2Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA
3Department of Electrical Engineering, Stanford University, Stanford, California 94305, USA
4I. Physikalisches Institut (IA), RWTH Aachen University, D-52056 Aachen, Germany
5Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, USA
6PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA

(Received 27 March 2013; accepted 10 May 2013; published online 22 May 2013)

Pump-probe optical reflectivity and terahertz transmission measurements have been used to investigate time resolved sub-threshold photo-induced effects in crystalline and amorphous GeSbTe films at MHz repetition rates. The reflectivity in both phases exhibits long-lived modulations consistent with the sign of the changes that occur upon switching but of smaller magnitude. These can be understood by the generation of acoustic strains with the crystalline phase response dominated by thermal effects and the amorphous phase response associated with electronically induced changes. Evidence for a photo-induced distortion is observed in the amorphous phase which develops homogeneously within the excited region on few-picosecond time scales. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4807731]

GeSbTe (GST) alloys are an important class of materials for phase change memory applications due to fast, reversible switching between the crystalline and amorphous phases, and the associated optical reflectivity and electrical resistivity contrast between the two phases.1 Preliminary evidence has been obtained in the last several years indicating that the nature of the phase change mechanism may be electronic in origin rather than thermally induced.2–4 In particular, it has been proposed that the amorphization process involves a transition from crystalline to amorphous order without passing through the liquid phase. This has been explained in terms of local atomic disorder caused by a change in the bonding environment due to carrier excitation. Simulations5 indicate an intermediate phase with optical properties different from the initial and final states (and from the liquid) and time-resolved experiments5,6 have suggested that this is a photo-assisted process. In contrast, the possibility of electronic effects occurring within amorphous GST has not been carefully investigated. Exciting a phase change sample with laser power below the switching threshold may help to elucidate the process by which the phase eventually switches. Additionally, photo-assisted mechanisms open up possibilities for driving structural rearrangements at high repetition rates and on time-scales significantly faster than the nanosecond switching time-scales that are conventionally regarded as the intrinsic speed limits for this process.

Earlier time-resolved pump-probe reflectivity experiments on GST alloys have shown varying results. Först et al.7 and Hernandez-Rueda et al.8 investigated Ge2Sb2Te5 films on a few-picosecond time scale and observed varying behaviors for different film preparations. Siegel et al. used single sub-threshold femtosecond laser pulses to induce a decrease in the reflectivity of a crystalline Ge2Sb2Te5 film on Si, which recovered to the initial value in over a nanosecond.9 In a similar experiment, Wang et al. saw an increase in the reflectivity of an amorphous Ge2Sb2Te5 film on polycarbonate substrate, which again recovered in over a nanosecond.10 Zhang et al., on the other hand, observed a decrease in the reflectivity of amorphous Ge2Sb2Te5 films on glass, which recovered with a time constant of 1 ns.11 Sokolowski-Tinten et al. and Callan et al. saw a transient reflectivity increase in Ge0.005Sb0.94 films on glass upon below-threshold excitation.12,13 The results of these previous experiments show that the behavior upon excitation of a thin GST film depends strongly on the substrate, film thickness, and possibly the stoichiometry of the GST. A clear understanding of the associated short-time-scale dynamics has not emerged from prior studies. Here we show that the short time-scale photo-induced effects in the sub-threshold regime exhibit an acoustic strain response, with an electronic response occurring on few-picosecond time scales dominating in the amorphous phase. These effects give rise to long-lived modulations to the reflectivity consistent with those that occur upon switching, with the amorphous phase increasing and the crystalline phase decreasing in reflectivity, a process which is fully reversible at MHz repetition rates. On short time-scales, evidence for electronically induced structural rearrangements modifying the amorphous phase optical constants is observed.

We have performed time-resolved optical reflectivity and terahertz (THz) transmission measurements on 250 nm Ge2Sb2Te5 films sputtered on silicon substrates. The amorphous film was in the as-deposited state, and the crystalline film was annealed at 225 °C. The choice of relatively thick films facilitated investigation of the short time-scale response without contributions from acoustic waves reflected from the film-substrate interface. The laser system for the reflectivity measurements provided pulses of 800 nm center wavelength (1.55 eV, well above the band gap of 0.39 eV for the crystalline phase and 0.76 eV for the amorphous phase)14 and 50 fs pulse duration at a repetition rate of 5.1 MHz. The beam was
split into a pump beam and a much weaker probe beam which passed through an optical delay line. The pump (probe) beam was focused to 150 µm (50 µm) for low fluence measurements and 50 µm (15 µm) for higher fluence measurements with pump fluences extending up to ~1 mJ/cm². The probe beam was incident near 45°, with about 10⁶ separating the pump and probe beams. The reflectivity changes were measured using a lock-in amplifier and an optical chopper operating at 400 Hz. The THz transmission measurements were performed with a 1 kHz amplified Ti:sapphire femtosecond laser system employing a plasma THz generation scheme and an electro-optic sampling detection scheme.¹⁵–¹⁷ The optical pump and THz probe beams were collinear at normal incidence.

Fig. 1(a) shows the typical time-resolved reflectivity change for the crystalline and amorphous films. Both the crystalline and amorphous phases show a fast decrease in reflectivity immediately following the pump excitation (marker I in Fig. 1(a)), which relaxes in a few picoseconds. Following the decay of this effect, a short-lived oscillation (II)—more evident in the amorphous film—is observed together with a long-lived (hundreds of picoseconds) response (III). In the crystalline phase, a long-lived decrease in reflectivity is seen, while in the amorphous phase the long-lived change is positive. These are consistent with the sign of the changes that occur upon switching but of smaller magnitude. The reflectivity gradually recovers its initial value between each pump pulse. Fig. 1(b) shows the long time-scale behavior, from which we extract a 1.45 ns time constant for the exponential decay of the long-lived reflectivity change in the crystalline sample, and a 280 ps time constant for the amorphous sample.

The magnitude of the response grows linearly with the fluence of the pump beam for low excitation powers. The left inset of Fig. 1(a) shows the linear fluence dependence of the response in each sample at a time delay indicated by the black arrows in Fig. 1(a). At higher fluences (above 1.2 mJ/cm²), cumulative heating effects result in permanent changes in the sample reflectivity and pump-probe response. These changes are associated with crystallization of the amorphous sample, or a transition towards the high temperature (hexagonal) phase of the crystalline sample. In the following, we investigate the low-fluence regime in which no permanent reflectivity change occurs in the samples.

The initial reflectivity dip observed in both the amorphous and crystalline phase can be explained as the free carrier effect using the Drude model, in which the excitation of carriers modulates the dielectric constant of the film. We estimate the excited carrier density \( N \) using the expression \( N = F \alpha (1 - R)/4\pi \),¹⁸ where \( F \) is the pump fluence, \( \alpha \) is the linear absorption, \( R \) is the reflectivity for the pump beam, and \( \hbar \omega \) is the photon energy. The right inset of Fig. 1(a) shows the value of the peak transient reflectivity decrease immediately following the pump excitation (delay time \( \sim 600 \text{ fs} \)) as a function of the excited carrier density in the crystalline sample. The values used are \( \alpha = 6.5 \times 10^7 \text{ cm}^{-1} \) and \( R = 0.47 \).¹⁴ The points qualitatively fit the Drude model prediction of reflectivity as a function of the excited carrier density (black line in inset) showing a decrease in reflectivity at low fluences, followed by a threshold-like increase in reflectivity at a higher fluence when the plasma frequency becomes comparable to the probe frequency—not associated with a structural response.¹⁹ Discrepancies between the data and model in the highest fluence range occur because the photo-excited region undergoes a permanent change to an unknown final state at a fluence similar to the threshold for the reflectivity increase. We used 800 nm pump-THz transmission probe measurements to further verify the source of the short reflectivity dip.²⁰ Since this technique is sensitive to the free carrier population in the sample, the time-resolved THz transmission can be used to measure the lifetime of the free carriers. Fig. 2 shows the time-resolved change in the normal incidence THz transmission caused by the optical pump pulse with a 0.9 mJ/cm² pump fluence. The time scale of the free carrier response measured by this technique roughly matches the lifetime of the initial reflectivity decrease (thin lines in Fig. 2), indicating that the drop comes from the free carrier response, with both the reflectivity and THz measurements consistently showing faster relaxation dynamics in the amorphous phase, consistent

---

**FIG. 1.** (a) Time resolved reflectivity change for the crystalline (light red) and amorphous (dark blue) sample at a fluence of 0.4 mJ/cm². Left inset: The fluence dependence showing the linearity of the effect. The data points are taken at the delay times indicated by the black arrows in (a). The color scheme is the same as in (a). Right inset: the value of \( \Delta R/R \) at 600 fs as a function of excited carrier density for the crystalline film. (b) Longer time scale data of the time resolved reflectivity change at a fluence of 0.26 mJ/cm².
with the increased disorder and trapping present in this phase.\textsuperscript{11}

We explain the reflectivity oscillations occurring within the tens of picoseconds following pump excitation (II), in addition to the long-lived effect (III), by an acoustic strain pulse generated at the sample surface, which locally modifies the refractive index as it propagates.\textsuperscript{21,22} The oscillations can be viewed as arising from a time-dependent interference of the scattered wave from the sample surface and from the acoustic strain pulse. Thomsen et al. provide a simple model to calculate the reflectivity modulations including both electronic and thermally induced effects. The sign of the reflectivity change induced by a strain wave is determined by the sign of the strain as well as the sign of the quantity $dE_g/dP$ (i.e., the change of the band-gap with pressure), which may be viewed as a contribution from an electronic or thermal Grüneisen parameter.\textsuperscript{21,23–25} Experiments on both amorphous\textsuperscript{26} and crystalline\textsuperscript{27} GST have indicated a negative value for $dE_g/dP$. Therefore, the different sign of the effect we observe in the two films should be caused by the sign of the strain with the crystalline phase expanding and the amorphous phase contracting overall (as occurs during switching). We note that a reflectivity decrease due to thermal expansion is consistent with our observation in both samples of a negative $\Delta R$ before time zero (not shown)—i.e., long (200 ns) after the previous pump pulse has passed, leaving only the residual heating—which grows in magnitude with pump fluence. For negative $dE_g/dP$, the electronic ($\sigma_e$) and thermal ($\sigma_{th}$) contributions to the stress have opposite signs, and the ratio of the contributions can be written\textsuperscript{21}

$$\frac{\sigma_e}{\sigma_{th}} = \frac{C}{3\beta(E - E_g)} \frac{dE_g}{dP} \tag{1}$$

with specific heat C, linear expansion coefficient $\beta$, band gap $E_g$, and photon energy $E$. For $C \sim 10^6$ J/m$^3$K, $\beta \sim 10^{-5}$ K$^{-1}$, and $(E - E_g) \sim 1$ eV,\textsuperscript{14,28,29} the electronic and thermal contributions are equal and opposite for $|dE_g/dP| \sim 0.03$ eV/GPa. This is on the order of previously measured results.\textsuperscript{27} Recent high pressure measurements indicate a stronger variation of the electronic conductivity with pressure in the amorphous phase, consistent with a larger value for $|dE_g/dP|$ and therefore a larger electronic contribution to the strain in the amorphous phase relative to the crystalline phase, consistent with our measured results.\textsuperscript{26}

The decay time of the long-lived effects indicate the time-scales of relaxation phenomena in the samples. We note that the decay times are inconsistent with simple heat diffusion out of the penetration depth of the film: the penetration depth is shorter and the thermal conductivity is higher in the crystalline phase compared to the amorphous phase,\textsuperscript{14,30} yet the long-lived effect takes several times longer to decay in the crystalline film. However, if the response of the amorphous sample is dominated by an electronic effect while the response of the crystalline film is dominated by a thermal effect, then we can understand the faster amorphous decay time as resulting from electronic rather than thermal diffusion.

As shown in Fig. 3, we fit our data using the model presented by Thomsen et al.\textsuperscript{21} in which the reflectivity is modulated by a propagating acoustic strain wave with expansive and compressive parts. The oscillation period is 34 ps for the amorphous film, matching the expression $\lambda/2nv$ for $\lambda = 800$ nm with index $n \sim 5$ and sound speed $v \sim 2.5$ mm/ps, close to values previously measured for GST films.\textsuperscript{14,30} The oscillation decays too quickly in the crystalline film to meaningfully extract a period. Also consistent with this model, the oscillatory part of the response decays on a 1/e time scale corresponding to the time for an acoustic pulse to travel through the optical penetration depth of the film: 6.4 ps ($\sim 16$ nm/$2500$ m/s) for the crystalline film and 12 ps ($\sim 30$ nm/$2500$ m/s) for the amorphous film.\textsuperscript{14,21}

While the acoustic model provides a good fit for the later portion of the data ($\sim 10$–70 ps), it is not adequate to explain the short time-scale onset of the effects following the free carrier response. In particular, the onset of the effect in the amorphous sample occurs on time-scales significantly faster than the optical penetration depth divided by the speed of sound, and is too fast to account for by acoustically propagating stresses (generated by either electronic or thermal mechanisms). The onset of the positive $\Delta R$ occurs within

![FIG. 2. Time-resolved change in terahertz transmission (thick lines) and optical reflectivity (thin lines) for crystalline (light red) and amorphous (dark blue) films, normalized to peak height.](image)

![FIG. 3. Time resolved reflectivity data (thin lines) with fits (thick lines) to the strain response model described, for crystalline (light red) and amorphous (dark blue) samples.](image)
3 ps, while the strain effect takes 10 ps to reach its maximum amplitude, determined by the speed of sound (see Fig. 3). This suggests that there is a contribution (marker IV in Fig. 3) other than the acoustic strain pulse, likely associated with an additional electronically driven effect caused by the change in bonding structure upon laser excitation, which turns on homogeneously within the optically excited region. It is also noteworthy that in the crystalline film the onset of the strain effect begins several picoseconds after zero pump-probe delay, indicating a slower transfer of energy to the lattice in the crystalline film which results in a delayed production of the strain pulse. This time delay is consistent with the relaxation time-scale extracted from the THz measurements as well as previous measurements in related GeSb thin films, indicating that this time can likely be associated with an electron-phonon coupling time.

Callan et al. suggested that a temporary phase was being generated for a short time when an amorphous GeSb film was excited below the crystallization threshold. Our data suggest that, similarly, sub-threshold photo-excitation of the amorphous GST film induces local rearrangements which may be associated with a precursor to the crystalline phase, with optical constants evolving toward the known crystalline values. The short time-scale on which this occurs is consistent with the electronic processes previously proposed to underlie the crystalline-to-amorphous transition, and in particular the onset of the effect is faster than acoustic propagation through the sample penetration depth, as has been observed in the past for non-thermal phase transformations induced by femtosecond optical pulses. Fig. 3 emphasizes the differences between the simple acoustic model and the observed temporal response. As noted above, the sign of the photo-induced strains (and thus the observed modulations in the reflectivity) are consistent with the changes in density that occur upon switching— the amorphous phase compresses and the crystalline phase expands. The fast effect in the amorphous phase may therefore be associated with a precursor to the formation of crystalline order in the excited region, and can be compared to the prestructural order hypothesized by Loke et al. to occur under electrical biasing conditions.

In conclusion, we have observed effects upon sub-threshold photo-excitation of crystalline and amorphous GST thin films which suggest a photo-induced excited state persisting for hundreds of picoseconds (amorphous) to over a nanosecond (crystalline). The qualitative response is simply explained by an acoustic strain model with electronic contributions dominating the induced stress in the amorphous phase. Deviations at short times to this model indicate processes consistent with precursors to hypothesized intermediate phases, particularly in the amorphous phase. Although much smaller than the distortions required to switch the phase of the material, these effects elucidate the first steps in the response of the material upon photo-excitation, which can eventually lead to a phase change at higher excitation intensities.

Research was supported by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. Y.K. was supported by DARPA grant N66001-10-1-4021. P.Z. wishes to acknowledge financial support by the Alexander von Humboldt foundation.

---