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Influence of pulse duration on the amorphization of GeSb thin films under ultrashort laser pulses

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Laser-induced amorphization of crystalline, 25-nm-thick, Sb-rich GeSb films has been studied for pump pulse durations in the range from 100 fs up to 6 ns. The dynamics of the phase change has been investigated using real-time reflectivity measurements with picosecond time resolution performed with a streak camera. For pulses in the femtosecond regime, the time required to complete the transformation is of the order of ~ 10 – 15 ns. When the pulse duration is increased to the 1.5–20 ps range, the transformation time decreases to values as short as 400 ps, while for nanosecond laser pulses amorphization is not achievable. This behavior is discussed in terms of the heat flow dynamics of the system and the influence of pulse duration on the initial supercooling and nucleation rate. © 2004 American Institute of Physics. [DOI: 10.1063/1.1759062]

Rewritable phase change optical recording systems typically utilize the different optical properties of the crystalline (*c*) and amorphous (*a*) states of a thin film recording material as the means for storing binary data.¹ Current trends in the development of this technology include the use of short wavelength laser systems,² multilevel recording,³ or near-field concepts^{4,5} in order to increase the storage density. Along with these, the optimization of recording materials for achieving increased recording speeds and data transfer rates is a topic of great interest.⁶ Since conventional storage systems like those based upon GeSbTe⁷ or AgInSbTe⁸ operate with laser pulse durations of the order of tens of nanoseconds (ns), the desired increase in the recording speed has motivated several studies involving the use of both picosecond (ps)^{6,9} and femtosecond (fs)^{6,9–12} pulses for recording applications while the search for faster crystallizing materials has mostly centred on antimony-rich compounds such as InSb,¹³ GaSb,¹³ and GeSb^{6,13} films. In particular, GeSb films with Sb content above the eutectic (85 at. % Sb) are very promising because, besides displaying suitable optical contrast between the crystalline and amorphous phases, reversible phase changes induced by ps and fs laser pulses have been demonstrated.^{14–16}

Most notably, in 25-nm-thick, Sb-rich films on glass substrates irradiated by single 30 ps laser pulses,¹⁶ the complete transformation time for amorphization and crystallization has been shown to be around only 400 ps. The same study showed that, with an increased film thickness of 50 nm, the *a*-to-*c* transformation time was drastically increased to ~ 70 ns and the re-amorphization of a crystalline area was not even possible. From these results, the authors concluded that bulk solidification was the dominant mechanism in these films under ps laser pulses and that the effect of decreasing the film thickness from 50 to 25 nm was to reduce the amount of latent heat released upon the bulk nucleation of the solid phase throughout the whole molten volume. As a consequence, recalescence effects, i.e., a substantial reduc-

tion of the initial supercooling leading to a slowing down of the solidification process,^{17,18} were minimized upon reduction of the film thickness, enabling the phase cyclability and reducing the solidification time to hundreds of ps. In contrast, studies performed on 50-nm-thick films under 100 fs pulses showed an *a*-to-*c* transformation time of ~ 30 ns.¹⁹ Globally, all these results indicate that phase reversibility and the transformation time under ultrashort pulses are essentially controlled by the heat flow dynamics of the system under each pulse duration. The aim of this work is to determine the influence of pulse duration on the dynamics of the *c*-to-*a* phase transformation in GeSb films, covering a span of pulse durations of five orders of magnitude, from the ns to the fs regime.

The samples are amorphous, 25-nm-thick Ge_{0.07}Sb_{0.93} films grown by dc sputtering on glass substrates. The irradiation pulses are delivered by two different sources. For pulses in the fs and ps ranges, the second harmonic of the signal output of an optical parametric amplifier pumped by Ti:Al₂O₃ fs regenerative amplifier has been used to produce ~ 100 fs at 600 nm. The use of either a grating pair stretcher or a series of glass blocks has allowed chirped pulses with durations up to 20 ps to be obtained. Nanosecond pulses of duration 3 and 6 ns at 583 nm have been obtained from the output of a pulsed dye amplifier seeded with a continuous-wave dye laser (Rhodamine 6G) pumped by a frequency-doubled Nd:YAG laser.

At each specific pulse duration and wavelength, the amorphous as-grown films have first been pre-crystallized by a series of low fluence (~ 15 mJ/cm²) pulses reaching the surface at normal incidence. The *c*-to-*a* phase transformation has then been induced by a single laser pulse at higher fluence. Real time reflectivity measurements have been carried out using 1- μ s-long pulses from a single mode Ar⁺ ion probe laser operating at 514.5 nm, incident at 19° to the sample and focused onto the center of the irradiated spot. The time evolution of the reflected probe beam intensity has been simultaneously measured with a fast photodiode coupled to a transient digitizer (ns-time resolution) and with a ps resolution streak camera. In the latter system, the longest

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FIG. 1. Reflectivity transients on crystalline GeSb induced by a single (a) 100 fs, (b) 20 ps, and (c) 6 ns pump pulse. Each arrow indicates the position of the pump pulse and the interval t indicates the crystalline to amorphous transformation time.

acquisition time window is 50 ns. Further details can be found elsewhere.²⁰

Figure 1 shows reflectivity transients induced by single pulses of (a) 100 fs, (b) 20 ps, and (c) 6 ns on *c*-GeSb. The first two have been obtained using the streak camera while the ns pulse induced transient has been measured with the photodiode, since the whole process occurs over a time interval longer than the longest acquisition time window of the streak camera. In each transient, the initially high reflectivity level corresponds to the crystalline phase. For the fs and ps pulses, the reflectivity (R) decreases upon irradiation as the film melts and re-solidifies in the amorphous phase⁶ while in the ns case [Fig. 1(c)] R increases substantially after the initial decrease, indicating a large amount of re-crystallization upon solidification. Obviously, amorphization is not achievable under this pulse duration due to the relatively slow rate of energy deposition which generates a cooling rate that is not fast enough to prevent the nucleation of the crystalline phase from the melt.

The most important difference in the behavior of the reflectivity when reducing pulse duration from ps to fs is the enormous increase in the time required to complete the amorphization process. Whereas it is ~ 400 ps in the former case [Fig. 1(b)], in agreement with the results previously reported in Ref. 16, it is ~ 15 ns for the latter [Fig. 1(a)]. The fluence thresholds for amorphization are, respectively, ~ 42 and ~ 30 mJ/cm² indicating a clear decrease of the threshold when the pulse duration is shorter than the carrier-lattice relaxation time, in agreement with an earlier report for the *a*-to-*c* phase transformation.²¹ The optimum 14% optical contrast between the two phases has been obtained under fs pumping. The slightly lower optical contrast of $\sim 11\%$ recorded for ps pulses is a consequence of the reduced pump-to-probe size ratio, since the energy loss in the pulse stretcher forced a tighter focusing of the pump pulse to achieve a sufficient fluence level for re-amorphisation.

FIG. 2. Dependence of the crystalline to amorphous transformation time t on the pump pulse duration. The dashed line is to guide the eye and the closed circles denote data at 1.5 ps.

The observed changes in the transformation time with pulse duration are more clearly seen in Fig. 2 where the dependence of the mean *c*-to-*a* transformation time on the pulse duration is presented. It is seen that ps pulse durations induce the minimum transformation time with a sudden increase occurring at 1.5 ps as the duration is decreased toward the fs pulse regime. The 1.5 ps duration represents the threshold between the fast, sub-ns (~ 400 ps) transformation induced by ps pulses and the slow, ~ 10 – 15 ns transformation induced by fs pulses. Right at the threshold, the transformation time depends very sensitively on the pump pulse fluence as illustrated in Fig. 3 for 1.5 ps pulses. Below ~ 50 mJ/cm², the transformation time is subnanosecond while, for higher fluences, the transformation is significantly slowed down. For all the other pulse durations studied, the transformation time is essentially independent of the pump fluence as can also be seen in Fig. 3 for 5 ps pulses.

The thermal diffusion length [$2(D\tau)^{1/2}$ where D is the thermal diffusivity and τ is the pulse duration] becomes equal to the optical penetration depth of *c*-GeSb (~ 11 nm at 600 nm) for $\tau \sim 2$ ps. Therefore, there is no significant diffusion during the pulse absorption for laser pulses shorter than this value and, considering a merely thermal transformation mechanism, the initial temperature gradient reaches its steepest value.²² For pulses shorter than or close to the carrier-lattice relaxation time t_R , however, the absorption of energy into the system can be enhanced, potentially giving rise to an even steeper thermal gradient once phonons are created. This time has been estimated to be ~ 800 fs for *a*-GeSb²¹ and is expected to be close to or shorter than this value for the crystalline phase. Therefore, the interval between 800 fs and 2 ps represents a pulse duration close to both t_R and the duration at which thermal diffusion during the laser pulse is

FIG. 3. Dependence of the crystalline to amorphous transformation time t on the pump pulse fluence for a pump duration of (○) 1.5 ps and (▲) 5 ps. Representative error bars are displayed for one data point and the dashed line is to guide the eye.

negligible. Consequently, a threshold behavior is expected in the initial thermal gradient and thus in the final solidification process such as the one observed in Fig. 2 for a pulse duration of 1.5 ps that can induce a fast (low fluences) or slow (high fluences) solidification process as seen in Fig. 3.

It has been reported that the dominant solidification mechanism for 25-nm-thick films under 30 ps pulses (that in our case induces fast solidification) is a bulk process.¹⁶ This means that upon complete melting of the film down to the film–substrate interface, solidification occurs via dense nucleation of the solid phase throughout the molten volume at homogeneous temperature.^{16,23} Due to the reduced thickness of the film, the amount of solidification enthalpy released in the initial nucleation stage does not substantially modify the initial supercooling prior to nucleation, thus promoting the solidification process to occur very rapidly. The present results for pulse durations between 5 and 20 ps are in perfect agreement with this reasoning.

When irradiating with pulses in the fs regime, nonthermal processes can be induced during the ultrarapid energy deposition that have consequences for the final process as reported earlier for crystallization processes in GeSb.^{19,21} However, solidification is still essentially a thermal process.^{24,25} The primary effect of reducing the pulse duration below 2 ps is to produce a strong increase in both the initial thermal gradient across the melt volume (the film is again completely melted) and the initial supercooling that leads to a sharp increase in the nucleation rate of the solid phase. The subsequent release of an enhanced amount of solidification heat increases the temperature of the surrounding liquid and slows down the bulk solidification process^{17,18} in a similar manner to what happens when the film thickness is increased as reported earlier.¹⁶

In conclusion, a minimum amorphization time close to 400 ps is achieved when irradiating *c*-GeSb films with pulse durations in the range 5–20 ps. Shorter pulse durations in the fs range for which the thermal diffusion length is shorter than the optical penetration depth of the crystalline phase and that are also close to or shorter than the carrier relaxation time induce much longer transformation times (around 10–15 ns). Further optimization of the thermo-physical properties of the system (film thickness and/or substrate thermal conductivity) in such a way as to limit the impact of the latent heat re-

leased upon solidification may finally enable sub-ns transformation times to be induced even upon fs pulse irradiation.

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