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Dynamics of ultrafast reversible phase transitions in GeSb films triggered by picosecond laser pulses

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The dynamics and the reversibility conditions of crystalline↔amorphous transitions induced in thin $Ge_{0.07}Sb_{0.93}$ films upon picosecond laser pulse melting were studied by *real-time* reflectivity measurements with nanosecond and picosecond resolution. The full transformation time could be resolved in a single exposure experiment using a novel setup based on a streak camera. It is shown that under optimum conditions both crystallization and amorphization are completed within 400 ps. The fundamental requirement for the occurrence of such ultrafast phase transformations is to reduce the latent heat released upon solidification. Amorphization is then achieved via bulk solidification of the fully molten film at a very large supercooling. © *1999 American Institute of Physics.* [S0003-6951(99)00946-8]

Amorphous GeSb films with a high Sb content have experimentally been demonstrated to be *fast* crystallizing media with potential interest for phase change optical recording.[1–4] Sb provides the rapidly crystallizing characteristics[5] while the addition of Ge enables the formation and stability of the amorphous phase.[2] It has been shown that *reversible* phase changes can be induced in GeSb films by ultrashort (ps and fs) laser pulses.[1] A dynamic study of these reversible phase changes induced by ps laser pulses in GeSb films on carbon coated mica substrates and based on real-time reflectivity measurements with ns resolution has recently been reported.[3] The full transformation time of both processes (amorphization/crystallization) was found to be ≈30 ns which was most likely overestimated due to limitations in the time response of the detection system. Similar tens of ns transformation times have usually been reported upon ns laser pulse phase transformation.[2,6–8]

The purpose of this letter is twofold. First, to show that ultrafast phase reversibility can be achieved by controlling the heat flow conditions imposed by the film configuration (thickness and substrate) and the laser fluence. Second, to demonstrate that both crystallization and amorphization in such a case occur with a full transformation time of hundreds of ps. The latter has been possible by means of a novel experimental setup based on a streak camera which allows us to monitor in real time the transformation dynamics in the ps time scale induced by a single ps pulse.

The samples used in this work are 25 and 50 nm thick amorphous $Ge_{0.07}Sb_{0.93}$ films grown by dc sputtering on glass and Si substrates. The specimens were irradiated by single 30 ps laser pulses at 583 nm. The transformation dynamics has been followed by measuring the reflectivity changes by means of a probe laser beam [either a He–Ne laser (633 nm) or a single mode Ar^+ laser (514 nm)], incident at a small angle (7°) and focused at the center of the irradiated area. The detection system used was either a fast photodetector connected to a transient digitizer for real-time reflectivity (RTR) measurements with ~5 resolution or a streak camera for RTR measurements in the ps time scale. Details can be found elsewhere.[9]

The RTR measurements can provide a direct measure of the structural state of a material provided that its optical constants depend on the phase.[10,11] In particular, the reflectivities of the liquid and the crystalline phases of Sb-rich GeSb films in the visible have been shown to be significantly higher than that of the amorphous phase.[2] Figure 1 shows several RTR transients recorded in 50-nm-thick films. Those transients that start at a low reflectivity value (amorphous GeSb) correspond to irradiations which attempted to induce crystallization, whereas those that start at a high value (precrystallized GeSb) attempted to achieve amorphization.

The irradiation of amorphous regions of the film on glass causes an initial reflectivity increase which is followed by a decrease to a minimum and a subsequent increase. The latter leads to a stable final reflectivity value well above the initial one, consistent with crystallization.[3] Similar RTR transients have previously been observed upon 250 ns laser pulse irra-

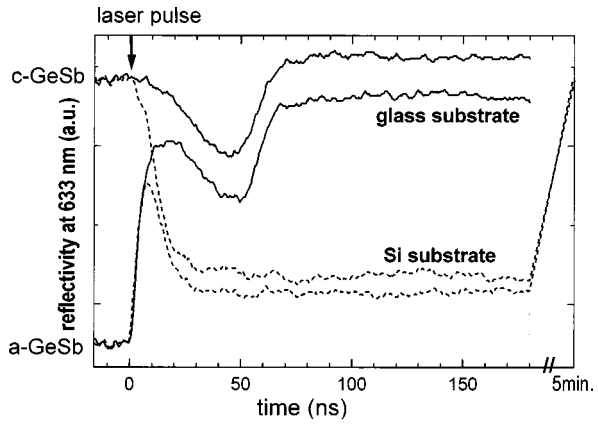

FIG. 1. RTR transients recorded at 633 nm in 50-nm-thick $Ge_{0.07}Sb_{0.93}$ films on glass (solid curves) and Si substrates (dashed curves) upon picosecond laser pulse irradiation of amorphous regions (*a*-GeSb) and precrystallized regions (*c*-GeSb). the static reflectivity levels recorded 5 min after irradiation in films on Si substrates are included and separated by a vertical line.

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diation and the initial increase was related to solid-state crystallization.[2] However, recent results obtained upon 100 fs laser pulse irradiation have evidenced that upon ultrashort pulse irradiation the final crystalline state is reached after a melting process occurring in the ps time scale.[4] It is important to emphasize that neither the melting process (within the pulse duration for ps pulses)[9] nor the initial part of the solidification process can actually be resolved with the ns resolution measurements shown in Fig. 1. The reflectivity decrease after the maximum in the case of picosecond laser pulses has thus to be related to the initial solidification process into an amorphous state. This amorphization process is frustrated by the release of the solidification enthalpy[11] which lowers the supercooling and promotes the nucleation and growth of the crystalline phase, as evidenced by the subsequent increase of the reflectivity. This recalescence-frustrated amorphization process has been reported to occur upon bulk solidification of Ge films under similar conditions.[9,12] Bulk solidification requires the homogenization of the temperature of the liquid prior to solidification which is favored by the low conductivity of the substrate. Upon ps laser pulse induced melting of the crystallized regions on glass substrate (*c*-GeSb in Fig. 1) the reflectivity undergoes a slow initial decrease followed by an increase until the initial reflectivity value is almost recovered, consistently with the formation of crystalline material. The similarity of the reflectivity minimum with the one observed upon irradiation of an amorphous region indicates that amorphization is prevented by the occurrence of recalescence.

One method to reduce the recalescence effects upon solidification which slow down the transformation process and favor crystallization, is to increase the heat flow towards the substrate. For that purpose we have used 50-nm-thick GeSb films on Si substrates having a thermal conductivity two orders of magnitude higher than that of glass. Figure 1 shows representative RTR transients recorded on such a film on Si. Upon irradiation of an amorphous region, the reflectivity shows a sharp increase which is again consistent with melting but is now followed by a rapid decay to a reflectivity level close to that of the initial one consistently with reamorphization. Nevertheless, this amorphous is not stable and converts to crystalline via an extremely slow solid-state transformation as evidenced by the reflectivity increase occurring within a much longer time scale ($\approx$5 min). The attempt to amorphize a crystalline region in these films on Si is also shown in Fig. 1. Upon melting, the rapid decay of the reflectivity indicates amorphization of the film although the initial reflectivity level and the crystalline phase are recovered within several minutes.

The comparison of the results of films on glass and Si substrates allows us to conclude that recalescence effects can effectively be prevented by the use of substrates with high thermal conductivity. Nevertheless, the amorphous phase obtained under these conditions is unstable. It is thus clear that another approach to prevent recalescence effects has to be found in order to promote ultrafast and stable reversible phase transitions. This has been done by reducing the film thickness, since the amount of latent heat released upon solidification is related to the amount of melted material.[13] The most promising results have been obtained in 25-nm-thick

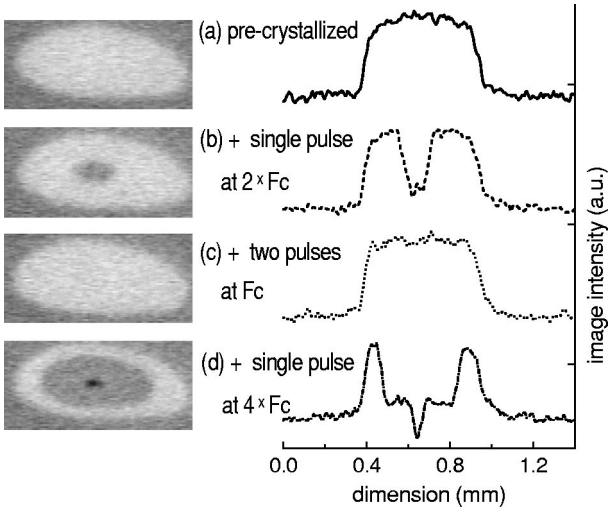

FIG. 2. *Left-hand side*: *consecutive* optical images of the same (a) precrystallized region of a 25-nm-thick $Ge_{0.07}Sb_{0.93}$ film on a glass substrate after (b)–(d) irradiation by subsequent picosecond laser pulses of a certain fluence. F_c denominates the fluence required for partial crystallization and is equal to 15 mJ/cm^2. *Right-hand side*: horizontal intensity profiles through the center of the images on the left-hand side.

$Ge_{0.07}Sb_{0.93}$ films on glass substrates that were initialized, i.e., crystallized by means of several laser pulses at low fluence. In order to visualize *in situ* the transformed regions, a video camera was installed at a small angle with respect to the specimen normal and connected to a frame grabber. Figure 2 shows images of (a) a precrystallized sample region, which has subsequently been irradiated with (b) a single pulse at a high fluence leading to reamorphization of the central region, then with (c) two pulses at low fluence which induced complete recrystallization and finally with (d) a single pulse at very high fluence inducing the reamorphization of a larger region and partial ablation at its center. The high contrast between the amorphous and crystalline regions and the sharp spatial transition between them can better be appreciated in the image intensity cross sections shown in Fig. 2. The intensities of the reamorphized regions of (b) and (d) are slightly higher than the intensity of the surrounding as-grown material, thus evidencing the formation of an amorphous phase with a different degree of relaxation.[3] In fact, that the reamorphized area in (d) is relatively large and of constant intensity although it has been exposed to a spatially Gaussian intensity distribution,[12] indicates that the fluence range for amorphization is relatively large ($2\times F_c - 3\times F_c$). This reversible phase transformation induced by varying the pulse fluence was found to be highly reproducible. Several cycles could be performed on the same region although an upper limit to the number of cycles could not be determined because the large energy fluctuations of the ps laser system output (20%).

The dynamics of the amorphization and crystallization processes in this 25-nm-thick GeSb film has been followed by measuring the RTR transients with the Streak Camera (ps resolution) and the results are shown in Fig. 3. The crystalline-to-amorphous transformation is shown in Fig. 3(a) and reveals that the actual transformation time is much shorter than the one measured with ns resolution (Fig. 1 and Ref. 3). The simultaneous measurement of the process with ns resolution as well as static reflectivity measurements 5

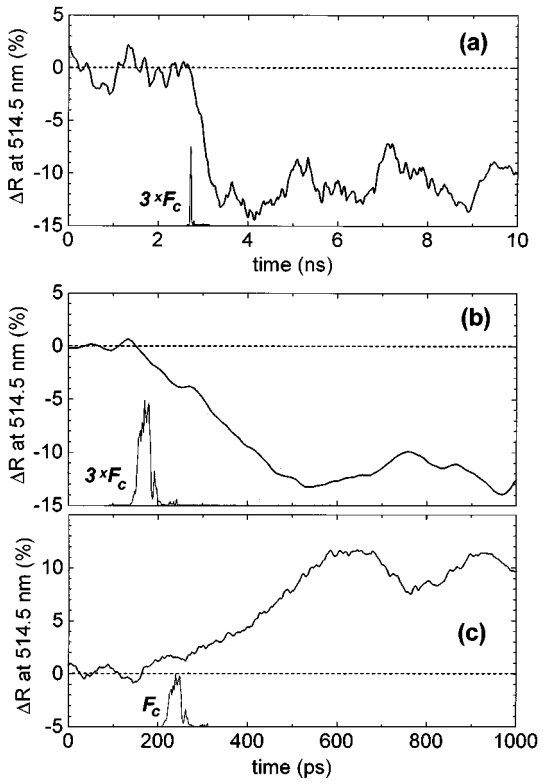

FIG. 3. RTR transients recorded with the streak camera at 514.5 nm of both, (a) and (b) the crystalline-to-amorphous transition at a fluence $3\times F_c$, and (c) the amorphous-to-crystalline transition at a fluence F_c induced in a 25-nm-thick $Ge_{0.07}Sb_{0.93}$ film on glass substrate upon picosecond laser pulse irradiation. The picosecond pulse (30 ps) measured by the Streak Camera is included in each figure to mark its temporal position.

min after the pulse showed that the final reflectivity level remains stable. An even better time resolution can be achieved by selecting a shorter time window (1 ns) of the streak camera [Fig. 3(b)], the RTR transient showing a full transformation time as short as 400 ps. Figure 3(c) shows the inverse transformation as measured in the same time window. It is evident that it is also completed within 400 ps, although the reflectivity contrast is lower (due to *partial* crystallization) than that for the amorphization process. To our knowledge, such an ultrafast completion of reversible and stable phase transformations has never been reported in literature.

In order to determine the mechanisms of these phase transformation processes it is important to notice that the pulse fluence required for amorphization is higher by a factor of 2–3 than that for crystallization. Even considering the different absorption coefficients of the amorphous and the crystalline phases at 583 nm (0.38 and 0.28, respectively), this means that a considerably higher amount of deposited energy and thus a larger melt depth is required for amorphization than for crystallization. This result indicates that amorphization requires melting of the whole film thickness whereas crystallization takes place through partial melting. The latter is further supported by the fact that the transformation times of both processes are approximately the same ($\approx$400 ps, see Fig. 3) which would be unlikely for a solid-state crystallization process. The present results are very similar to those reported by Sameshima *et al.* for ultrathin (6–36 nm) Si films on glass substrates upon excimer laser irradiation ($\lambda=308$ nm, $\tau=30$ ns).[13] The authors have demonstrated that complete melting of crystalline films was required for amorphization through a bulk solidification process, and that melting of only a thin surface layer of amorphous films leads to partial crystallization through an interfacial solidification process. The authors also reported that the amorphization threshold for 24-nm-thick Si films was 1.6 times higher than the crystallization threshold and that complete amorphization of films thicker than 36 nm was prevented due to the release of the latent heat (recalescence). These results support that in the case of our 25-nm-thick GeSb film on glass, amorphization is achieved by melting the whole film thickness because: (i) Interfacial solidification is prevented since no solid film material is in contact with the melt, thus enabling large supercoolings prior to solidification. (ii) The amount of latent heat released during the bulk solidification process is not enough to promote the nucleation of the crystalline material due to the small film thickness. The striking agreement of our results with those of Ref. 13 in spite of the completely different film material suggests that in ultrathin films the phase change scenario taking place is mainly defined by the heat flow conditions, i.e., the film thickness and the substrate.

In summary, ultrafast reversible and stable phase transformations triggered by ps laser pulses in GeSb films could be achieved by a proper control of the heat flow conditions imposed by the film thickness and the substrate through its thermal conductivity. The transformation times required to complete both the amorphization and crystallization processes are approximately the same and close to 400 ps. Melting of the whole film thickness was found to be essential for achieving amorphization and thus the threshold for amorphization is 2–3 times higher than that for crystallization.

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