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Laser-induced structural relaxation and crystallization phenomena in the picosecond time scale in GeSbO thin films

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Structural relaxation phenomena in the ps time scale have been observed upon pulsed laser irradiation of (GeSb)O amorphous films. The transformation of the irradiated surfaces has been temporally resolved by means of *in situ* optical techniques with ns and ps resolution. The results show the occurrence of structural relaxation phenomena in a time shorter than 600 ps in the as-deposited material or about 200 ps in thermally relaxed samples. In the latter case, a substantial amount of crystalline material is nucleated at the initial stage of the transformation. © 1998 American Institute of Physics. [S0021-8979(98)07021-2]

I. INTRODUCTION

Changes in both the topological and/or the chemical short range order within the amorphous phase are usually referred to as structural relaxation phenomena. Such changes are accompanied by the modification of the free energy of the system and normally by changes in its physical properties which have been intensively studied in the case of elementary amorphous semiconductors.^{1,2} There has been particular interest in the relation between structural relaxation and point defects in the amorphous phase of elementary amorphous semiconductors.²⁻⁵ If relaxation of amorphous Si (*a*-Si) occurs through the diffusion of point defects,² structural relaxation effects would be observable in the ps time scale upon irradiation with sufficiently short laser pulses. Nevertheless, this prediction has not been experimentally confirmed to date.

Other types of structural transformations induced by pulsed laser radiation have been reported both in the ps and fs time scales. Ultrafast melting processes in Si and GaAs have been thoroughly studied^{6,7} and subnanosecond crystallization phenomena have been reported in noble metals undergoing rapid solidification under ps laser pulses.⁸ To the best of our knowledge, no attempt has been made to resolve structural relaxation processes in the ps time scale. The recent demonstration of electronic excitation enhancement effects during fs laser pulse induced crystallization of GeSb films⁹ and the occurrence of relaxation in (GeSb)O films upon ps laser pulse irradiation¹⁰ suggests that structural relaxation and solid state crystallization might occur at ultrafast speeds in several material systems.

This work provides evidence for the occurrence of both structural relaxation and crystallization phenomena in the ps time scale upon laser irradiation of amorphous (GeSb)O (Ref. 11) thin films. It has been reported that Sb-rich amorphous films, such as GeSb, (GeSb)O, or SbO, can be crystallized upon ultrashort laser pulse irradiation and exhibit a large optical contrast between the amorphous and the crystalline phases,^{9,12,13} thus having a high potential for the de-

velopment of ultrashort laser pulse driven optical memories.¹⁴ The study of the crystallization kinetics in these materials under isothermal annealing conditions has revealed that this process is diffusionless and interface controlled and occurs at higher velocities in the (SbGe)O films.¹⁰

II. EXPERIMENT

Amorphous (Sb_{0.90}Ge_{0.10})O_{0.16} thin films, 60 nm thick, were grown on glass and carbon-coated mica substrates using a multitarget dc reactive magnetron sputtering system. Some of the films were partially relaxed by annealing at 100 °C for 10 min in vacuum (10⁻³ Pa). The films were irradiated in air with 30 ps laser pulses at a wavelength of 583 nm. The time evolution of the reflectivity of the irradiated surfaces was recorded in the ns time scale at 633 nm by means of a HeNe laser focused to a size of about 50 μm at nearly normal incidence in the center of the irradiated region (≈600 μm diameter). The reflected light was collected by a fast photodiode connected to a transient digitizer with a time resolution of a few ns. The energy density of the pulse at the sample site was determined within 10%. After each single pulse exposure, the sample was moved to a fresh region. Further details can be found elsewhere.^{10,15}

The time evolution of the reflectivity with ps resolution was determined using a “pump and probe” configuration with a variable delay between the pump and the probe pulses in the $\tau = -100$ –1200 ps range. The pump pulse is focused at the sample site to a size of ≈300 μm while the probe beam is focused to a size about eight times smaller. Since the effect of a single pump pulse may induce a permanent change in the state of relaxation of the surface, the reconstruction of the time evolution of the reflectivity was performed in single exposure steps,⁷ unlike the normal situation in experiments aimed at studying carrier relaxation dynamics.¹⁶ For a given delay ($\tau = t$), and a prefixed value of the pulse energy (E), the reflectivity of the surface before irradiation [$R(\tau = -\infty)$], the instantaneous reflectivity value [$R(\tau = t)$] and the reflectivity after irradiation [$R(\tau = \infty)$] are measured exposing a region of the surface to the pump pulse only once. The sample is then moved to a fresh region and the procedure is repeated until the instantaneous reflectivity change

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FIG. 1. Evolution in the ns time scale of the reflectivity at 633 nm of (a) as-deposited and (b) thermally annealed $(\text{Sb}_{0.90}\text{Ge}_{0.10})\text{O}_{0.16}$ films upon irradiation with a 30 ps laser pulse at several energy densities. The reflectivity values have been normalized to that of the surface before laser exposure and are given in terms of the percentage change. The arrow denotes the temporal position of the irradiation pulse. The corresponding laser pulse energy densities at the sample site are: (1) 4.0 mJ/cm^2 , (2) 4.5 mJ/cm^2 , (3) 6.0 mJ/cm^2 , (4) 10.0 mJ/cm^2 , and (5) 16.5 mJ/cm^2 in (a) and (1) 14.0 mJ/cm^2 and (2) 18.0 mJ/cm^2 in (b).

caused by at least ten pump pulses of energies within 10% of E are recorded. The values $R(\tau = -\infty, t, \infty)$ corresponding to the ten irradiation events are then averaged and the delay is changed to a new value. The reconstruction of a reflectivity transient under these conditions normally requires the irradiation of about 500 spots. In spite of the large statistics performed, experimental errors mainly related to the large fluctuations of the laser energy output tend to hinder the quality of the reconstructed signal. Under these conditions the energy density at the sample site is determined within 20%–30%; this value can rise to 40% for very low energies. Surface morphology and structural changes were analyzed by optical and transmission electron microscopy (TEM), as described in Ref. 13.

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows some representative examples of the evolution in the ns time scale of the reflectivity at 633 nm of the as-deposited films upon irradiation. The instantaneous reflectivity values have been normalized to the reflectivity of the surface before laser exposure according to the formula $R_n(t) = 100 \times [R(t) - R_0]/R_0$ where $R(t)$ is the instantaneous reflectivity value and R_0 is the sample reflectivity before laser exposure. In all cases, the effect of the pulse is to induce an initial reflectivity increase occurring in a time scale close to the time resolution of the experiment. The reflectivity then reaches a maximum that increases with the

pulse energy density. At low energy densities (3–9 mJ/cm^2 , transients 1–3), the maximum is followed by a more or less decay until a stable reflectivity value 3%–5% higher than R_0 is reached. Similar reflectivity transients have been reported upon both ns and ps laser pulse irradiation of $\text{Ge}_{1-x}\text{Sb}_x$ ($x > 0.85$) films and have been correlated to changes in the degree of relaxation of the irradiated surface.^{14,17} This was confirmed by TEM observation and electron diffraction analyses of the irradiated spots that are formed by amorphous material and show small ripples like those shown in Refs. 10 and 17. In this fluence regime, the initial reflectivity maximum observed in the transients is related to the cumulative effect of structural relaxation and the dependence of the reflectivity of the amorphous phase on temperature.¹⁷ Notice that electron-hole plasma effects in the reflectivity of the material are not expected to be observable in a time scale longer than a few ps since the carrier-lattice relaxation time estimated in very similar materials is about 800 fs.⁹ When the energy density is increased (9–15 mJ/cm^2 , transient 4), the evolution of the reflectivity is similar to that observed at lower energy densities but the final reflectivity values are 5%–10% above R_0 . These higher values are related to the partial crystallization of the irradiated region as evidenced by the small crystalline nuclei observed by TEM. Finally, at even higher energy densities (15–32 mJ/cm^2 , transient 5), the pulse induces the complete crystallization of the film. The initial increase of the reflectivity is followed by a decrease to a minimum and by a subsequent increase which leads to a final value 25%–30% higher than R_0 . This behavior has also been widely observed in $\text{Ge}_{1-x}\text{Sb}_x$ (where $x > 0.85$) thin films upon irradiation under similar conditions and is related to an initial fast solid state crystallization process (initial reflectivity increase) followed by melting and rapid solidification.^{12,13} The melting process is evidenced by the existence of the transient minimum and the final increase of the reflectivity corresponds to the solidification process into a crystalline phase.¹³

Representative examples of the ps time scale evolution of the reflectivity of the as-deposited films upon irradiation are shown in Figs. 2(a) and 2(b), together with the average $R(\tau = \infty)$. Figure 2(a) shows the behavior of a film irradiated with an average energy density below 10 mJ/cm^2 under a condition similar to that of transients 1–3 in Fig. 1(a), corresponding to a structural relaxation process without crystal nucleation. The reflectivity is observed to increase up to a value which is nearly identical to the final one. This change occurs at approximately 600 ps. In spite of the slightly different wavelength used in this case (583 nm), it is remarkable that the average value of $R(t = \infty)$ is very similar to the one observed in Fig. 1(a) at 633 nm upon relaxation (4% and 3%–5% above R_0 , respectively, at both wavelengths). Therefore, the results clearly evidence that the structural relaxation of the film under these experimental conditions occurs in the subnanosecond time scale.

Figure 2(b) shows the corresponding evolution of the reflectivity for an average energy density of $26 \pm 3 \text{ mJ}/\text{cm}^2$. This situation corresponds to the highest fluence regime (15–32 mJ/cm^2) and thus the evolution in Fig. 2(b) should be compared to the behavior in the ns time scale illustrated by

FIG. 2. (●) Evolution in the ps time scale of the reflectivity at 583 nm of (a),(b) as-deposited and (c) thermally annealed $(\text{Sb}_{0.90}\text{Ge}_{0.10})\text{O}_{0.16}$ films upon irradiation with 30 ps laser pulses. The reflectivity values have been normalized as in Fig. 1. Each data point corresponds to the average of at least ten irradiations each of them performed in a fresh region. (Δ) Final reflectivity level [$R(t=\infty)$] obtained by averaging the values at the different regions irradiated in order to determine the instantaneous reflectivity for a fixed delay. The dashed line indicates the reflectivity of the surface before laser exposure, the dot line denotes the average reflectivity value after laser exposure for all the irradiation events, and the solid line is a guide to the eye. The average energy densities at the sample site are (a) below 10 mJ/cm^2 , (b) $26 \pm 3 \text{ mJ}/\text{cm}^2$, and (c) $30 \pm 3 \text{ mJ}/\text{cm}^2$.

the transient labeled 5 in Fig. 1(a) corresponding to a crystallization process. In this case, the reflectivity changes seem to occur in three stages: (i) an initial and fast increase lasting about 400 ps in which the reflectivity reaches a value $\sim 12\%$ higher than the initial one; (ii) a plateau in which the reflectivity remains approximately constant for delays between ≈ 400 ps and ≈ 1 ns; (iii) a final reflectivity increase for delays longer than 1 ns. A comparison of this behavior to the one observed at lower energies when only relaxation is induced [Fig. 2(a)] indicates that the fast initial increase is most likely related to the relaxation of the amorphous material, which occurs faster at higher energy densities. However, the reflectivity at the plateau (10%–14% above R_0) is higher than $R(t=\infty)$ upon relaxation ($\approx 4\%$ at 583 nm and 3%–5% at 633 nm, both above R_0). This suggests that a significant amount of crystalline phase nucleation might take place during the first stage of the transformation together with the relaxation process. If this is the case, the crystalline nuclei formed would need an incubation time to reach the critical radius¹⁸ before the onset of crystal growth, which would explain the observed reflectivity plateau. Afterwards, the onset of the growth process from the already developed stable nu-

clei would lead to the reflectivity increase observed for delays > 1 ns.

Since both the relaxation and the crystallization kinetics can be largely influenced by the initial state of relaxation of the films, part of the samples were partially relaxed by thermal annealing. The behavior of these samples in the ns time scale upon irradiation can be seen in Fig. 1(b). Both at high ($15\text{--}36 \text{ mJ}/\text{cm}^2$, transient 2) and low ($4\text{--}15 \text{ mJ}/\text{cm}^2$, transient 1) energy densities the results are very similar to the ones obtained in the as-deposited films [Fig. 1(a)]. The only significant difference is that in the low energy regime, $R(t=\infty)$ is always above the values observed in the as-deposited films upon relaxation, which is consistent with the occurrence of crystallization under the former conditions. TEM observations confirmed this point.

The behavior of the thermally relaxed samples in the ps time scale is illustrated in Fig. 2(c) for an average pulse energy density of $30 \pm 3 \text{ mJ}/\text{cm}^2$. The increase of the reflectivity again takes place in three stages as in the case of the as-deposited films [Fig. 2(b)] but the initial reflectivity increase occurs ≈ 200 ps earlier and now seems to be faster. The reflectivity at the plateau is also higher than the values observed in a pure relaxation process as it occurs in Fig. 2(a) and even higher than the value at the plateau obtained upon relaxation plus some crystal nucleation as it occurs in Fig. 2(c). This result clearly indicates that a very substantial amount of crystalline material is now formed during the early stage of the transformation. It is worth noting that the plateau has a duration similar to the one observed in the as-deposited film [Fig. 2(b)] which further supports its relation to a characteristic time for crystalline nuclei incubation. Finally, an additional reflectivity increase is observed for delays > 900 ps which, according to the previous discussion, corresponds to the onset of crystal growth.

The present results thus provide direct evidence for laser-induced structural relaxation phenomena of amorphous materials in the ps time scale. This fast structural relaxation process can be partially understood by considering the crystallization mechanism of this and similar materials such as Sb-rich $\text{Sb}_x\text{Ge}_{1-x}$ films.^{10,13} In these films, laser-induced crystallization occurs in a fast diffusionless process in which the small amount of Ge atoms compared to Sb are incorporated into the Sb crystalline lattice. This process should require relatively small bond rearrangements which can explain the fact that a large degree of relaxation can be produced by very minor changes in the bond configuration. These changes could be induced in the observed time scale if the temperature of the system is high enough. The presence of a mechanism involving bond angle rearrangements through point defect migration within the amorphous phase, as proposed for *a*-Si (Ref. 2) can contribute further to this fast relaxation process. Carrier plasma screening effects have also been claimed to favor relaxation processes in *a*-Si,¹⁹ although in our case the expected carrier lifetimes (≤ 1 ps) (Ref. 9) are clearly below the observed time for completing the relaxation process (≈ 600 ps).

The results in Figs. 2(b) and 2(c) also show that the crystalline phase nucleation occurs in the subnanosecond time scale. The maximum speed at which both the complete

relaxation of the amorphous and the initial nucleation of the crystalline phase may occur (200–600 ps) depends on the initial state of structural relaxation of the amorphous material. The results obtained indicate that the initial relaxation and nucleation stage is followed by a nuclei incubation time in the sub-ns time scale. It is nevertheless uncertain whether nuclei incubation effects impose a limit for the maximum speed of the amorphous to crystalline phase transformation and whether such a limit could be overcome in the presence of carrier plasma effects which might be present under irradiation with much shorter pulses in the hundreds of fs range.⁹

IV. CONCLUSION

In summary, structural relaxation phenomena have been observed in an amorphous system in the ps time scale. Depending on the initial degree of relaxation of the system, this process can be accompanied by subnanosecond crystal nucleation even when the minimum time limit for the whole process of relaxation and complete crystallization remains uncertain.

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