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Citation: J. Appl. Phys. 80, 6677 (1996); doi: 10.1063/1.363815

View online: http://dx.doi.org/10.1063/1.363815

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Bulk solidification and recalescence phenomena in amorphous Ge films upon picosecond pulsed laser irradiation

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(Received 6 March 1996; accepted for publication 5 September 1996)

Melting and rapid solidification are induced in amorphous Ge films upon irradiation with 10 ps laser pulses at 583 nm. The role of heat flow during the solidification process was investigated by comparing the behavior of films grown on substrates with different thermal properties. The melting and solidification kinetics are followed in real time by reflectivity measurements in the nanosecond time scale and the induced structural changes are analyzed by means of Raman spectroscopy in micro-Raman configuration. If the thermal diffusivity of the substrate is high enough, the film reamorizes via bulk nucleation of the amorphous phase from the melt. When the thermal diffusivity of the substrate is reduced, the initial nucleation of the solid phase leads to an increase in the liquid temperature (recalescence) and in the melt duration, thus promoting the formation of the crystalline phase. © 1996 American Institute of Physics. [S0021-8979(96)03024-1]

INTRODUCTION

Pulsed laser-induced melting and rapid solidification phenomena in elementary semiconductors have been subject of longstanding interest in material science.1–7 The literature published in this field covers a variety of topics that include, among others, laser induced crystallization of amorphous semiconductors,8–10 laser-induced annealing of ion-implanted Si,9,10 rapid melting, regrowth, and amorphization,1–3,5,11,12 or nucleation of solid phases from supercooled melts.4,13,14 A particularly intensive experimental effort has been expended on the last subject in order to establish the validity of various models1,3,14 for the transformation among amorphous, liquid, and crystalline phases. Experiments aimed at determining the solidification scenario for different supercoolings16 and quench rates have also been performed.4 Complete amorphization of polycrystalline Si films through bulk solidification17 following pulsed laser-induced melting has been reported.18,19 But complete amorphization of Ge films through this mechanism has not yet been observed in spite of the large supercoolings reported in earlier rapid solidification experiments.14 This work reports a study on rapid solidification phenomena induced in Ge films upon irradiation with picosecond laser pulses. The role of heat flow during the solidification process was investigated by comparing the behavior of films grown on substrates with different thermal properties. If the thermal diffusivity of the substrate is not large enough, release of the solidification enthalpy during the initial nucleation stages may lead to a decrease in the supercooling (a phenomenon usually referred to as recalescence) and give rise to the formation of crystalline material. When the thermal diffusivity of the substrate is increased, recalescence is suppressed and the molten layer reamorizes through bulk nucleation from the melt, this being the first time to the best of our knowledge such behavior has been observed for Ge.

EXPERIMENT

The samples used for the present study are 50-nm-thick amorphous Ge (a-Ge) films grown at room temperature either on glass or on Si(100) wafers covered by their native oxide. The films are deposited by dc sputtering from a Ge (99.999%) target in a vacuum system with a residual pressure of $3 \times 10^{-6}$ Torr and with an Ar operating pressure of $4 \times 10^{-3}$ Torr. Transmission electron microscopy and spectroscopic ellipsometry of films deposited under the same conditions show that the films are amorphous and have a low density of voids.20 The samples are irradiated in air with 10 ps laser pulses at a wavelength of 583 nm. The pulses are delivered by a synchronously pumped dye laser (rhodamine 6G) whose output is amplified by a pulsed dye amplifier (Kitton red-620) pumped by a frequency-doubled Nd–YAG laser. The amplified beam is spatially filtered and focused onto the sample surface. The spatial profile of the beam at the sample site is Gaussian elliptical with 1.0 and 0.7 mm $1/e^2$ diameter axes. The fluences at the maximum of the intensity distribution are in the range 0–200 mJ/cm$^2$. The fluence is determined within 10%.

The evolution of the reflectivity of the irradiated surface is measured in real time with a resolution of about 1 ns by means of a HeNe probe laser (633 nm). It is focused, at nearly normal incidence, at the center of the irradiated region to a size of approximately 50 $\mu$m ($1/e^2$ diameter). The ratio between the size of the irradiation and the probe beam ($\approx 1/20$) ensures that the reflectivity is measured over a homogeneously irradiated region. Further details can be found elsewhere.21,22 After irradiation, the surface of the samples was inspected by optical microscopy and the structure of both the as-deposited and the irradiated materials were ana-

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lyzed by means of Raman spectroscopy in micro-Raman configuration\textsuperscript{23,24} using an Ar\textsuperscript{+} laser excitation beam at 514 nm. The beam is focused onto the sample to a size of about 10 μm, and it is sufficiently attenuated to prevent any transformation of the surface. The spectra of the irradiated regions are recorded at the center of the irradiated spots.

RESULTS

Figure 1 shows the time evolution of the reflectivity of amorphous Ge films grown on (a) Si and on (b) glass substrates upon irradiation with 10 ps laser pulses at several fluences. The reflectivity transients were arbitrarily shifted and the zero of the horizontal axis scale corresponds to the temporal position of the irradiation pulse. The number on each transient corresponds to the irradiation fluence. The transients plotted with a dashed line correspond to fluences above the surface ablation threshold.

The reflectivity of the films grown on glass [Fig. 1(b)] shows a behavior similar to that of the films on Si for low fluences. For higher fluences, above 55 mJ/cm\textsuperscript{2}, a shoulder is observed in the decreasing part of the curve after the maximum. Its temporal position (10±2 ns after the maximum) and duration (3±1 ns) do not depend on laser fluence. After the shoulder, the reflectivity decreases again but at a slower rate, and the final reflectivity value observed is always clearly smaller than the initial one. For fluences higher than ~75 mJ/cm\textsuperscript{2} surface ablation is induced (dashed line transient).

The evolution of the key features of the reflectivity transients versus the laser fluence can be seen in more detail in Figs. 2 and 3. The evolution of both the maximum transient reflectivity value ($R_{\text{max}}$) and the reflectivity after irradiation ($R_{\text{fin}}$) as functions of the laser pulse fluence for films grown on Si substrates.

Fig. 1. Time evolution of the reflectivity of amorphous Ge films grown on (a) Si and on (b) glass substrates upon irradiation with 10 ps laser pulses at several fluences. The reflectivity transients were arbitrarily shifted and the zero of the horizontal axis scale corresponds to the temporal position of the irradiation pulse. The number on each transient corresponds to the irradiation fluence. The transients plotted with a dashed line correspond to fluences above the surface ablation threshold.

Fig. 2. (a) Maximum transient reflectivity ($R_{\text{max}}$) ($\blacksquare$) and reflectivity after irradiation ($R_{\text{fin}}$) (○) and (b) melt duration (▲) as functions of the laser pulse fluence for films grown on Si substrates.
similar to that observed in the films on Si although the characteristic inflections occur in a compressed fluence scale and show a different amplitude. More significant differences are observed in the behavior of $R_{\text{fin}}$ since for fluences above 55 mJ/cm$^2$ and up to the ablation threshold; a clear decrease is observed for the films on glass.

Since the reflectivity at 633 nm of amorphous Ge at the melting temperature is known to be 13%–14% higher than the value at room temperature and molten Ge is metallic, any reflectivity increase above 14% of the initial value in the reflectivity transients can be interpreted in terms of surface melting. The time the reflectivity remains above that value thus corresponds to the melt duration that is plotted as a function of laser fluence in Figs. 2(b) and 3(b) for the films on Si and on glass substrates, respectively. In both cases, the melt duration follows a similar trend for increasing fluences but the melt durations observed are always longer for the films grown on glass. It is remarkable in this latter case [Fig. 3(b)] the existence of a sharp change of slope in the curve that occurs when the fluence is increased above 55 mJ/cm$^2$ and therefore when the shoulder is first observed in the reflectivity transients.

The time interval between the maximum of the reflectivity transient and the point at which it decreases to a value 14% higher than the initial one provides a reasonably good measurement of the solidification time since the optical properties of the liquid do not depend significantly on temperature. The measured solidification times are in the range of 10–15 ns for the films on glass and 5–10 ns for the films on Si. The former might be slightly underestimated for fluences higher than 55 mJ/cm$^2$ due to the fact that the material obtained upon solidification has a reflectivity ($R_{\text{fin}}$) lower than the initial one [Figs. 1(b) and 3(a)]. The results thus show that both the melt durations and solidification times are longer in the films grown on glass substrates.

Figure 4 shows several representative Raman spectra from Ge films on Si (dashed lines) and glass (solid lines) substrates before and after irradiation. The spectra of the as-deposited films [(a) and (c)] show the characteristic broad transverse optic (TO) band of amorphous Ge at 270 cm$^{-1}$. Upon irradiation of the films on Si with fluences up to the ablation threshold, the spectra remain essentially unchanged as can be seen in spectrum (b). This result evidences that the material reamorphizes upon melting and rapid solidification. The same behavior is observed in the films on glass irradiated at low fluences [spectrum (d)]. For fluences above 55 mJ/cm$^2$, [spectrum (e)], the TO phonon peak of crystalline Ge at 298 cm$^{-1}$ is clearly observed, indicating that the resolidified material is partially crystalline. However, the presence of crystalline material was already observed, but in a much smaller amount, for fluences higher than $\approx 50$ mJ/cm$^2$.

The decrease observed in $R_{\text{fin}}$ upon irradiation with fluences above this value [Fig. 3(a)] is therefore related to the formation of crystalline material. The changes observed for smaller fluences are most likely related to differences in the state of relaxation of the resolidified amorphous material with respect to the as-deposited one.

**DISCUSSION**

The most important difference between the behavior of Ge films on glass and on Si substrates is the fact that crystallization can be induced upon irradiation in the former. For fluences above 55 mJ/cm$^2$, crystallization occurs upon solidi-
Our results also show a clear increase of the melt duration for fluences above this value [see Fig. 3(b)] that is related to a slower solidification process. The latter is in agreement with an increase in the liquid temperature during solidification, most likely due to the release of the solidification enthalpy. The enthalpy released during solidification heats the material, thus decreasing strongly the rate at which the liquid is consumed. This interpretation is in agreement with the presence of the shoulder in the reflectivity transients [Fig. 1(b)], which indicates that the liquid consumption is reduced enough to maintain nearly constant, during a few nanoseconds, the solid to liquid material ratio in the volume probed by the HeNe laser beam. At the end of the process, the temperature of the liquid is close to the melting point of crystalline Ge (the undercooling/supercooling is smaller), thus promoting the formation of the crystalline phase.

Shameshima and Usui\(^5\) studied, among other parameters, the influence of heat diffusion on the laser-induced amorphization of polycrystalline Si films. They observed that crystallization can be prevented for a given film thickness if the heat flow to the substrate is fast enough. It is worth noting that the thermal diffusivity of Si is about two orders of magnitude higher than that of glass. Therefore, the heat released upon solidification in films on Si can be efficiently extracted and the large supercooling initially achieved can be maintained. A comparison of our results to those in Ref. 4 and 14, taking into account the higher cooling rates involved in our experiment due to use of shorter laser pulses, shows that the minimum supercooling achieved prior to solidification in the films on Si has to be higher than 540 K and probably close to or above 600 K since we observe complete reamorphization of the molten films. For the films on glass substrates, the slower heat flow allows the liquid temperature to increase as a consequence of the initial nucleation of the solid phase, thus promoting the formation of crystalline material either nucleated in a hotter liquid or formed by crystallization of pre-existent amorphous nuclei. The fact that there is a fluence threshold (55 mJ/cm\(^2\)) below which recrystallization is not observed in the films on glass suggests that the heat released depends on the amount of material initially solidified which is turn depends on the volume of molten material and its supercooling, and therefore on the fluence. Only when the heat released upon the initial solidification is large enough and/or the efficiency of heat extraction to the substrate is not sufficient does the liquid temperature increase substantially and recrystallization effects become dominant.

There is a number of earlier studies focused on nucleation phenomena in Ge and Si supercooled melts produced by laser melting. These studies combined electrical conductivity and optical reflectivity measurements in real time.\(^1,4,5,13,14\) Amorphization either via interfacial\(^7\) or bulk solidification\(^5\) has been reported in different experiments in Si. In order to estimate the average liquid–solid interface velocity upon solidification in our case, we have estimated the induced melt depth by comparing the experimental \(R_{\text{max}}\) values to the evolution of the reflectivity at 633 nm of a 50 nm an-Ge film as a surface molten layer progresses in depth. This evolution is shown in Fig. 5 and was obtained from numerical simulations performed using a home developed computer program based on the theory of Abeles for calculating the reflectivity of an isotropic planar multilayer system, and using the optical constants for amorphous Ge(\(a\)-\(\text{Ge}\)) and liquid Ge(\(l\)-\(\text{Ge}\)) reported elsewhere.\(^20,26\) Obviously this method is valid if we assume that a homogeneous molten layer is produced in the surface upon irradiation,\(^21,29,30\) which is a very reasonable assumption for fluences just below the ablation threshold. Comparison of the highest experimental \(R_{\text{max}}\) values to the simulated ones leads to maximum melt depths of about 10 and 15 nm for Ge films on Si and on glass, respectively. Since this estimation of the maximum melt depth critically depends on the experimental measurement of the maximum transient reflectivity level (\(R_{\text{max}}\)), the possible influence of the rise time of the detection system was checked by measuring the response of a crystalline Ge wafer upon melting. It was found that the reflectivity value of an optically thick \(l\)-Ge layer could be observed within the first few ns after the irradiation pulse. Considering a very conservative maximum error of 5% in reflectivity measurements, the resulting maximum melt depths in the films on Si and on glass would not be substantially affected, leading to maximum values below 15 and 20 nm, respectively. The combination of these extreme values with the experimental solidification times provides a maximum upper limit of 3 m/s (films on Si substrate) and 2 m/s (films on glass substrate) for the solid–liquid interface velocity upon solidification. These velocities are still nearly one order of magnitude smaller than the minimum interface velocity required for amorphization in elementary semiconductors (15–20 m/s),\(^1,31\) thus evidencing that reamorphization has to occur through a different mechanism, i.e., via bulk solidification. This is, to our knowledge, the first time that reamorphization of Ge layers through bulk nucleation of the amorphous phase from the melt has been reported.
The shallow melt depths observed in the present experiments are not unexpected since there are significant differences between our experimental conditions and those reported in Refs. 4, 5, and 14. The optical penetration depth of amorphous Ge at 583 nm is about 23 nm (Ref. 20) while the thermal diffusion length for a 10 ps laser pulse is about 4 nm. The temperature distribution in depth immediately after the pulse thus follows the exponentially decreasing light absorption profile. This makes the initial temperature of the surface much higher than that of the few tens of nm layer below; therefore surface ablation occurs before an optically thick liquid layer can be formed. The thermal diffusivity of the liquid material (0.3 W/cm K) is, however, large enough to efficiently reduce, after a few nanoseconds, the thermal gradient in the very thin liquid layer induced, thus promoting solidification throughout the full liquid volume. This reasoning agrees with the calculations of Sameshima and Usui that indicated that homogenous bulk solidification of the amorphous phase has to occur under a uniform temperature distribution in the liquid.

In films grown on glass and for fluences higher than 55 mJ/cm², recrystallization phenomena appear and lead to the formation of crystalline phases upon solidification. The thickness of the crystalline layer can be estimated by comparing the reflectivity of the films upon crystallization [R_m in Fig. 3(a)] to the evolution of the reflectivity at 633 nm of a 50 nm a-Ge film when a surface polycrystalline layer progresses in depth. The simulated values are also included in Fig. 5, where the optical constants of p-Ge were assumed to be the same than those of c-Ge. It can be seen that the presence of a very shallow p-Ge layer at the surface produces a clear decrease of film reflectivity which is in agreement with the experimentally observed behavior of R_m in films on glass substrates upon irradiation with laser fluences above 55 mJ/cm² [Fig. 3(a)]. By comparing the minimum experimental R_m values before ablation to the simulated reflectivity evolution, the thickness of the crystalline layer is estimated to be below 10 nm. This thickness is significantly smaller than the maximum melt depth estimated (~20 nm), thus suggesting that the resolidified material is formed by either a mixture of amorphous and crystalline phases or by a p-Ge layer on top of a reamorphized layer. Both alternatives would be quite unlikely in a pure interfacial solidification process occurring at a presumed maximum interface velocity of 3 m/s. These results thus suggest that solidification of the films on glass for high fluences (and leading to crystallization) also occurs via bulk nucleation or, at least, through a mixed mechanism involving simultaneous bulk and interfacial solidification. If bulk nucleation is assumed, an estimation of the minimum nucleation rate can be made by assuming spherical crystalline nuclei with diameters equal to the crystalline layer thickness and using the observed solidification time. This leads to a value of the order of 10⁸ cm⁻³ s⁻¹ that is well above those previously reported for rapid solidification phenomena in elementary semiconductors and also likely above the limit where homogeneous nucleation theory applies.¹³

CONCLUSIONS

Bulk nucleation of amorphous Ge from the melt leading to complete reamorphization of the molten layer was observed for the first time in Ge films on Si substrates upon irradiation with 10 ps laser pulses. The strong influence of the thermal properties of the film–substrate system is evidenced by the change in the solidification behavior observed in films on glass, for which the initial nucleation leads to recrystallization and promotes the formation of the crystalline phase for fluences above a threshold value. In this latter situation it is most likely that bulk and interfacial solidification occur simultaneously.

ACKNOWLEDGMENTS

This work was partially supported by CICYT (Spain) under the TIC93-0125 project. The authors are grateful to Dr. J. Jiménez and Dr. C. Prieto for very helpful discussions during the preparation of this article.

¹⁶ We use the term undercooling to refer to the deviation of an interface from the melting temperature and the term supercooling to refer to the deviation of a “bulk liquid” from the melting temperature, following the criterion given in Ref. 13.
¹⁷ We use the term “bulk solidification” to refer to a solidification process that takes place throughout the full volume of the liquid.
32 Defined as $\sqrt{Dt}$, where the $D$ is the thermal diffusivity and $t$ is the time lapse from the pulse onset. The value of $D$ was taken from Ref. 33.