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On the origin of recalescence in amorphous Ge films melted with nanosecond laser pulses

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Rapid solidification phenomena have been studied in amorphous germanium films on silicon substrates by means of real time reflectivity measurements performed during irradiation with nanosecond laser pulses. The influence of the thermal response of the film/substrate system has been investigated by comparing the behavior of films with thicknesses in the range of 30–180 nm. Two different solidification scenarios are observed depending on the ratio between film thickness (d) and the thermal diffusion length (l) of amorphous germanium ($l \approx 80$ nm for 12 ns laser pulses). In the thinner films ($d < l$), reamorphization occurs upon solidification. Recalescence is observed in the thicker ones ($d \geq l$) when the melt depth induced is above of ≈ 80 nm. Above this threshold, crystalline phases are nucleated upon solidification. The origin of this melt depth threshold is discussed in terms of the heat flow into the substrate, the supercooling prior to solidification, and the need of a minimum amount of initially solidified material. © 1997 American Institute of Physics. [S0021-8979(97)07317-9]

INTRODUCTION

Pulsed laser induced melting and rapid solidification of amorphous semiconductors is a topic of lasting interest to the materials science community. Several articles dealing with this issue have been focused to the formation of either crystalline^{1–3} or amorphous^{4,5} phases. It has been reported that incomplete melting of amorphous silicon (a -Si) layers leads to the formation of a large-grained polycrystalline Si (p -Si) layer near the surface and fine-grained p -Si at greater depth.^{1,6} Although there was some controversy about the mechanism responsible of the formation of the fine-grained polycrystalline layer, it is now well established that explosive crystallization mediated by a buried thin liquid layer explains its formation.^{6–8}

More recently several studies have been focused on the nucleation mechanisms involved in rapid solidification phenomena under large undercoolings. The dominant role of both the undercooling/supercooling degree prior to solidification and the presence of recalescence in the formation of either crystalline or amorphous phases is widely recognized.^{9–12} It has been suggested that the films thickness is a key parameter controlling both the heat flow to the substrate¹⁰ and the occurrence of recalescence¹² upon laser-induced melting of Si films on insulating substrates. These works deal however with Si films on substrates of very low thermal conductivity (mainly SiO₂) and film thicknesses much smaller than the thermal diffusion length of Si. In the

case of Ge, recalescence and crystalline phase formation were reported to occur in films with a fixed thickness of 350 nm on SiO₂ substrates.¹¹ This result is in contrast with the recent experiments carried out on 50-nm-thick amorphous Ge films on Si substrates which have shown that reamorphization of the molten layer was produced.⁵ Since the thermal conductivity of the a -Ge is about two orders of magnitude smaller than that of the c -Si substrate, it is not surprising that the cooling rate can be strongly modified by varying the film thickness around the a -Ge thermal diffusion length. Different solidification scenarios should then be accessible thus leading either to amorphization or crystallization upon solidification.

The aim of this work is to study the role of the film thickness on the rapid solidification kinetics of thin a -Ge films on Si substrates. Films with thicknesses ranging from 30 to 180 nm were melted by irradiation with ns laser pulses of energy densities up to the ablation threshold. The experimental conditions to observe recalescence together with the reflectivity changes after solidification are determined from real-time reflectivity (RTR) measurements. The induced melt depths are calculated by solving the one dimensional heat flow equation. The occurrence of recalescence, i.e., the release of the solidification enthalpy and subsequent heating of the surrounding liquid, which leads to the formation of crystalline phases upon solidification, is discussed in terms of both, the thermal diffusion length to the film thickness ratio and the induced melt depth.

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EXPERIMENT

The films were grown at room temperature in a dc magnetron sputtering system onto single crystalline Si (100) substrates covered by their native oxide. The films were amorphous and had thicknesses of 30, 50, 100, 130, and 180 nm. Further details on the film preparation as well as their optical and structural properties can be found elsewhere.¹³

The films were irradiated in air at normal incidence using an ArF excimer laser ($\lambda = 193$ nm, $\tau = 12$ ns). A HeNe laser beam ($\lambda = 633$ nm, $\tau = 1$ μ s) was focused to the center of the irradiated area at $\approx 20^\circ$ off its normal in order to record in real time the evolution of the reflectivity of the irradiated surface. A detailed description of the experimental setup is provided in Ref. 14.

The occurrence of recalescence is directly evaluated from the RTR transients as shown in Refs. 9–11 and 15. The melt depth as a function of the laser energy density is calculated for each film thickness in the frame of a thermal model based on one dimensional heat-flow equation. The code is described in detail elsewhere¹⁶ and is based on the finite element method together with the temperature dependence optical and thermal parameters used. The maximum melt depth for each energy density is obtained from the calculation as the maximum thickness of material over which the temperature reaches a value $T_m \geq 965$ K, the melting temperature of *a*-Ge.

RESULTS

Figure 1 shows some representative RTR transients obtained upon irradiation at increasing energy densities in the thinnest [30 nm thick, Fig. 1(a)] and the thickest [180 nm thick, Fig. 1(b)] films studied. If the pulse energy density is large enough, the arrival of the laser pulse induces a reflectivity increase related to the heating and melting of the surface. The maximum transient reflectivity value then observed for all the films corresponds to the development of an optically thick liquid ($> \approx 20$ nm at $\lambda = 633$ nm) layer at the surface. After the maximum, the reflectivity decreases due to the solidification and cooling processes, these features being similar to those widely reported upon laser induced melting of both amorphous^{5,14} and crystalline^{17,18} semiconductors. The final reflectivity value observed upon cooling is similar to the initial one in the transients recorded in the 30 nm film and those labelled (1') and (2') in the 180 nm film. The RTR transients obtained in all the studied films show the same features when irradiating with low energy densities above the melting threshold. The thinner films (30 and 50 nm thick) show these features even for energy densities up to the ablation threshold.

The transient shown for the 180-nm-thick film at high energy densities (3') exhibits new features. A shoulder appears on the solidification tail of the RTR transient and the whole cooling process lasts longer than 200 ns and is not shown in the figure. This shoulder indicates that immediately after the initial solidification, the consumption of liquid is reduced enough so as to maintain nearly constant within the near surface region the solid to liquid material ratio during a few nanoseconds. The reflectivity decreases again after the

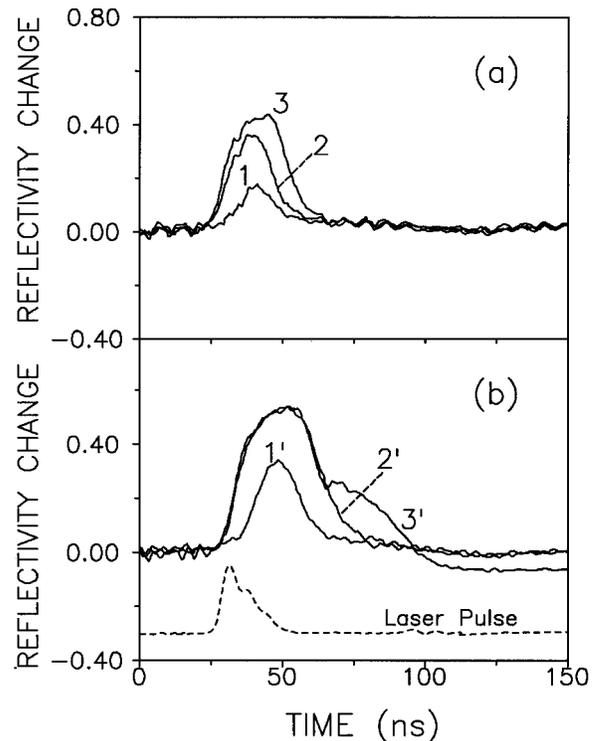


FIG. 1. Reflectivity transients normalized to the initial film reflectivity obtained in a 30-nm-thick (a), and in a 180-nm-thick (b) *a*-Ge film. Each transient is recorded in a virgin area and the energy density used was: (1) 91, (2) 115, and (3) 408 mJ/cm^2 for the 30-nm-thick film and (1') 45, (2') 88, and (3') 366 mJ/cm^2 for the 180 nm film. The temporal profile of the irradiation laser pulse is also included.

shoulder but at a slower rate. These features are consistent with an increase of the liquid temperature produced by the release of solidification enthalpy, and thus the occurrence of recalescence.^{9–11,15} The reflectivity after the shoulder decreases again down to a final value that is always smaller than the initial one.

From these measurements, it was determined that recalescence is only observed in films with a thickness $d \geq 80$ nm and irradiated with energy densities above a threshold value. This threshold has been plotted in Fig. 2(a) as a function of the film thickness where it is seen that the higher the film thickness the lower the energy density required to observe recalescence. The melt depths calculated as a function of the pulse energy density for each film thickness showing recalescence (80, 100, 130, and 180 nm) have been plotted for comparison in Fig. 2(b). As expected, the melt depth increases as the energy density increases up to a value for which the whole film is melted. When comparing the simulated results in Fig. 2(b) to the experimentally determined energy density threshold for recalescence [Fig. 2(a)], it is clearly seen that the latter corresponds in all cases to the minimum energy density required to produce a molten layer of ≈ 80 nm.

Finally, Fig. 3 shows the reflectivity changes upon solidification, normalized to the initial film reflectivity, as a function of the energy density and for films of different thicknesses. It is seen that no reflectivity changes are ob-

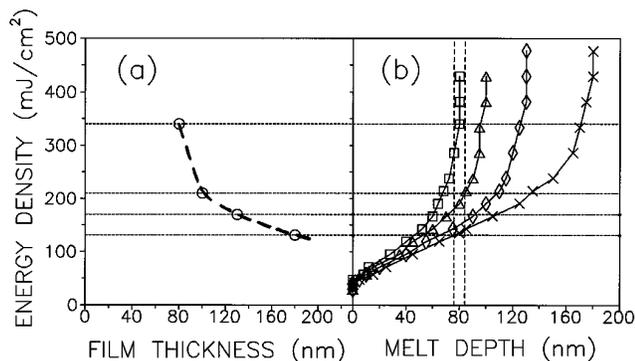


FIG. 2. Energy density threshold to observe recalescence as a function of the film thickness (a), and calculated melt depth achieved (b). Calculated results obtained in *a*-Ge films of thickness 80(□), 100(△), 130(◇), and 180(×) nm are shown.

served within experimental resolution in the thinnest film (30 nm). The same result applies for the 50-nm-thick film, but the results are not plotted for the sake of clarity. This result is in contrast with the behavior observed in the thicker films for which the final reflectivity is a decreasing function of the pulse fluence which is more pronounced as the film thickness is increased. It is worth noticing that the reflectivity changes induced are relatively small in all cases ($\approx 15\%$ at the most).

DISCUSSION

The results show that the solidification process is clearly dependent on the thickness of the *a*-Ge film and therefore on the rate of the heat transfer to the *c*-Si substrate. The thermal diffusion length in the *a*-Ge film can be estimated as $l \sim (D\tau)^{1/2}$, where $D = k/\rho c_p$ is the heat diffusion coefficient and τ the pulse length. By using the thermal parameters of *a*-Ge reported in Ref. 16 ($k = 0.01 \text{ W cm}^{-1} \text{ K}^{-1}$, $\rho = 5.3 \text{ g/cm}^3$, $c_p = 0.29 + 17.5 \times 10^{-5} \text{ T J/gK}$) and $\tau = 12 \text{ ns}$, the thermal diffusion length ranges from 81 nm at room temperature to 70 nm at the melting temperature of *a*-Ge (T_m

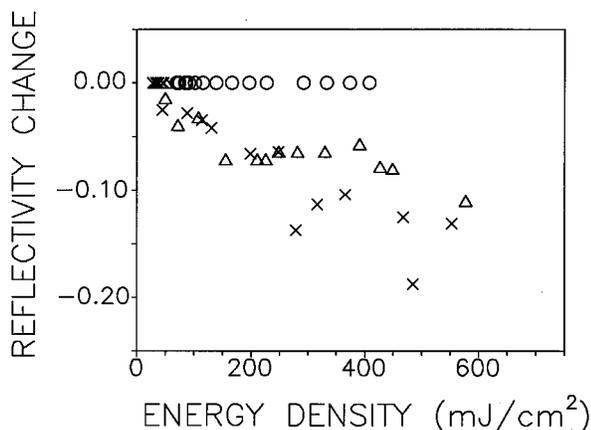


FIG. 3. Reflectivity after irradiation normalized to the initial film reflectivity as a function of the laser energy density. Results obtained in *a*-Ge films of thickness 30(○), 100(△), and 180(×) nm are shown.

$= 965 \text{ k}$). By assuming an averaged value of $l \approx 76 \text{ nm}$ and taking into account the very different thermal properties of *a*-Ge and *c*-Si, it is not unexpected that the thickness of 80 nm represents a boundary condition between a heat flow process controlled by the thermal properties of the substrate or by those of the remanent amorphous film. Different solidification scenarios are therefore expected for films whose thicknesses are at either side of $\approx 80 \text{ nm}$ as experimentally observed.

In the thinner films (30- and 50-nm-thick films), the heat released during the initial solidification stages is efficiently transferred to the Si substrate. The thermal conductivity of *c*-Si is two orders of magnitude higher than that of *a*-Ge and therefore recalescence is prevented since the liquid cannot increase significantly its temperature after the release of the solidification enthalpy during the initial stages of solidification. Consequently, the large initial supercooling is maintained and the material resolidifies into the amorphous phase. This reasoning is also supported by the fact that no reflectivity changes are observed upon solidification and cooling for energy densities up to the ablation threshold (Fig. 3) and it is in agreement with what has already been reported.⁵ A comparison of the results presented here for the thinner films to those reported by Stiffler and co-workers in Ref. 11, where complete reamorphization of Ge films could not be achieved, indicates that the maximum supercooling induced upon rapid solidification in the thinner films (30–50 nm) should be above 500 K. A somewhat smaller undercooling (445 K with respect to the melting temperature of *c*-Ge) has been estimated in Ref. 16 from heat flow calculations of the solidification process of 50-nm-thick amorphous films on Si substrates assuming an interfacial solidification model. These large values evidence the extremely large heat flow rates that can be achieved for film thicknesses smaller than the thermal diffusion length when a substrate with a large thermal conductivity is used.

The heat transfer to the substrate is significantly slower in *a*-Ge films of thicknesses higher than the thermal diffusion length of the amorphous material. This gives an appreciable increase in the liquid temperature as a result of the initial nucleation of the solid phase and the release of the solidification enthalpy, which is evidenced by a decrease in the rate at which the liquid is consumed. A shoulder appears in the RTR transients [Fig. 1(b) transient (3')] thus indicating that the liquid to solid ratio in the volume probed by the HeNe laser remains nearly constant during a short time interval. The supercooling is then reduced thus promoting the formation of *c*-Ge which is evidenced by the lower reflectivity level of the resolidified material when compared to the as-deposited one. The relationship between the reflectivity decrease and the formation of crystalline phases has been earlier demonstrated by means of Raman spectroscopy.^{5,15}

In order to analyze if crystallization has been induced upon recalescence over the full volume of the molten layer, we have simulated the reflectivity of an *a*-Ge film as a surface layer of *c*-Ge grows in depth. We have developed a computer program based on the theory of Abeles for calculating the reflectivity of an isotropic planar multilayer system together with the optical constants of *a*-Ge¹⁴ and *c*-Ge¹⁹ re-

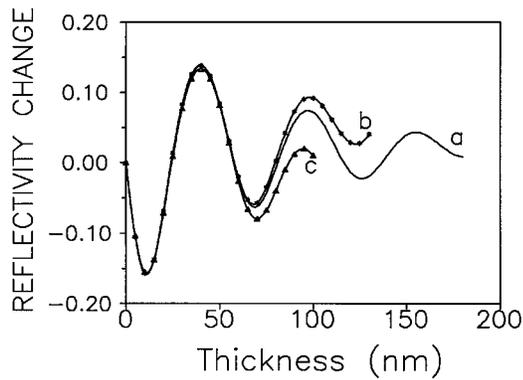


FIG. 4. Simulation of the variation of the reflectivity at $\lambda=633$ nm as a *c*-Ge layer progresses in depth in a 180 (a), 130 (b), and 100 (c) nm *a*-Ge film. Results are normalized to the initial reflectivity of the film.

ported elsewhere. The results obtained in 100, 130, and 180-nm-thick *a*-Ge films are shown in Fig. 4. The comparison of the 15% decrease of reflectivity observed experimentally (Fig. 3) to the theoretical curves suggests that the thickness of the crystallized layer formed at the surface is ≈ 10 nm. This thickness is however much smaller than the melt depths achieved for film thicknesses in the 100–180 nm range. A similar situation has been recently reported during ps laser induced melting of *a*-Ge films on glass and Si substrates¹⁵ and has been interpreted in terms of the formation of a mixture of amorphous and crystalline phases upon solidification.

Our results show that recalescence is only observed in the thicker films and for fluences above an energy density threshold [Fig. 2(a)]. This is related to the existence of a minimum molten layer thickness required for the occurrence of observable recalescence effects, this thickness being comparable to the thermal diffusion length in the amorphous material. One approach to explain this behavior is the assumption that the molten layer thickness inversely limits the maximum value of the thermal gradient in the liquid layer. The lower thermal gradient expected for melt depths above 80 nm is most likely necessary for promoting the bulk solidification of the molten layer as already pointed out by Sameshima and co-workers.¹² Moreover, recalescence effects can only become significant if the liquid temperature is substantially increased following the initial nucleation of the solid phase. Such an increase can only be achieved if a sufficient amount of solid material is nucleated during the first few ns of the solidification process. It is clear that both requirements for the occurrence of observable recalescence effects, namely bulk solidification and enough amount of initial nucleation, are not independent since the nucleation rate is in itself supercooling dependent. The critical melt depth ob-

served (≈ 80 nm) has to thus be related to the supercooling window accessible in the present experimental conditions.

CONCLUSIONS

Two solidification scenarios have been shown to occur in *a*-Ge films on Si depending of the film thickness d to thermal diffusion length l ratio. In the thinner films ($d < l$), reamorphization occurs since the solidification process is controlled by the Si substrate and the heat is efficiently extracted from the melted layer preventing recalescence. In thicker films, ($d > l$) the solidification process is partially controlled by the film itself, and recalescence takes place once a critical volume of molten material is produced. The molten layer thickness threshold for recalescence to occur (≈ 80 nm) is approximately equal to the thermal diffusion length in *a*-Ge and the occurrence of recalescence leads to a solidification process at higher temperatures which promotes the nucleation of the crystalline phase.

ACKNOWLEDGMENT

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