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Relaxation and crystallization kinetics of amorphous germanium films by nanosecond laser pulses

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Relaxation and crystallization of amorphous germanium films on silicon are induced by nanosecond laser pulses. Real time reflectivity measurements and Raman spectroscopy show that amorphous regrowth occurs upon melting and rapid solidification of the film because the thermal conductivity of the silicon substrate is high enough to extract the laser energy absorbed by the film in a very efficient way. The amorphous regrown film is in a relaxed state when compared to the as-grown amorphous material. Further pulses induce fast crystallization of the film. An increase of the melting threshold is found upon relaxation and crystallization of the film.

I. INTRODUCTION

Crystallization of amorphous semiconductors has been the subject of many studies either to produce crystalline material or to study the stability of the amorphous phase. It has been shown that the crystallization process can be initiated by the relaxation of the amorphous phase. The continuous release of heat upon stress relaxation leads to an amorphous state of lower Gibbs free energy.¹ Different stress states (unrelaxed, partially relaxed, and fully relaxed) have been found in amorphous Si depending on the preparation method and thermal treatments. These stress states have different melting temperature^{2,3} and thermal conductivities.⁴

Several attempts have been made to study nucleation phenomena in amorphous semiconductors⁵⁻⁸ since it has been pointed out they have a critical influence on the formation of grained or single-crystalline material. Pulsed laser annealing is very suitable to study such nucleation phenomena^{7,8} in addition to relaxation processes.^{2,4} It is possible to study the behavior of the amorphous materials close to their melting temperature^{4,7} and melting—rapid solidification processes at very high rates and involving very large undercoolings.⁸ Pulsed laser melting of Si films has shown that above a critical thickness, the solidified material crystallizes due to recalescence leading to polycrystalline films with a grain size which depends on the film thickness.⁹

The aim of this work is to study the crystallization kinetics of amorphous Ge films under nanosecond laser irradiation and to analyze the presence of relaxation processes in the amorphous phase. Since the melting threshold under short pulses is very sensitive to the initial state of the material (amorphous—relaxed or unrelaxed—or crystalline), several pulses will be accumulated in the same irradiated area. Real time reflectivity measurements during irradiation will allow us to determine any change in the transformation thresholds in addition to studying crystalline phase incubation phenomena and to follow the melting-rapid solidification kinetics. Since Raman spectroscopy is a noninvasive technique and requires no specific specimen preparation as opposed to electron microscopy analytical techniques, it will be used to study the structural transformations induced upon

laser irradiation. It will be shown that amorphous regrowth in a relaxed state occurs upon melting and rapid solidification under the first pulse. The irradiation with a second pulse results in a fast crystallization process and three pulses are enough to saturate the crystallization process. The dependence of the degree of crystallization achieved on the laser energy density and number of pulses is studied.

II. EXPERIMENT

Amorphous 50 ± 1 nm thick Ge (*a*-Ge) films are grown in a dc magnetron sputtering system from a Ge (99.999%) target. The residual pressure is 3×10^{-6} Torr and the operating Ar pressure is 4×10^{-3} Torr. The *a*-Ge films are deposited on Si (100) substrates covered by their SiO₂ native oxide layer and cleaned with organic solvents. During film deposition the substrates are held at room temperature. Their characterization by spectroscopic ellipsometry and transmission electron microscopy (TEM) has shown that the as-grown films are amorphous, homogeneous, and dense with a low fraction of voids.¹⁰

Samples are irradiated in air, by using an ArF excimer laser ($\lambda = 193$ nm, $\tau = 12$ ns). The laser beam impinges the sample at normal incidence, and it is focused by means of a 104 mm focal length cylindrical lens. Energy densities at the target site are up to 320 mJ/cm² with pulse to pulse energy fluctuations of $\pm 5\%$. A pulsed He-Ne probe beam ($\lambda = 633$ nm, $\tau = 1$ μ s) is focused at the center of the irradiated area $\approx 20^\circ$ off its normal and synchronized with the irradiation pulse to record in real time the reflectivity of the sample. A more detailed description of the experimental set-up can be found elsewhere.¹¹

Raman spectroscopy is used to analyze the as-grown film as well as the irradiated areas. A Jharrel–Ash double monochromator spectrometer is used for spectra recording. The exciting radiation is provided by a Spectra Physics-171 Ar⁺ laser emitting at 514 nm. The 500 mW beam is focused on the sample by means of a 30 cm focal length cylindrical lens at an external incidence angle of $\approx 60^\circ$. The exciting light was *p*-polarized whereas the polarization scattered light was not analyzed.

III. RESULTS

Figure 1 shows the reflectivity transients obtained at increasing pulse energy densities (E). Each transient is recorded in a virgin area and its shape is similar to that previously reported in single-crystal materials like Ge,¹² Si,^{11,12} and GaAs.¹³ The arrival of the laser pulse induces an increase of the reflectivity at room temperature (R_s) upon heating and melting of the surface which is followed by a reflectivity decrease due to the cooling and solidification process. There is an inflection in the cooling tail for a fixed value of the reflectivity after which it decreases at a lower rate. This inflection is related to the total disappearance of the liquid phase and hence the reflectivity at this inflection must correspond to that of the solid material at the melting temperature.¹¹⁻¹³ The experimentally determined value is 0.55 ± 0.07 which is 14% higher than the initial reflectivity $R_s = 0.48$. This value is in good agreement with the $\sim 13\%$ increase reported in Ref. 14 for the reflectivity of α -Ge films at the melting temperature. The final reflectivity level is similar or slightly lower ($\leq 4\%$) than the initial one in the whole range of studied energy densities.

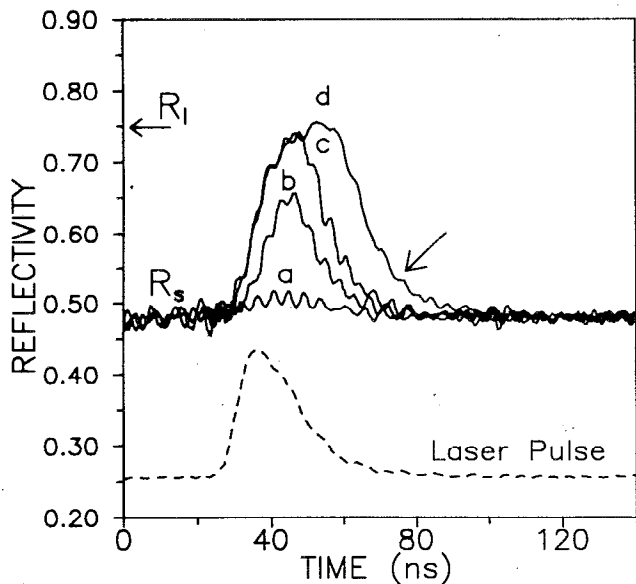


FIG. 1. Reflectivity transients obtained in the as-deposited α -Ge film with a pulse energy density of (a) 35, (b) 69, (c) 98, and (d) 307 mJ/cm^2 . The arrow points out the inflection in the cooling tail. The temporal profile of the laser pulse is also included.

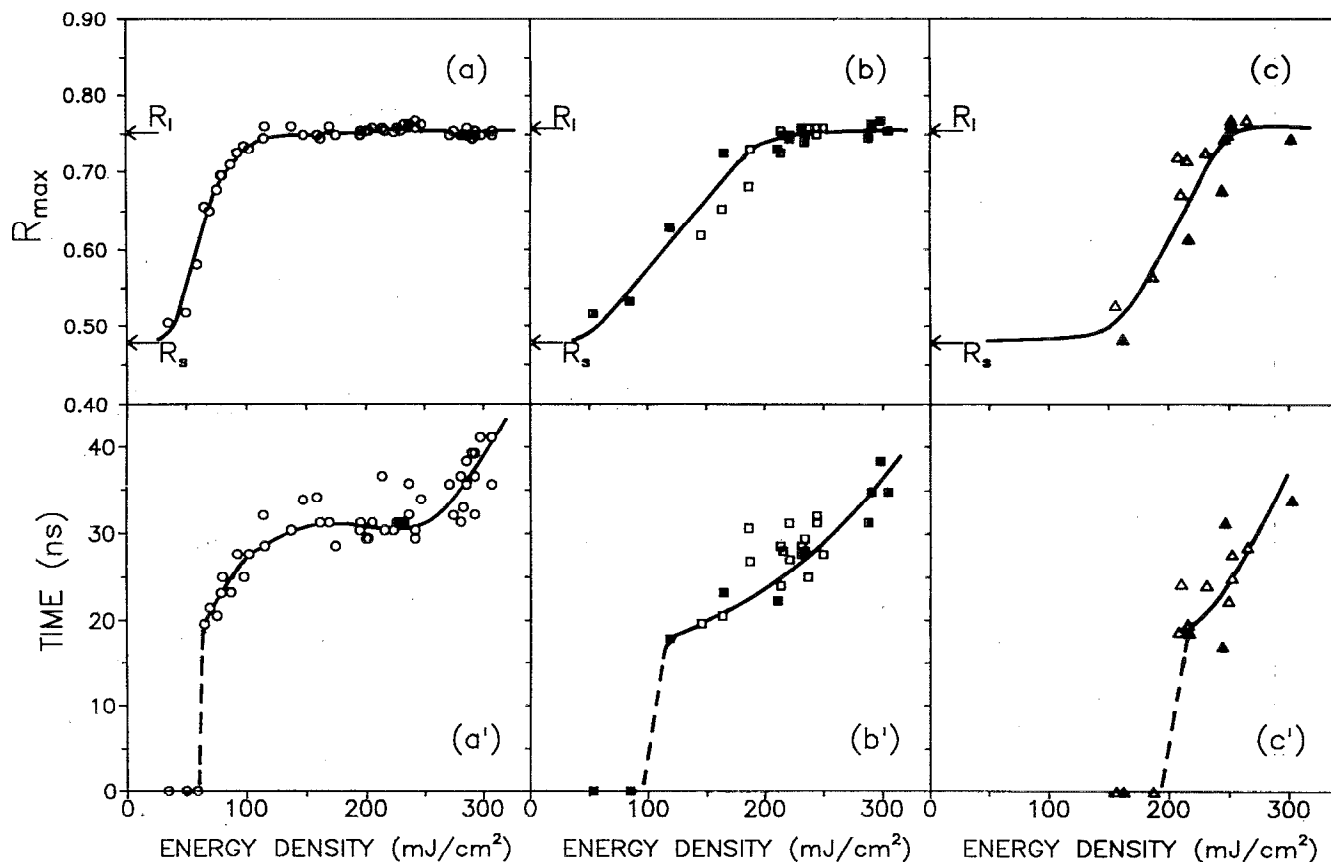


FIG. 2. Maximum reflectivity (a), (b), (c) and melt duration (a'), (b'), (c') as a function of the pulse energy density. Results obtained in the as-deposited α -Ge film (a), (a'), in film areas "pre-treated" with a pulse of 180 (\square) or 290 (\blacksquare) mJ/cm^2 (b), (b') and in film areas "pre-treated" with two pulses of 231 (\triangle) or 290 mJ/cm^2 (\blacktriangle) (c), (c') are plotted.

The maximum of the reflectivity transient as a function of E is plotted in Fig. 2(a). For $E \geq 125$ mJ/cm² all the transients reach a maximum value of 0.75 ± 0.02 . Since the reflectivity of a continuous Ge liquid layer as thick as the penetration depth of the He-Ne probe beam (≈ 20 nm) is $R_l = 0.75$,¹² it is most likely that pulses of $E \geq 125$ mJ/cm² induce the formation of a Ge liquid layer equal to or thicker than 20 nm. This energy density will be referred to hereafter as “continuous” melting threshold. When $60 \leq E \leq 125$ mJ/cm² the maximum of the reflectivity transients shows a strong dependence on the pulse energy density and is always below R_l (0.75) but above the value at the inflection (0.55) which is always observed. Finally, when $E \leq 60$ mJ/cm², the maximum of the reflectivity is lower than 0.55 and no clear inflection is observed after it. All these features support the fact that the melting threshold^{11,12} of the as-deposited films is ≈ 60 mJ/cm².

The melt duration is defined as the temporal width of the transients, with the criteria that the material is molten whenever the reflectivity is above 0.55. In Fig. 2(a') the melt duration is plotted as a function of the pulse energy density. Melt durations shorter than ≈ 20 ns are not observed, strongly supporting the fact that the nucleation of melting proceeds inhomogeneously.^{11,12} Above a pulse energy density of ≈ 125 mJ/cm², a plateau becomes evident in Fig. 2(a'). Once the pulse energy density is increased above ≥ 250 mJ/cm² the melt duration starts to increase again.

The lack of significant differences between the reflectivity of the film before and after irradiation (Fig. 1) indicates that the optical properties at the probe beam wavelength of the irradiated areas are very similar to the ones of the as-grown sample. Since the melting threshold is very sensitive to the existence of structural microscopic changes, the material behavior under multi-pulse irradiation is studied. Several areas of the as-grown sample are “pre-treated” with a pulse of energy density above the “continuous” melting threshold (180 and 290 mJ/cm²). These areas are subsequently irradiated with a second pulse of increasing energy density. Although the reflectivity transient shape by the second pulse is the same as that shown in Fig. 1, the dependence of both maximum reflectivity and melt duration on the pulse energy density is clearly different as can be seen in Figs. 2(b) and 2(b'), respectively. The melt duration increases now continuously while melting threshold (≈ 112 mJ/cm²) and “continuous” melting threshold (≈ 215 mJ/cm²) have shifted to higher energy densities. Moreover the results do not depend on the energy density of the first “pre-treating” pulse, provided that the energy density of this pulse is enough to melt the material surface.

An additional shift of the melting thresholds is induced when the as-grown sample is “pre-treated” with two laser pulses of equal energy density above the “continuous” melting threshold (231 or 290 mJ/cm²). From Figs. 2(c) and 2(c') it can be seen that both the melting threshold and “continuous” melting thresholds have shifted to even higher values, ≈ 212 mJ/cm² and ≈ 250 mJ/cm², respectively, and this shift is again independent of the energy density of the “pre-treating” pulses. The accumulation of further “pre-treating” pulses induces no additional increase of the melting thresh-

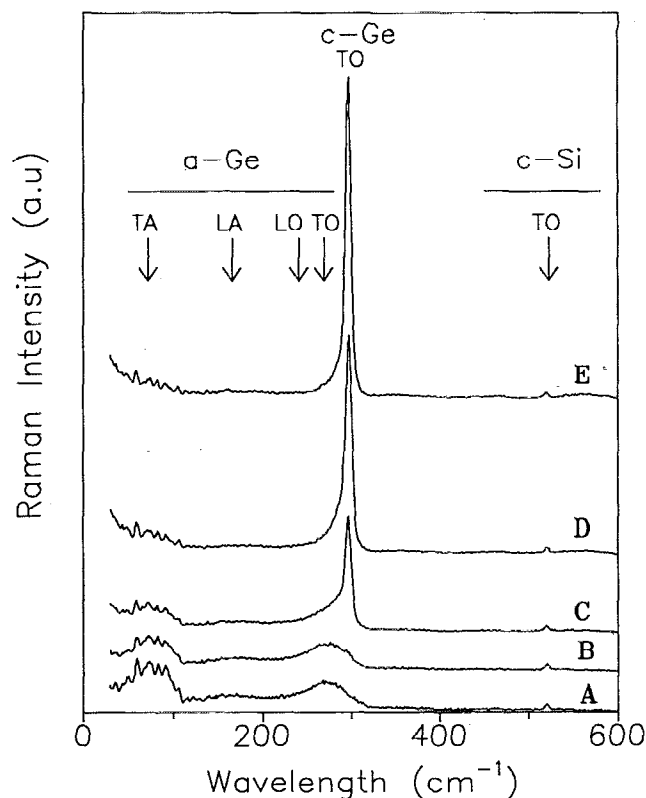


FIG. 3. Raman spectra of as-deposited (A) *a*-Ge film, (B) a film area irradiated with a pulse of 290 mJ/cm², and (C–E) film areas “pre-treated” with a pulse of 290 mJ/cm² and a second pulse of (C) 53, (D) 85, and (E) 164 mJ/cm².

olds which indicates that the process of transformation has reached a saturation.

The irradiated areas are analyzed by Raman spectroscopy which is a technique sensitive to the presence of structural changes beyond resolution of other techniques. In Fig. 3 some representative spectra are plotted. The small peak at 520 cm⁻¹ corresponds to the transverse optic (TO) phonon of the single crystalline Si substrate (*c*-Si) and has been used to normalize the intensity of the spectra shown. The spectrum labeled A corresponds to the as-deposited sample. The structure overlapping the Ge transverse acoustic (TA) peak is due to the pure rotational spectrum of air. Spectrum B is taken in an area irradiated with one pulse of 290 mJ/cm², thus well above the “continuous” melting threshold of the as-grown film (125 mJ/cm²). Although there is no clear evidence of crystalline structure and the spectrum shape is fairly close to that of the as-grown film, some differences can be mentioned. In spectrum B, the half width $\Gamma/2$ of the Ge TO peak measured at the high wavenumber side to avoid influences of the nearby longitudinal optic (LO) peak is 25.5 cm⁻¹ which is again lower than the corresponding value of the as-grown film (28.0 cm⁻¹).

Spectra C, D, and E are obtained in areas which have been “pre-treated” with a pulse of 290 mJ/cm² and have received a second pulse with increasing energy densities. The TO peak due to crystalline Ge (298 cm⁻¹) becomes evident in these spectra, being more intense as the energy density of

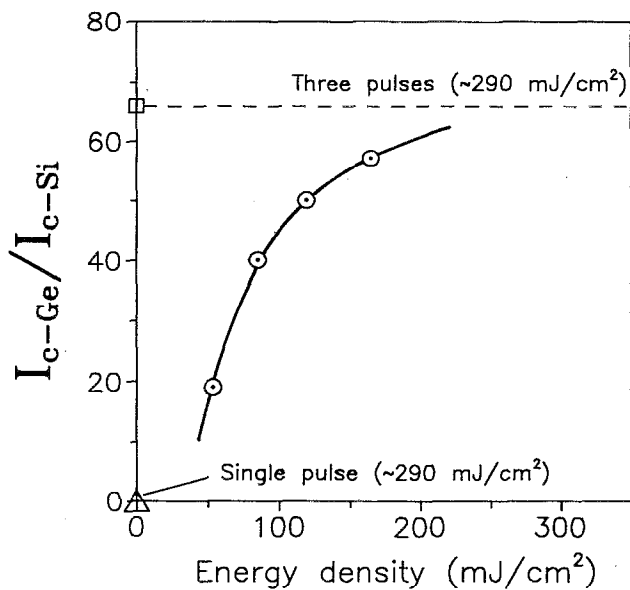


FIG. 4. Intensity ratio between the TO crystalline Ge peak to TO c-Si peak obtained in film areas "pre-treated" with a pulse of 290 mJ/cm² and irradiated with a second pulse, as a function of the energy density of the second pulse. Results obtained in areas irradiated with a single 290 mJ/cm² pulse (Δ), and three pulses of 290 mJ/cm² (\square) are also included. Line is to guide the eye.

the second pulse is increased. Furthermore, a broad structure centered at ≈ 580 cm⁻¹ appears, which corresponds to the second order spectrum of crystalline Ge.¹⁵ In addition, the TA, longitudinal acoustic (LA), and LO structures decrease. In spectrum E the crystalline Ge TO peak is the main feature but there is still some amorphous structure which is evidenced in the tail of the TO peak at the short wavelength side. This tail is due to TO phonons not centered in the Brillouin zone and it is a clear indication of some remaining disorder in the Ge film.¹⁶ The degree of crystallization after the second pulse can be evaluated through the evolution of the intensity of the crystalline Ge TO peak normalized to the c-Si substrate peak intensity. The results plotted in Fig. 4 are obtained in film areas "pre-treated" with a pulse of 290 mJ/cm². It is seen that the degree of crystallization tends to a saturation value. This value is fully reached upon irradiation with three pulses of 290 mJ/cm².

IV. DISCUSSION

Upon single nanosecond laser pulse irradiation of amorphous layers of Ge and Si, both crystallization and reamorphization, have been reported.^{9,17,18} Regarding the laser induced crystallization, it has been shown that the local temperature increase produced because the release of the solidification heat during nucleation of *a*-Ge from supercooled melts may induce nucleation of crystalline Ge and explosive crystallization.¹⁷ This process results in a complex polycrystalline structure in depth. On the other hand, amorphous regrowth of laser melted polycrystalline Si films deposited on quartz substrates has been shown to depend on both laser energy density and film thickness.⁹

Our measurements show that the reflectivity of the Ge films at the probe wavelength before and after irradiation with a single pulse are similar. Moreover, the reflectivity value at the inflection in the cooling tail of the transients is in good agreement with the value reported¹⁴ for *a*-Ge at the melting temperature. In addition, Raman spectra show no evidence of crystalline structure after the first laser pulse independently of the irradiation pulse energy density. These results evidence that a 50 nm thick *a*-Ge film deposited on c-Si does not crystallize under irradiation with a single nanosecond laser pulse in a wide energy density range. This suggests that the absorbed energy from the laser is very efficiently transferred from the film to the Si substrate due to the small thickness of the film compared to the heat diffusion length. Then, the heat flow is controlled by the Si substrate⁴ and because of its high thermal conductivity, the cooling and solidification of the film is faster enough to avoid its crystallization. This explanation holds for all the studied energy densities and as a consequence, solidification in amorphous phase is found.

The amorphous film formed upon irradiation exhibits nevertheless different properties than the as-grown film. The melting and "continuous" melting thresholds increase from 60 to 112 mJ/cm² and from 125 to 215 mJ/cm², respectively [Figs. 2(a) and 2(b)]. The Raman spectra show that the half width $\Gamma/2$ of the Ge TO peak has decreased from ≈ 28.0 to ≈ 25.5 cm⁻¹. Since $\Gamma/2$ is related to the average bond angle distortion $\Delta\theta$ (in degrees) through^{19,20}

$$\Gamma/2 \approx [(2.65\Delta\theta)^2 + 9^2]^{1/2},$$

we estimate $\Delta\theta \approx 10.0^\circ$ for the as-deposited film and $\Delta\theta \approx 9.0^\circ$ for the irradiated film. By using the expression given in Ref. 3 for the stored strain energy due to bond angle distortion, values of ≈ 14 kJ/mole and ≈ 11 kJ/mole are found for the as-grown and the irradiated material, respectively, which evidence that a net amount of energy (≈ 3 kJ/mole) has been released upon melting and amorphous regrowth. Calorimetric studies carried out on *a*-Ge samples prepared by ion implantation¹ as well as Raman spectroscopy studies of rf sputtered *a*-Ge films deposited at several substrate temperatures²¹ have shown that the structural relaxation of the films is accompanied by a release of heat in the 6–9 kJ/mole range. As a consequence, the Gibbs free energy is lowered and the melting point increases. Moreover it has been shown that structural relaxation in *a*-Si involves both a heat release³ and an increase of the thermal conductivity of the film⁴ and then a higher melting threshold upon relaxation is found.^{3,4} These findings point out that in our case the as-grown amorphous Ge structure has been relaxed upon irradiation.

The relaxed material must be considered as an intermediate state between the as-grown amorphous material and the crystalline material since a low energy density pulse (53 mJ/cm²—well below the melting threshold) is enough to induce some crystallization (see spectrum C in Fig. 3). The reflectivity transient obtained under these conditions is typical for a solid-state heating process¹⁴ with a maximum transient reflectivity change of $\approx 7\%$ above the initial value and no inflection in the cooling tail. The heating time is estimated

to be ≈ 27 ns from the full width half maximum (FWHM) of the reflectivity transient which gives an upper limit for the time needed to trigger the crystallization process. This value is several orders of magnitude lower than the incubation time of *a*-Ge films determined by *in situ* TEM annealing,²² even when the data are extrapolated to temperatures around the melting point of *a*-Ge (965 K).

This "fast" crystallization seems to be different from the explosive crystallization which has been widely reported in *a*-Ge²³ and *a*-Si obtained by ion-implantation.²⁴ In our case in order to induce the crystallization process, the film has been previously modified by a "pre-treating" pulse. Therefore, the most likely explanation for the "fast" crystallization is the presence of a high density of preferential sites for crystallization ("nucleants") produced upon melting and amorphous regrowth under the first pulse. The differences found on the crystallization triggering time in *a*-Si layers¹⁸ have provided evidence of these nucleants even when the size and/or the concentration of possible crystalline clusters are resolvable neither by Raman²⁵ nor by Rutherford backscattering channeling measurements.¹⁸

Finally, when the *a*-Ge film is "pre-treated" with two 290 mJ/cm² pulses a new shift of the melting thresholds is observed [see Figs. 2(c) and 2(c')]. The extrapolation of results of Fig. 4 indicates that *a*-Ge is completely crystallized after being irradiated with two pulses of 290 mJ/cm². Then, a third pulse is impinging on a crystalline material. It is well known that crystalline Ge has a melting temperature above that of the amorphous phase.¹ Moreover, as it has been reported in Si,⁴ a thermal conductivity of the crystalline Ge phase higher than that of the amorphous Ge phase is expected. Therefore a shift to higher energies of the melting threshold upon crystallization is also expected as experimentally observed.

V. CONCLUSIONS

Amorphous regrowth occurs upon nanosecond laser induced melting and rapid solidification of *a*-Ge films on *c*-Si due to the efficient heat flow through the *c*-Si substrate. Raman spectroscopy shows that the amorphous regrown film is in a structural relaxed state. Further pulses induce fast crys-

tallization of the film which suggests the presence of preferential sites for crystallization in the relaxed amorphous film. The melting threshold of the Ge film shifts to higher values upon relaxation and crystallization.

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