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Excimer laser melting of GaAs: Real-time optical study

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In situ real-time reflectivity measurements have been made in GaAs under ArF excimer laser ($\lambda = 193$ nm) irradiation. The results obtained provide a reflectivity value for the solid material at the melting temperature of 0.44 and for the liquid of 0.63, both at 633 nm. The reflectivity values obtained for fluences just above the melting threshold ($E = 225$ mJ/cm²) show that melting proceeds inhomogeneously, the near-surface region being formed by a mixture of solid and liquid phases. The comparison of these results to those obtained previously for irradiation of single-crystalline Si and Ge shows that inhomogeneous melting can be a general phenomenon at least in semiconductors. Higher fluences ($E > 300$ mJ/cm²) are necessary to induce an homogeneous melted layer on the surface of the irradiated material.

In this communication we report for the first time results of real-time reflectivity measurements during the irradiation of crystalline GaAs with ArF excimer laser ($\lambda = 193$ nm) pulses. In spite of the technological interest of this material, the poor knowledge or the lack of data about its thermal properties has prevented detailed studies of pulsed laser annealing (PLA) in GaAs.¹ Experimental studies providing data about the evolution of the optical properties of the material, the melting threshold, or the evolution of the melt duration as a function of the pulse energy density are necessary both to achieve a proper knowledge of the physical properties of GaAs via thermal model calculations and to improve the capability of controlling dopant profiles in laser-induced diffusion applications.²

In a previous work³ a systematic study on the characteristics of the early stages of melting in crystalline Si under ultraviolet (uv) and visible nanosecond laser pulse irradiation was reported. It was shown that laser-induced melting in Si proceeds inhomogeneously and that only for fluences above a threshold, is an homogeneous melted layer formed at the surface. The work reported here also aims to analyze if inhomogeneous melting is a more general phenomenon occurring in other semiconductors such as GaAs.

The irradiations and real-time optical measurements are performed using a two-beam system. The irradiation beam is provided by an ArF excimer laser ($\lambda = 193$ nm, pulse length = 12 ns) which is partially focused on the sample using a 104-mm focal length cylindrical lens. The optical reflectivity of the sample is monitored in real time using a HeNe laser ($\lambda = 633$ nm) pulsed to 2800 ns. It is incident at 12° off the surface normal and is focused to a $1/e$ beam radius of ≈ 160 μ m in the center of the irradiated region. The irradiation beam is homogeneous in the probed area within 5% and its energy density is varied during the experiment in the range of 125–450 mJ/cm². A narrow-band interferential filter at 633 nm is located in front of the

detector in order to suppress any spurious contribution caused by near-band-gap laser-induced photoluminescence (PL) (see Ref. 4, for example). Further details can be found elsewhere.^{3,5}

The samples used are Zn⁺-doped, *p*-type ($p = 1 \times 10^{17}$ cm⁻³), (111) GaAs wafers chemically etched a few minutes before irradiation in 3H₂SO₄:1H₂O₂:1H₂O and later in HCl to remove residual oxides. A preliminary set of irradiations both in vacuum (4×10^{-5} Torr) and in air are performed. For a given energy density above the melting threshold, the melt duration is longer in the former case and the irradiations induce nonreversible changes in the reflectivity of the sample surface which shows damage by visual inspection. Furthermore, when irradiations are made in vacuum, only the first pulse induces strong PL emission from the sample. The observed features are most likely related to a degradation of photoluminescence efficiency due to a strong preferential As loss. This interpretation is consistent with earlier results obtained when irradiating GaAs with ruby laser pulses in ultrahigh-vacuum (UHV) conditions. The ratio of As/Ga evaporated atoms was found to be as high as 10 for fluences slightly higher than the energy density melting threshold.⁶

Upon irradiation in air the sample recovers its initial reflectivity level, no significant damage is appreciated in the irradiated surface, and PL emission is still observed after multishot irradiation. It can be then concluded that, when irradiating in air in the studied energy density interval, the preferential As loss, if any, is extremely low. The present study is therefore performed at atmospheric pressure. However, in order to avoid both cumulative damage in the irradiated region and possible oxidation effects,⁷ each region is irradiated only once.

In Fig. 1 several reflectivity transients obtained for increasing pulse energy densities are plotted. The initial and final reflectivity levels in the transients seem to be different because the material requires times longer than those shown in Fig. 1 to recover the initial reflectivity value. It

FIG. 1. Reflectivity transients obtained upon irradiation with ArF excimer laser pulses with increasing energy densities: (a) 181 mJ/cm², (b) 252 mJ/cm², (c) 374 mJ/cm², (d) 412 mJ/cm², and (e) 438 mJ/cm². The dashed line corresponds to the irradiation pulse temporal profile. The inset shows how the reflectivity value at the inflection R_{inf} is determined. R_{max} indicates the maximum transient reflectivity level.

can also be seen in Fig. 1 that both the “width” and the maximum level (R_{max}) of the reflectivity transients are a function of the pulse energy density E . Three different regimes can be distinguished.

In regime A ($E \geq 300$ mJ/cm²) all the transients induced reach a maximum reflectivity level equal to 0.63 ± 0.02 which is consistent with the developing of an homogeneous melted layer on the surface. The observed value is in rather good agreement with the one reported previously (0.67) for the reflectivity of liquid GaAs at 633 nm.⁶ The small discrepancy between the two values may be related to a Ga enrichment of the melted surface layer when the experiment is performed in UHV conditions.⁶ Therefore, from now on we will assume $R_L = 0.63$ as the reflectivity of liquid GaAs at 633 nm.

The reflectivity maximum is followed by a decay caused by the solidification process. The decay follows a straight line and an inflection is observed when the reflectivity reaches a certain value. This can be more clearly appreciated in the inset which also shows schematically the procedure followed to determine the reflectivity value at the inflection R_{inf} . These values are plotted in Fig. 2 and it is seen that within this energy regime, the reflectivity value at the inflection is nearly constant, $R_{\text{inf}} = 0.44 \pm 0.02$. The temporal position of the inflection depends on the pulse energy density but the shape of the transients is not dependent on E once the inflection is reached. The presence of an inflection in the cooling tail of the reflectivity transients related to the end of the solidification process has been observed before for the case of Si and Ge under uv and visible nanosecond laser pulse irradiation.^{3,8}

In regime B ($225 \text{ mJ/cm}^2 < E < 300 \text{ mJ/cm}^2$) the maximum transient reflectivity level is always below R_L and above 0.44 and it is a strongly increasing function of the pulse energy density. The decay of the transients presents the characteristic inflection described for the previous regime. R_{inf} is again constant and has the same value found in regime A (see Fig. 2). Once the inflection is reached the subsequent behavior of the reflectivity does not depend on the pulse energy density.

FIG. 2. Reflectivity value at the inflection R_{inf} as a function of the pulse energy density. A, B, and C denote the three different regimes observed as the pulse energy density decreases.

Finally in regime C ($E \lesssim 225$ mJ/cm²) the maximum of the reflectivity transients is always below 0.44 and no clear inflection is observed after the transient maximum.

In Fig. 3 we have plotted the maximum transient reflectivity values R_{max} as a function of the pulse energy density. The comparison of Figs. 2 and 3 strongly suggests that the energy density melting threshold is ≈ 225 mJ/cm². The inflection (regimes A and B) occurs at the time at which the liquid phase completely disappears³ leaving a solid material at the melting point. When energy absorption ends (see the pulse profile in Fig. 1), the material cools down, its cooling rate being determined only by the thermal properties of the material. This behavior is mirrored by the behavior of the reflectivity after the inflection which, as we have mentioned above, does not depend on the pulse energy density. The absence of inflection when the maximum of the reflectivity transient is below 0.44 and the sharp increase of reflectivity observed in Fig. 3 for

FIG. 3. Maximum transient reflectivity R_{max} as a function of the pulse energy density. A, B, and C denote the three different regimes observed as the pulse energy density decreases.

FIG. 4. Melt duration τ_m as a function of the pulse energy density E .

$E > 225 \text{ mJ/cm}^2$ and related to the presence of the liquid phase at the surface give further support for this reasoning. It allows us to conclude that the reflectivity of the solid material at the melting point is $R_s(T_m = 1515 \text{ K (Ref. 9)}) = 0.44 \pm 0.02$. The reflectivity changes observed in regime C obey the temperature-related changes in the optical constants of the material with no phase transformation.

Once the reflectivity of the solid at the melting point has been determined, $R_s(T_m) = 0.44$, we can analyze the physical meaning of the existence of reflectivity values between $R_s(T_m)$ and $R_L(T_m)$. It is clear from Fig. 3 that the laser-induced transition between solid and liquid in GaAs is not optically abrupt but occurs instead over a finite energy density interval ($225\text{--}300 \text{ mJ/cm}^2$). A similar behavior has been reported for irradiation of single-crystalline Si and Ge under uv and visible nanosecond laser pulses^{3,8} and has been explained in terms of inhomogeneous melting. A proper addressing of this topic can be found there but basically it is assumed that the near-surface region does not melt homogeneously, being formed, rather, by a mixture of solid and liquid phases with a non-well-defined solid/liquid interface. Another possible explanation of this behavior, is related to the evolution of the reflectivity of the liquid/solid bilayer as a function of the liquid layer thickness.¹⁰

The final evidence of whether this behavior obeys the former or the latter model is provided by the evolution of the melt duration τ_m as a function of the pulse energy density. τ_m has been determined considering that the material is melted when its reflectivity is above that of the solid at the melting temperature. The optical model yields to a melt duration continuously increasing from zero as the energy density increases whereas the inhomogeneous melting model is consistent with a non-null minimum melt duration.⁸ Figure 4 shows the evolution of τ_m vs E . Melt durations shorter than $\approx 16 \text{ ns}$ are not experimentally observed giving support to the inhomogeneous melting

model. It is also seen in Fig. 4 that the melt duration follows a near-linear behavior with two different slopes. The slope change ($E \approx 300 \text{ mJ/cm}^2$) occurs when the energy density is high enough to induce an homogeneous melted layer on the surface. The existence of a slope change separating the homogeneous and inhomogeneous melting regimes in the evolution of τ_m vs E has been reported earlier for crystalline Si.³

In laser-induced diffusion experiments the strong concentration of diffusant species may strongly reinforce both the inhomogeneous melting and solidification phenomena. Therefore, in the inhomogeneous melting regime, diffusivities intermediate between those corresponding to solid- and liquid-state diffusion processes are expected. The inhomogeneous impurity distribution for energies slightly above the melting threshold and long diffusion tails at the end of the melted layer in pulsed laser-induced diffusion experiments² can be explained on this basis. This effect has also been observed in cw laser-induced diffusion when processing around the melting threshold¹¹ or at the end of the diffusion profiles when processing above the melting threshold.¹²

In summary, a real-time optical study on uv laser irradiation of GaAs has been performed. We have determined the reflectivities at 633 nm of both solid and liquid GaAs at the melting temperature to be, respectively, 0.44 and 0.63. It has also been established that melting proceeds inhomogeneously, the energy density melting threshold at 193 nm being $E = 225 \text{ mJ/cm}^2$. An homogeneous melted layer is formed on the surface of the irradiated material only for fluences above 300 mJ/cm^2 . The observed behavior indicates that inhomogeneous melting can be a general phenomenon at least in semiconductors.

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