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Recalcescence \textit{after} solidification in Ge films melted by picosecond laser pulses

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Thin amorphous Ge films on glass substrates are irradiated by single picosecond (ps) laser pulses and the induced melting and solidification process is followed by means of real-time reflectivity measurements with ps resolution using a setup based on a streak camera. Due to the excellent time resolution achieved in single exposure, the recalcescence process occurring upon solidification can be completely resolved by means of an all-optical technique. The results are consistent with the bulk nucleation of the amorphous phase in the supercooled liquid at an extremely large nucleation rate. The massive release of solidification heat causes the reheating and partial remelting of the film after its complete solidification. The occurrence of recalcescence \textit{after} solidification is responsible for the formation of the crystalline phase finally obtained. ©1999 American Institute of Physics.

Pulsed-laser melting of semiconductors may lead to a variety of different solidification mechanisms.\textsuperscript{1–11} In this context, the importance of recalcescence phenomena, i.e., the reheating of the material due to the release of latent heat during solidification, has already been pointed out by several authors.\textsuperscript{3,6,7,9,10,11} In a comprehensive work, Sameshima and Usui\textsuperscript{7} demonstrated that recalcescence effects can be reduced or enhanced by a proper variation of the film thickness and the thermal conductivity of the substrate. But only by means of real-time reflectivity (RTR) and real-time conductance (RTC) measurements the dynamics of recalcescence phenomena could be studied. All authors appear to agree on a model which assumes that recalcescence effects take place \textit{during} the solidification process, thus slowing it down and favoring the formation of the crystalline phase. The time resolution of these techniques is several nanoseconds (ns), which is generally considered to be sufficient to follow the main features of the solidification processes. Nevertheless, solidification processes might occur much faster than the duration of the ns laser pulses\textsuperscript{7} used in most of the experiments reported, and thus, their complete understanding might require sub-ns resolution measurements.

In this letter, we provide direct evidence for the occurrence of massive recalcescence \textit{after} the complete solidification of the material. This has been possible by means of RTR measurements with picosecond (ps) resolution. The excellent time resolution achieved also enables us to determine the high nucleation rate at the early stage of solidification. The results obtained imply that the amorphous phase is nucleated directly from the supercooled melt through a bulk solidification process. The occurrence of massive recalcescence is found to catalyze the subsequent amorphous-to-crystalline transformation.

The material system under study is formed by a 50-nm-thick amorphous Ge film grown by dc sputtering on a glass substrate. As-grown areas of the specimen were irradiated by single 30 ps laser pulses at 583 nm. The dynamics of the induced transformations has been followed in real time by measuring the reflectivity changes at the air/film interface by means of a probe laser beam incident at a small angle (7°) and focused at the center of the irradiated area. The probe beam used was either by a He–Ne laser (633 nm) or by a single-mode Ar$^+$ laser (514 nm). The detection system used was either a fast photodetector connected to a transient digitizer for RTR measurements with ns resolution or a streak camera for RTC measurements with ps resolution. More details about the experimental setup can be found elsewhere.\textsuperscript{11} Unlike the common experimental setup based on a pump-and-probe scheme,\textsuperscript{12} our streak camera-based setup permits the measurement of ultrafast processes upon \textit{single laser pulse exposure}.

Figure 1 shows a RTR transient recorded at 514 nm upon irradiation with a single laser pulse at a fluence of 65 mJ/cm$^2$. The actual duration of the laser pulse itself (30 ps) can be resolved in an entire time window of 1 ns, which confirms the excellent time resolution of the experimental setup. The induced increase of the reflectivity by $\approx$50% is consistent with the melting of the material surface.\textsuperscript{11,13} It is remarkable that the reflectivity rise, and thus, the melting process, occurs within the pulse duration as predicted by several authors.\textsuperscript{14,15} Similar results (fs laser pulse melting of...
also the maximum values obtained by ps-resolution measurements. This recalescence process, which involves par- 

The solidification process indeed occurs mainly in the ns time scale, which permits, even by means of ns-resolution measurements, estimating the solidification time and the initial melt depths with high precision. The $t_s$ values are defined as the time during which the reflectivity remains 14% above the initial value and the $z_s$ values can directly be deduced from the $R_s$ values with the help of optical calculations and following the description.

At low fluences [Fig. 2(a)], solidification occurs interfa-

The solidification process indeed occurs mainly in the ns time scale, which permits, even by means of ns-resolution measurements, estimating the solidification time and the observation of film recalescence at high fluences [the shoulder in Fig. 2(b)]. Nevertheless, substantial differences in the dynamics of recalescence can be observed when measured with ps resolution. What has seemed to be a shoulder in the ns-resolution RTR transient [Fig. 2(b)]. The dip between the two maxima is well below the 14% level, which corresponds to the reflectivity of the amorphous solid film at the melting temperature, and thus evidences that the film has solidified completely before massive recalescence occurs. Such a recalescence process taking place after the complete solidification of the material has not earlier been reported in the literature. Whether this fact is a consequence of the use of ps laser pulses or a general feature of the solidification dynamics in thin semiconductor films, and thus occurring also under ns laser pulse irradiation, cannot be decided at this point. Nevertheless, it is clear that measurements with sub-ns resolution are also essential in ns laser pulse irradiation experiments in order to study in detail the recalescence process.

A very detailed description of the entire melting and solidification process at high fluences can be obtained following the ps-resolution transient shown in Fig. 2(b). Melting occurs within the pulse duration, and during the following few ns the molten volume cools down by heat conduction to the substrate, leading to a highly supercooled liquid. Due to the high thermal conductivity of liquid Ge, the liquid reaches an internal thermal gradient as low as 0.01 K/nm during the cooling process, as reported elsewhere. Then, massive nucleation of the solid phase throughout the supercooled liquid initiates solidification, which leads to a fast decrease of the reflectivity to a level consistent with a completely solidified, although still hot material. The release of the solidification enthalpy then becomes dominant, leading to an increase of the temperature to the melting point ($\Delta R = 14\%$). This recalescence process, which involves partial remelting of the solid phase obtaining a state of reduced supercooling, promotes the formation of the crystalline phase. The final state of the material consists of a mixture of amorphous and crystalline phases with a maximum crystalline fraction of ~60%, as shown in Ref. 11.

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FIG. 2. Comparison between reflectivity transients at (a) 19 mJ/cm$^2$ and (b) 65 mJ/cm$^2$ measured at 633 nm with ns resolution (dashed curves) and at 514 nm with ps resolution (solid curves). The dotted lines indicate the reflectivity change predicted for $\alpha$-Ge at its melting temperature.

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in Ref. 11. From these data, the solidification velocities $v_s = z_s/t_s$ have been calculated and plotted in Fig. 3 as a function of fluence. Their evolution shows clearly that there are two solidification regimes separated by the recalescence threshold at 54 mJ/cm$^2$, which can distinctly be appreciated by a change in the trend of $v_s$: In the interfacial reamor-
phization regime at low fluences, $v_s$ increases linearly from
1.7 to 4 m/s. In the high fluence regime, where partial crys-
tallization occurs via bulk solidification, and thus, no solidi-
fication front propagates, the behavior of $v_s$ remains appar-
tently constant. The continuous transition of the behavior of
$v_s$ from the low to the high fluence regime clearly indicates
that also in the latter regime solidification is initiated by the
nucleation of the amorphous phase, which then is partially
transformed into the crystalline phase through recalescence.
This interpretation is further supported by our observation
that the transient shape changes only by the appearance of
the second maximum when increasing the fluence above the
recalescence threshold. The presence of a still considerable
amount of amorphous material (40\%) in the finally solidified
film also indicates that the amount of latent heat released
during the initial nucleation and growth process of the amor-
phous phase is not sufficient to promote the crystallization of
the entire film.

In the case of bulk solidification, an estimation of the
minimum nucleation rate in the supercooled liquid can be
made following the calculations of Sameshima and Usui.\textsuperscript{7}
Assuming that the solid nuclei grow spherically with a diam-
eter $d$, a minimum value for the nucleation density is given
by the inverse of the sphere volume $[4\pi(d/2)^3]/3$. Taking
into account the fact that the mean value of the crystal size
has been determined\textsuperscript{16} to be $\approx 10$ nm, a minimum nucleation
density of $1.9 \times 10^{24}$ events/m$^3$ is obtained. Dividing this
value by the mean value of the solidification time, a mini-
imum value of $1.8 \times 10^{32}$ events/m$^3$s for the nucleation rate is
obtained. This value is more than one order of magnitude
above those earlier reported for rapid solidification in el-

dimentary semiconductors. This indicates that the degree of
supercooling prior to bulk solidification has to be higher than
the 530 K value reported by Stiffler, Thompson, and Peercy\textsuperscript{6}
on ns laser pulse irradiation of 300-nm-thick $\omega$-Ge films
on a SiO$_2$ substrate. The same authors found evidence for
solidification being initiated by nucleation of the amorphous
phase, which subsequently transformed to crystalline, cata-
lyzed by recalescence. Our results are thus in good agree-
ment with their observations, although they could not ob-
serve a temporal separation between the solidification and
the recalescence process, either due to the limited time reso-

dition or the larger thickness of the films they used.

In summary, RTR measurements with ps resolution in
single exposure improve considerably our understanding of
pulsed-laser melting and solidification processes in semicon-
ductors and reveal exciting features. Ge films are found to
solidify completely before recalescence takes place, cata-
lizing the amorphous-to-crystalline transformation. The
supercooling prior to solid-phase nucleation and the minimum
nucleation rate are $> 530$ K and $2 \times 10^{32}$ events/m$^3$s, re-
spectively. The interface velocity of the reamorphization front
at low fluences could be determined precisely, showing a lin-
early increasing behavior with fluence from 1.7 to 4 m/s up
to the recalescence threshold at 54 mJ/cm$^2$. This work has been partially supported by CICYT
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