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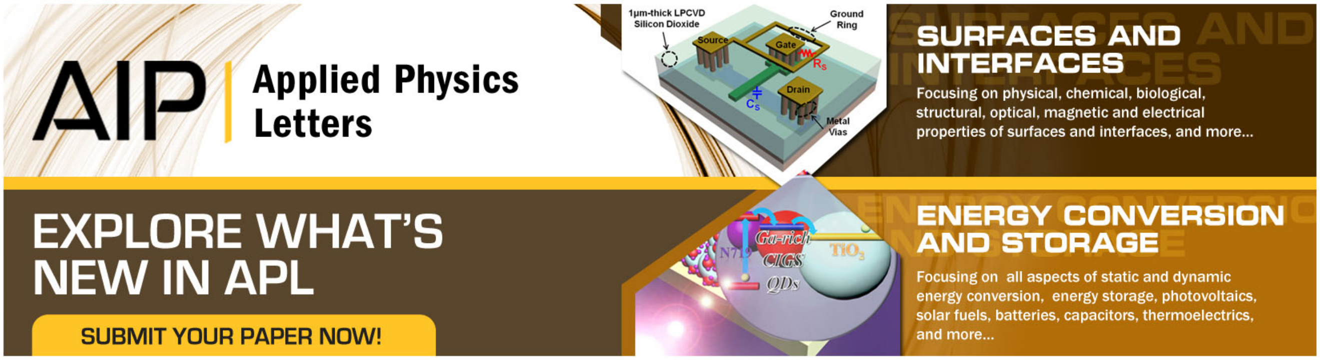

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Pressure-induced transient structural change of liquid germanium induced by high-energy picosecond laser pulses

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The temporal evolution of the reflectivity of germanium at 514 nm upon irradiation with single high-energy picosecond laser pulses has been measured using a streak camera. It is found that, for a well-defined high fluence range, the reflectivity of the laser-induced molten phase attains a value of 0.85, considerably above the value reported for liquid Ge in thermal equilibrium (0.75). This behavior is consistent with a strong densification of the liquid phase remaining after the explosive vaporization of a thin surface layer. Within the specified fluence interval, this anomalously high reflectivity state is independent of the fluence and lasts tens of nanoseconds. Both characteristics point to the presence of a pressure-induced transient structural change in liquid germanium. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1940117]

The interaction of ultrashort laser pulses with semiconductor materials has been a subject of increasing interest over the last decades. Ultrafast phase transitions have been observed in several materials like Si,[1,2] GaAs[2] and Ge[3] using pump-and-probe experiments aimed at analyzing the structural transformation dynamics for laser pulse durations in the fs and ps ranges. Along with ultrafast phase transitions, the appearance of solid or liquid phase overheating phenomena have received considerable attention. For instance, the reflectivity of overheated liquid Si was reported to remain below that of the equilibrium phase over a time lapse of ~10 ps, comparable to the pulse duration used.[4] Since the liquid phase of covalent semiconductors is metallic, the decrease of reflectivity was attributed to an increase of the electron collision frequency with temperature.

The relaxation behavior of these and other types of laser-induced metastable phases over longer time windows has been much less investigated, the studies being restricted in most cases to time windows of the order of hundreds of ps. In this work we have explored the existence of long-lasting metastable phenomena during laser-induced phase transitions in Ge. For this purpose, we have measured the time evolution of the reflectivity of crystalline Ge (*c*-Ge) over a time interval of about 40 ns after excitation with high-energy ps laser pulses using a streak camera. Since the duration of laser-induced transformations can extend over tens of ns, the use of a streak camera provides an excellent compromise between time resolution and available time window for performing real time reflectivity (RTR) measurements.[5,6] In addition, this approach provides the complete evolution of the reflectivity in a single exposure measurement, unlike pump-and-probe measurements, which require multiple exposures.

The sample studied was an optically polished (100) 0.02 Ω cm *p*-type Ge wafer. Before irradiation, the sample was cleaned to remove organic contaminants using a conventional chemical cleaning procedure. A detailed description of the experimental setup used to carry out the transient reflectivity measurements with sub-ns resolution can be found elsewhere.[6] Essentially, it consists of a ps-pulsed pump laser (584 nm, 30 ps), a μs-pulsed single-mode probe laser (514 nm, 1 μs) and a light detection system used to monitor the time evolution of the sample reflectivity. The probe beam, incident at an angle of 15°, is focused at the center of the area irradiated by the pump beam. The intensity of the reflected probe beam is then measured simultaneously by a single sweep streak camera with sub-ns resolution (350 ps) in a time window of 40 ns and by a fast photodiode connected to a transient digitizer with ns resolution over a longer time window (200 ns). In all cases, an unexposed region of the sample is irradiated by a single laser pulse. The absolute reflectivity values quoted in this work have been obtained by multiplying the experimentally measured relative changes of reflectivity by the reflectivity of *c*-Ge at 514 nm at room temperature. The linearity of the detection system and the accuracy of the normalization procedure used for obtaining absolute reflectivity values have been demonstrated in a previous work[7] in which the known reflectivity values of the molten phases of Ge and Si were routinely reproduced upon ns laser pulse irradiation.

Figures 1(a)–1(c) show several representative reflectivity transients recorded with the streak camera upon ps laser irradiation of the sample at fluences above the melting threshold of *c*-Ge ($F_m = 30\ \mathrm{mJ/cm^2}$). For a fluence of $5.3 \times F_m$ [Fig. 1(a)], the sample reflectivity is observed to increase after the laser pulse within approximately 600 ps, up to a constant reflectivity level (plateau) that lasts a few ns. Subsequently, the reflectivity decreases and reaches a final value, slightly lower than the initial one. Similar features have been widely described in previous studies on laser-induced melting of semiconductors.[5–8] The rapid reflectivity increase corresponds to the formation of an optically thick, highly reflective (metallic) molten layer at the surface. Upon solidification, the reflectivity decreases as the solidification front approaches the surface. Therefore, to a good approximation, the time duration of the reflectivity plateau corresponds to the duration of the melting process (t_{melt}). The reflectivity value reached at the plateau, $R = 0.75$, is in excel-

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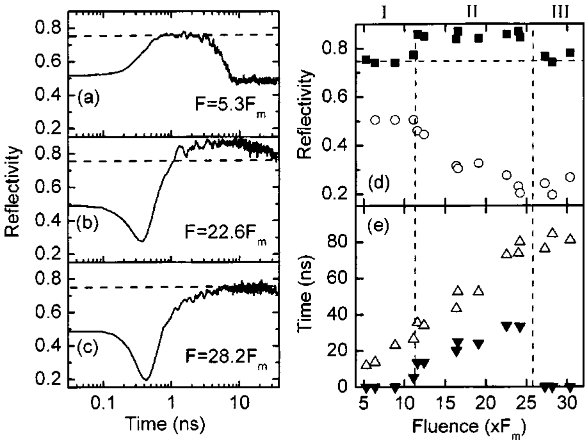

FIG. 1. [(a)–(c)] Time evolution of the reflectivity at 514 nm of *c*-Ge upon 30 ps, 584 nm laser exposure at three fluences normalized to the melting threshold $F_m = 30$ mJ/cm^2. (d) Maximum reflectivity ($R_{\max}$) of the reflectivity transients at the plateau (■) and reflectivity minimum $R_{\min}$ (○) as function of laser fluence. (e) Melt duration t_{melt} (△) and period of time $t_{R>R\ell\text{-Ge}}$ over which $R > R_{\ell\text{-Ge}}$ (▼) as function of fluence. The horizontal dashed lines in (a)-(d) indicate the thermal equilibrium reflectivity level of ℓ-Ge, $R_{\ell\text{-Ge}} = 0.75$. The vertical dashed lines in (d)-(e) divide the fluence scale into Regime I ($<11\times F_m$), Regime II ($11\times F_m$–$25\times F_m$) and Regime III ($>25\times F_m$).

lent agreement with the one expected from the optical constants of liquid germanium (ℓ-Ge) ($n=2.51, k=5.12$) reported by Hodgson[9] and Jellison[8] at 514.5 nm. In the following we will refer to this value as $R_{\ell\text{-Ge}}$, as indicated in the plot by a horizontal dashed line. When the pump fluence is increased further [$22.6\times F_m$, Fig. 1(b)] the evolution of the reflectivity shows several features that differ strongly from the behavior observed at lower fluences. First, the reflectivity increase is preceded by a minimum, indicative of the presence of surface ablation. Subsequently, the reflectivity increases, reaching a plateau value after several ns. Most importantly, this value (~ 0.85) is anomalously high (15% above $R_{\ell\text{-Ge}}$). For even higher fluences [$28.2\times F_m$, Fig. 1(c)], the plateau value decreases back to $R_{\ell\text{-Ge}}$ and occurs even later.

The evolution of the most characteristic reflectivity values of the RTR transients is plotted as a function of fluence in Fig. 1(d): the maximum reflectivity level ($R_{\max}$) reached at the plateau and the reflectivity level at the minimum ($R_{\min}$). Figure 1(e) shows the fluence dependence of the melt duration t_{melt} and of the time $t_{R>R\ell\text{-Ge}}$ that the reflectivity remains above $R_{\ell\text{-Ge}}$. The evolution of these quantities can be divided into three distinct fluence regimes; Regime I ($\mathrm{F}<11\times F_m$), Regime II ($11\times F_m<F<25\times F_m$) and Regime III ($F>25\times F_m$). Within Regime I, $R_{\max}$ is constant and equal to $R_{\ell\text{-Ge}}$, whereas t_{melt} increases linearly with fluence, reaching values up to ~ 30 ns. This is consistent with the widely reported behavior of molten Ge upon ns laser irradiation.[8] Within Regime II, $R_{\max}$ jumps up to the high-reflectivity state that is fluence independent, accompanied by a linear decrease of $R_{\min}$ with fluence. Simultaneously, $t_{R>R\ell\text{-Ge}}$ shows a smooth increase and t_{melt} continues its linear increase. Finally, within Regime III, $R_{\max}$ decreases back to $R_{\ell\text{-Ge}}$, being constant with fluence, and t_{melt} shows a nearly saturated value of about 80 ns.

Jellison and Lowndes[8] have shown that the optical properties of Ge melts obtained by ns pulsed laser irradiation of *c*-Ge are the same as those of liquid Ge obtained by more conventional heating procedures. They can be described in the frame of the Drude model that assumes a fully ionized liquid with a complex dielectric function given by[9]

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\omega_c)},$$

where the plasma frequency ω_p ($\omega_p^2 = n_e e^2/\varepsilon_0 m_e$, with n_e being the electron density, ε_0 the permittivity constant, and m_e the electron mass) and the electron collision frequency ω_c are the dominant parameters that control the reflectivity. Under thermal equilibrium conditions, ω_c and ω_p have been determined[9] to be $\omega_c = 3.9\times 10^{15}$ s^{-1} (2.56 eV) and $\omega_p = 2.5\times 10^{16}$ s^{-1} (16.5 eV).

According to this simple model, a temperature increase of the melt should lead to a decrease of the liquid-phase reflectivity due to the increase of ω_c with temperature. Such behavior has been observed experimentally in liquid Si[10] and Ge[11] upon ns laser pulse irradiation. In contrast to this we observe that, under ps pulsed laser irradiation over a well-determined fluence interval, the reflectivity of the molten phase shows values clearly exceeding the one corresponding to the equilibrium molten phase of Ge. This indicates a shift of ω_p to higher values caused by an increase of the electron population and/or the density of the melt. However, such an increase in electron density, whatever its origin, would have to compensate not only for the increase of ω_c with temperature but also for the density decrease of molten Ge. In the temperature range between 1210 and 1873 K, the density of molten Ge scales linearly as $\rho(T)[\mathrm{g/cm^3}] = 5.51 - 0.498\times 10^{-3}\,(T - T_m)$,[12] yielding an electron density reduction of $\sim 16\%$ when extrapolated to the boiling point. In this context, our experimental observation of an anomalously high reflectivity state in Regime II is a clear indication of the presence of a mechanism that compensates for the thermal expansion of the liquid.

It is worth noting that experimental evidence has been found for strong structural transformations to occur in both liquid Ge and Si under pressures exceeding ≈ 10 GPa, resulting in structures substantially denser than those corresponding to the liquid phase at atmospheric pressure.[13] In addition, tight-binding molecular dynamics simulations show that in liquid Ge, the molten phase bonding can be considered as a mixture of covalent and metallic bonds with a fraction of covalent bonds that decreases with pressure.[14] Both works[13,14] indicate that the local structure of liquid Ge changes from a distorted beta-tin structure to the denser "pure" beta-tin structure in the high-pressure region ($>\approx 10$ Gpa). We can expect that this denser and more metal-like (less-covalent) structure should show a reflectivity higher than the one observed at much lower pressures, which is in agreement with our experimental observations.

The open question still remaining is whether the pressures involved in the ablation of the surface are sufficient to trigger a structural change in the liquid phase. The features of the reflectivity transients in Regime II provide hints for the occurrence of an ablation process accompanied by a strong recoil pressure. The high-reflectivity state is in all cases preceded by a reflectivity minimum. The combination of a very short laser pulse, a very shallow optical penetration depth (~ 26 nm), a shallow thermal diffusion length during the pulse absorption (~ 65 nm), and the high fluences used within Regime II, lead to the formation of a thin molten layer

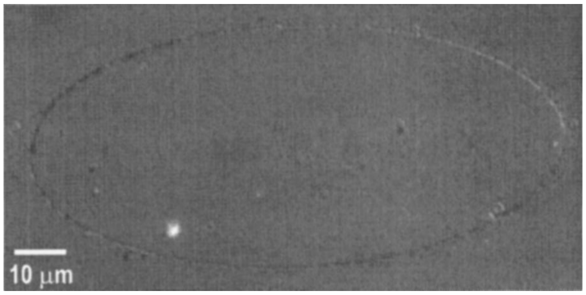

FIG. 2. Phase contrast optical micrograph of the area ablated by a single ps pulse at $22.6\times F_m$.

at the surface whose temperature rapidly rises beyond the boiling point. The subsequent explosive vaporization and ablation of this thin surface layer is likely to be the origin of the observed reflectivity minimum. A similar drop of reflectivity has been observed during ps and fs laser irradiation of Si,[15] GaAs[3] and other materials[15] and could be identified as the onset of ablation, occurring tens or hundreds of ps after the solid-liquid phase transition has taken place. As a consequence of the explosive evaporation of the surface layer, an intense shock wave leads to the compression of the liquid layer underneath, thus increasing its density and its reflectivity in a transient manner. However, such a transient reflectivity increase can only be detected if the compressed liquid layer is optically flat. Figure 2 shows an optical micrograph of the ablated area at $22.6\times F_m$. The almost perfect flatness of the ablation crater is evident when considering that we used phase contrast microscopy to record the micrograph. Von der Linde and Sokolowski-Tinten have reported interferometrically flat craters also *during* the ablation process in Si and other materials, using pulse durations of 120 fs and much lower fluences.[15] By means of fs-resolved photography, the authors were able to resolve Newton fringes after approximately 1 ns, due to interference effects of the probe laser reflected at the ablation front and at the nonablating dense melt. As our technique is not space resolved, we would be averaging over any Newton fringes present which could lead to a reduction of the measured reflectivity value. However, simulations have shown that, under no circumstances could interference effects cause the high-reflectivity state observed in Regime II. As for the pressures involved during the ablation processes, von der Linde and Sokolowski-Tinten give an estimation of several tens of GPa.[15] Taking into account our much higher fluences and longer pulse duration, we estimate somewhat lower pressures, in the ten GPa range, leading to a highly densified layer of liquid Ge with a structure similar to that described in Refs. 13 and 14 for similar pressures (10–20 GPa). This denser and more metal-like structure is responsible for the anomalous reflectivity level observed in Regime II and the duration of the anomalously high-reflectivity state corresponds to the time required for the high-density state to relax to the low-pressure structure

In summary, we have experimentally shown the existence of an anomalously high reflectivity state of molten Ge after high-energy ps laser irradiation. This reflectivity increase is consistent with a higher electron density in the liquid phase, which we attribute to a pressure-induced densification following the explosive vaporization of a thin surface layer. The fact that the anomalously high-reflectivity state is fluence independent, long lived (tens of ns), and occurs over a well-defined fluence interval (11–25 times the melt threshold) strongly points to the formation of a pressure induced, transient, high-density structural state of ℓ-Ge.

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