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Nanosecond dynamics of a gallium mirror's light-induced reflectivity change

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Transient pump-probe optical reflectivity measurements of the nano- to microsecond dynamics of a fully reversible, light-induced, surface-assisted metallization of gallium interfaced with silica are reported. The metallization leads to a considerable increase in the interface's reflectivity when solid α-gallium is on the verge of melting. The reflectivity change was found to be a cumulative effect that grows with light intensity and pulse duration. The reflectivity relaxes back to that of α-gallium when the excitation is withdrawn in a time that increases critically at gallium's melting point. It is shown that thermal processes cannot account for the effect and so a mechanism based on a nonthermal light-induced structural phase transition is proposed.

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The search for materials with large optical nonlinearities or that show a marked response to low-power optical excitation, as required for applications such as all-optical switching, has concentrated on media whose optical electrons exhibit a highly anharmonic response; most notably semiconductors, which exploit free excitonic and near-band-gap effects, and organic materials with weakly bound electrons. Here we report on a study of a novel type of reversible optical response associated with a surface-assisted, light-induced transition between structural phases with significantly different optical properties. One can illustrate this type of reversible response to optical stimulation by considering an ice cube at a temperature just below the bulk melting point. A skin of water develops on the ice because the energy of a water/air interface is lower than that of one between ice and air. This is known as premelting. The delicate balance between water and ice may be shifted very easily, for example by heating with light, thus inducing a change in the water skin depth. Water and ice have similar optical properties but if they were different, such an excitation would lead to a change in the sample's reflectivity and transmission. Recently we found that gallium confined at an interface with silica exhibits this type of response via light-assisted surface metallization.[1] This transformation engages only a few atomic layers but leads to a very considerable change in optical properties. In this paper we report on the transient dynamic characteristics of the response, measured with nanosecond time resolution at various excitation intensities and interface temperatures, and we propose a microscopic mechanism for the observed behavior.

We investigated gallium/silica interfaces formed by inserting a freshly cleaved single-mode optical fiber, with a mode radius of $r_0 = 4\ \mu$m, into an initially molten bead (~1 mm diameter) of $6N$ purity gallium (see the inset to Fig. 1). The gallium was then frozen to form a mirror at the end of the fiber. The bead's temperature was controlled to a nominal precision of 0.01 °C. We studied the interface's response using pump-probe techniques: pump light, at 1536 nm, was used to modify the interface's reflectivity whilst it was being continuously measured with a much weaker probe beam, at 1550 nm. The pump and probe were generated by distributed-feedback laser diodes with the pump radiation subsequently amplified by an erbium-doped fiber amplifier and modulated with an acousto-optic modulator. The overall frequency bandwidth of the probe detection system was 125 MHz. Figure 1 shows the dependence of the interface's reflectivity on temperature around gallium's melting point in both the "ground" (no pump beam present) and "excited" regimes. In the absence of pump light a significant and abrupt reflectivity change is seen at the melting and solidifi-

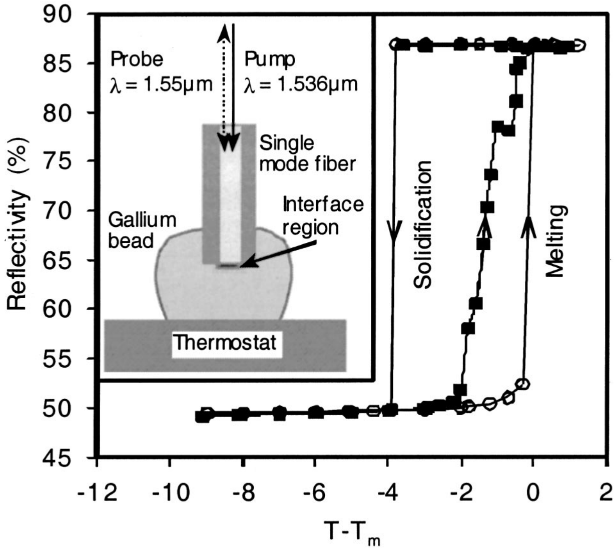

FIG. 1. Interface reflectivity as a function of temperature T relative to gallium's melting point T_m as measured by the probe beam in the absence of a pump beam (○) and in the presence of a 5-mW cw pump beam (■). The inset shows a schematic of the gallium/silica interface.

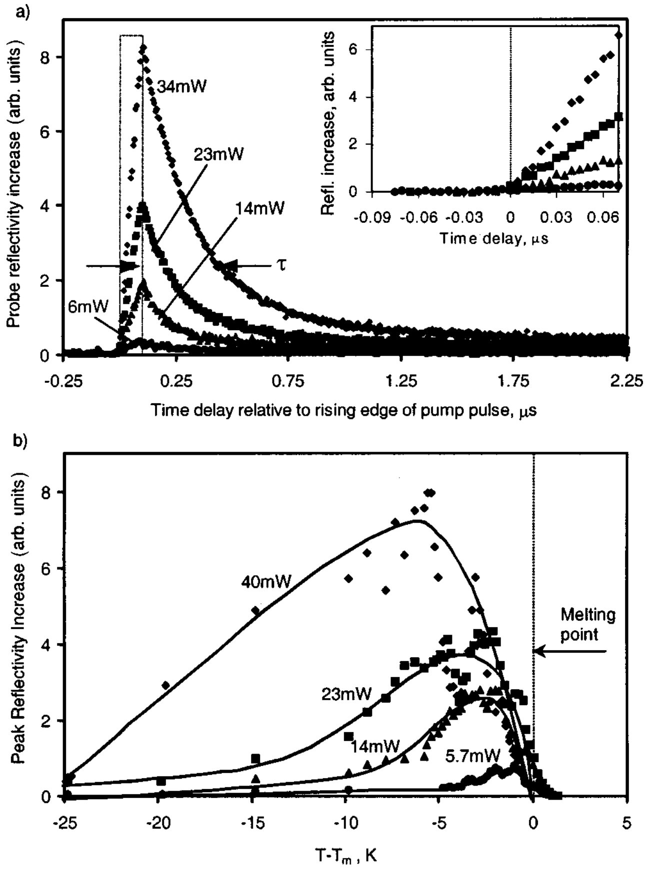

FIG. 2. (a) Dynamics of the reflectivity change after excitation with 100-ns pump pulses (dashed line) of varying peak power, at a temperature $T = 24$ °C. The inset shows dynamics near the rising edge of the pump pulse with an enlarged time scale. (b) Amplitude of the induced reflectivity change as a function of temperature T relative to gallium's melting temperature T_m for a range of peak pump powers.

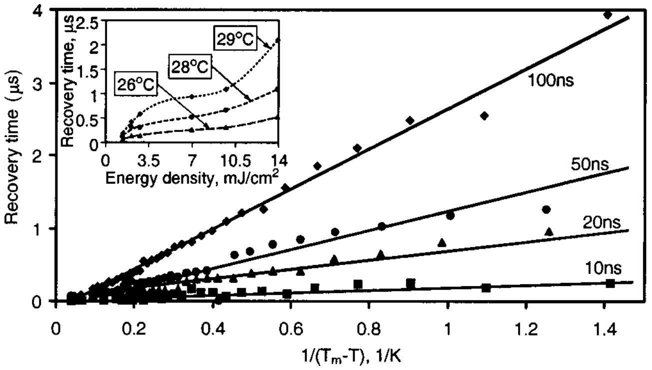

FIG. 3. Induced reflectivity change recovery time τ as a function of temperature T relative to gallium's melting temperature T_m for different pump pulse durations at a peak pump power $P = 70$ mW. Inset: induced reflectivity change recovery time τ as a function of energy density for different temperatures of the gallium drop.

cation points. Supercooling is clearly seen, resulting in a well-defined hysteresis curve. On heating, a small reflectivity increase can be seen just below the bulk melting point indicating the presence of premelting at the interface. Application of a cw pump beam modifies the hysteresis curve, making the melting transition far less abrupt. Considerable reflectivity changes (>30%) were induced by only a few milliwatts of laser power and were fully reversible. We studied the reflectivity change's dynamics by initiating it with nanosecond pump pulses of varying peak power and duration. These transient measurements show the reflectivity's fast response to optical excitation. Recent measurements performed with a femtosecond laser reveal that the intrinsic response time can be just a few picoseconds.[19] [see Fig. 2(a)]. Importantly, the reflectivity starts to increase *immediately* after commencement of the pump pulse [see the inset to Fig. 2(a)]. For the range of pump pulse parameters available in our experiment the effect accumulates with time and increases with laser power. The peak response for various excitation levels is presented as a function of temperature in Fig. 2(b). These data show that the effect is much more pronounced at temperatures just below the melting point of gallium and disappears completely above the melting point. Immediately after termination of the pump pulse the reflectivity level begins to recover to the initial level. The effect is fully repeatable and *perfectly reproducible* for at least 10^5 pulses. The recovery time is relatively slow (ns to μs) and, importantly, temperature dependent. Figure 3 presents induced reflectivity change recovery time as a function of temperature. This graph shows the remarkably accurate proportionality of the recovery time τ to $(T_m - T)^{-1}$, indicating a ''critical'' enhancement of the effect: the closer the sample temperature is to the melting point, the longer the relaxation time. For a given temperature the relaxation time steadily increases with pump pulse energy density (see the inset to Fig. 3).

The laser-induced reflectivity change can be explained by conversion of α-gallium (the normal crystalline form at room temperature and pressure) to a new, more metallic, more reflective phase. This new phase could be molten (liquid) gallium or a highly reflective crystalline phase. We begin by assuming that such a conversion is the result of laser-induced thermal melting. To evaluate the temperature change due to laser heating we solved the three-dimensional heat propagation problem in the time domain using a method based on Green's function.[2] Our heat propagation model described the experimental conditions very closely—accurately accounting for the geometry of the experiment and the materials' thermal characteristics. The incident radiation is absorbed within the optical skin depth, α^{-1}, which in gallium is only ~38 nm at a wavelength of 1.55 μm. The reflectivity of the α-gallium/silica interface was taken to be 60%. α-gallium manifests considerable anisotropy in its thermal conductivity. It was established recently that gallium dimers in the liquid phase tend to be oriented perpendicular to an interface.[3] Therefore, we expect that after solidification this orientation would prevail near the interface. This expectation is supported by our measurements of interface reflectivity levels for the solid phase. In the direction perpendicular to the interface the thermal conductivity is $\lambda_c = 15.9\,\mathrm{W\,m^{-1}\,K^{-1}}$ and in the plane of the interface it is anisotropic with principal coefficients $\lambda_a = 41\,\mathrm{W\,m^{-1}\,K^{-1}}$ and $\lambda_b = 88\,\mathrm{W\,m^{-1}\,K^{-1}}$.[4] All of these parameters were used in our calculations. Using this model we were able to calculate,

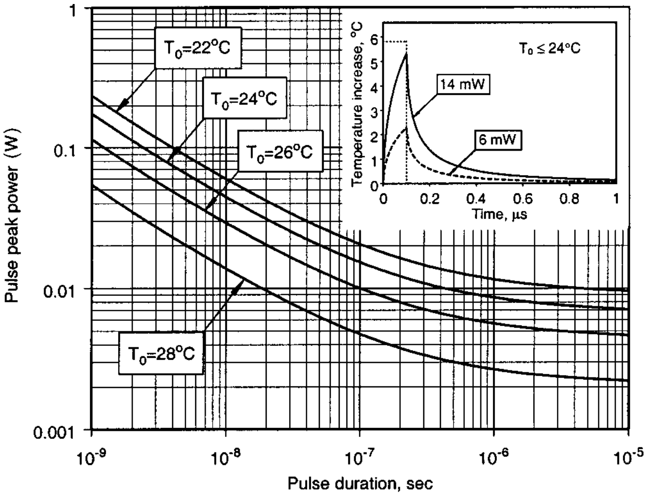

FIG. 4. Duration and peak power of the optical excitation pulse necessary to achieve gallium's melting temperature (29.8 °C) at the interface for different initial temperatures (T_0 $= 22$ °C,24 °C,26 °C,28 °C) of the gallium drop. Inset: dynamics of the interface temperature increase due to 100-ns excitation pulses of 14- and 6-mW peak power ($T_0 \leqslant 24.3$ °C).

for a given initial sample temperature, the optical power levels and laser pulse durations at which the melting temperature is reached (see Fig. 4). Since we neglected the thermal conductivity of the optical fiber, the values shown are upper estimates of the temperature increase. The assumption that thermal melting causes the reflectivity increase is clearly in conflict with our experimental observations (Figs. 2 and 3). For example, with an initial temperature of 24 °C we would have seen no reflectivity change at powers below 14 mW even with 100-ns pulses (the longest used in our experiments) and at higher power levels the reflectivity would only begin to change after a delay during which the interface is heated to the melting temperature and the latent heat of melting is accumulated. In contrast, we see reflectivity changes at intensities below 14 mW and we see in all cases that the change starts as soon as the pump pulse starts. Therefore, the laser-induced thermal melting mechanism does not explain the reflectivity behavior observed experimentally.

Let us now suppose that another hypothetical nonmelting mechanism exists wherein reflectivity depends on interface temperature (which changes due to laser heating) but does not involve a change in the phase of gallium. Reflectivity would then relax as temperature relaxes. According to our calculations, this would happen within approximately 60 ns following a 100-ns pulse (see the inset to Fig. 4). Importantly, this relaxation time would be *independent* of the thermostat temperature or laser power level. In contrast, our experiments show that the relaxation time is a strong function of the excitation level [see Fig. 2(a)] and background temperature (see Fig. 3). This leads us to conclude that a temperature-dependent mechanism that does not involve a change in the structural phase of gallium at the interface is also not possible. There must therefore be another mechanism behind the reflectivity increase, whereby α-gallium is converted into a different phase.

Here we propose such a mechanism involving a nonthermal light-induced transition from α-gallium to a phase that only becomes stable in the presence of light. This process naturally *restricts energy dissipation into the bulk*, confining it to the optical skin depth α^{-1}. The light-matter interaction is thus confined within a volume $\pi r_0^2 \alpha^{-1} = 1.9 \times 10^{-18}\,\mathrm{m}^3$. The equilibrium energy difference between α-gallium and the metastable metallic phases is of the order 8.3×10^{-2} eV/atom (1.3×10^{-20} J/atom) (Ref. 5) and so to transform this volume, which contains 14.2×10^{10} atoms, to the metallic phase, a total energy of 2 nJ is needed. Comparing this with the 5–10 nJ typically absorbed from the light pulse in our experiments confirms that the energy balance allows such a transition. The metastable phase could be quasi-liquid or amorphous gallium, or one of several ''metallic'' crystalline phases of the metal, which is known for its polymorphism.[6–11]

We believe that the light-induced transition is made possible by the unique structure of α-gallium in which molecular and metallic properties coexist—some interatomic bonds are strong covalent bonds, forming well-defined Ga_2 dimers (molecules), and the rest are metallic.[5,7,12] Absorption results in highly localized excitation of the dimers from the bonding to the antibonding state, reducing the stability of the surrounding crystalline cell. α-gallium subsequently undergoes a transition to a new configuration (crystalline or disordered), creating a microscopic inclusion of the new phase without achieving the melting temperature. The rapid increase in reflectivity, which follows excitation, is then a result of the increased density of the metallic phase in the skin layer. It is not quite clear yet whether, within the duration of the excitation pulse, the metallic phase inclusions form a well-defined metallic layer at the interface that grows during the pulse. If this is the case, the increase in the velocity of the α-gallium/metallic-gallium interface upon approaching the melting point explains why the light-induced effect increases with temperature towards the melting point as shown in Fig. 2(b). It should be noted that this scenario of light-induced metallic film formation was recently found to be a very accurate model for the behavior of a gallium/silica interface subjected to cw excitation.[13]

When the excitation is withdrawn, the metallic phase becomes metastable and recrystallizes back to the α phase. Correspondingly, the reflectivity is restored to its initial value. The reflectivity relaxation time is a function of the growth velocity v_r of the α-gallium phase (i.e., the rate at which energy is released due to solidification) and the rate of thermal diffusion. Under the conditions used in our experiments, the former is dominant because the characteristic thermal diffusion time is shorter than the recrystallization time. The growth velocity depends on temperature: $v_r = g(1 - T/T_m)$, where g is a function of the recrystallization mechanism.[14,15] The recovery time $\tau = d/v_r$ therefore increases critically on approaching T_m. One thus expects longer recovery times for larger induced reflectivity changes, i.e., thicker metallized layers, at a fixed temperature, and a slowing of the response at fixed optical excitation strength as the temperature is increased towards α-gallium's melting point. All of these features have been seen in our experiments, in particular, the recovery time increases as $\sim 1/(T_m - T)$ (see Fig. 3). Our data are not, however, sufficient to conclude that the metastable phase is liquid. Indeed, it has been suggested that α-gallium melting is in fact a continuous transition through several of the crystalline phases that are energetically very close[5] and therefore, the metastable phase could be one of these.

The light-induced transition in gallium is different from those observed in semiconductors such as Si and GaAs (see Ref. 16 for a review) and recently in Al.[17] To achieve nonthermal effects in these materials high-intensity femtosecond optical excitation is needed. In crystalline silicon, for instance, all of the bonds are covalent and so its specific enthalpy of melting is 8–10 times higher than that of α-gallium. Furthermore, the above-band-gap absorption depth in Si is 20–70 times greater than in gallium. Importantly, in silicon and GaAs the result of optical excitation is highly delocalized and the phase transition occurs through plasma-induced instability in the acoustic phonon modes, typically on a subpicosecond time scale. In gallium localization of the excitation is possibly an important factor, which could lead to local transformation of the structure. This allows us to discuss the transition in terms of the much slower nucleation and growth mechanisms.

In conclusion, the observed response of gallium to low power optical excitation is of considerable interest for applications requiring light-by-light control at low power levels, and in particular for photonic switching devices. The recent demonstration of gallium mirrors as effective *Q*-switching elements in fiber lasers[18] convincingly confirms this point.

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