Femtosecond X-Ray Measurement of Ultrafast Melting and Large Acoustic Transients

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Time-resolved x-ray diffraction with ultrashort (≈300 fs), multi-keV x-ray pulses has been used to study the femtosecond laser-induced solid-to-liquid phase transition in a thin crystalline layer of germanium. Nonthermal melting is observed to take place within 300–500 fs. Following ultrafast melting we observe strong acoustic perturbations evolving on a picosecond time scale.

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Femtosecond laser excitation is an ideal tool for driving materials into extremely high nonequilibrium states. Excitation conditions corresponding to one excited electron per atom can be achieved in a time determined by the duration of the laser pulses. Both these states and also the short-lived states of high pressures and temperatures resulting from the thermalization of the initial energy distribution represent exciting areas of study.

One interesting example of this class of phenomena is the electronically induced solid-to-liquid transition in semiconductors, or nonthermal melting [1–3]. This process is triggered by interband excitation of a dense electron-hole plasma ($\approx 10^{22}$ cm^{-3}) leading to ultrafast disordering of the semiconductor crystal [4,5] and the formation of a hot liquid at high pressure. A complex chain of phenomena follows on a picosecond time scale, including strong density perturbations propagating away from the molten layer, and the ablation of macroscopic amounts of material [6] at higher laser fluences.

Until recently, ultrafast processes could be measured only by using optical techniques. With the advent of ultrashort x-ray pulses, powerful tools such as time-resolved x-ray diffraction have become available, enabling much deeper investigation into the phenomena of interest here. So far, the power of this new experimental technique has been demonstrated in studies on lattice dynamics [7–10] and ultrafast disordering [11]. Two recent experimental studies have shown that ultrafast melting occurs homogeneously over macroscopic volumes of material [12] and on a subpicosecond time scale [13].

Here we report on a set of experiments that extend the scope of this research both in terms of the investigated phenomena and experimental capabilities. By measuring femtosecond x-ray diffraction from a Ge-Si heterostructure undergoing ultrafast melting at the surface, we directly measure the disordering dynamics, similarly to what has recently been reported [13]. Further, we directly observe large amplitude compression and rarefaction waves that are launched into the bulk beneath the energized volume and propagate across the buried Ge-Si interface. Our study clearly demonstrates that femtosecond x-ray diffraction using laser-plasma-based x-ray sources can be extended to the multi-keV range. In comparison with longer wavelength sources this results in a tool that is generally suitable for determining changes in the atomic structure on a subpicosecond time scale. The use of bent crystals [14] to collect, monochromatize, and focus the x rays from the plasma source enables us to greatly improve the spot size, photon flux, and spectral line shape of the x rays incident on the samples.

One of the principal difficulties of using x rays to study laser-induced phase transitions is that usually the thickness of the transformed layer is much less than the penetration depth of the x-ray probe pulses. Thus special precautions are necessary in order to detect the small changes in the x-ray diffraction efficiency due to structural changes in a thin surface layer, and to distinguish them from the strong background due to diffraction from the unmodified bulk.

In the experiments described here we study the solid-to-liquid phase transition of a 170 nm thick crystalline layer of Ge. Germanium films of (111) surface orientation can be grown on large Si wafers using surfactant-mediated heteroepitaxy [15]. One obtains highly perfect crystal layers (rms surface roughness 0.3 nm [16], density of threading dislocations $<10^{8}$ cm^{-3} [15]) whose lattice constant does not match that of the substrate. This type of sample enables us to optically excite and x-ray probe similar depths of material and to distinguish x-ray diffraction out of the Ge layer and from the Si substrate.

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The x-ray pulses are generated by focusing the output of a titanium sapphire laser (repetition rate 10 Hz) on a thin moving wire of titanium metal to produce a microplasma. The energy, duration and wavelength of the laser pulses are 100 mJ, 120 fs, and 800 nm, respectively. We use the characteristic titanium K_α line emission at 4.51 keV ($\lambda = 0.275$ nm) from the Ti microplasma. A portion of this incoherent line emission is collected and focused by an x-ray mirror consisting of a toroidally bent crystal platelet of Si with (311) orientation. The number of incident K_α photons in the focal plane of the toroidal mirror is a few times 10^4, in an approximately circular spot of 80 μm diameter. To produce the transient structural change of the Ge crystal a small fraction of the laser pulse (800 nm) is split off and combined on the sample with the x-ray beam, after introducing a variable time delay. The x-ray spot is positioned in the center of the oval-shaped laser-excited area (long and short axis 500 μm by 250 μm, respectively).

In a separate experiment we have measured the changes of the optical reflectivity to determine the threshold laser fluence for the onset of the phase transition in Ge and to verify the temporal evolution of the reflectivity. The threshold was measured to be 0.050 J/cm^2 for p-polarized excitation pulses at $\approx 80°$ angle of incidence. We observed a transition to the high reflectivity phase indicative of the liquid state within about 250 fs. This result is well in line with previous observations in other semiconductor crystals [3].

In the optical pump/x-ray probe experiments the Bragg diffraction from (111) lattice planes of Ge and Si are measured using a CCD camera as an x-ray detector. The x rays incident from the mirror onto the sample cover an angular range of about 2.5°, centered around the (111) Bragg angles (Ge: $\theta_B = 24.9°$; Si: $\theta_B = 26.0°$). The angular range is large enough to cover the Bragg diffraction, both from the Ge layer and the Si substrate. Thus, the time-dependent angular characteristics of the Bragg diffraction (rocking curves) of Ge and Si can be recorded simultaneously with a time resolution determined by the duration of the x-ray pulses.

First, let us consider the results depicted in Fig. 1 concerning the Ge layer. Shown are the angular-integrated x-ray diffraction signals measured over the first few picoseconds for two different laser excitations. The inset illustrates the evolution of the diffraction signal over a larger time span of 30 ps. In fact, we extended our measurement for longer than 100 ps, and within this rather large time range a number of other interesting physical phenomena could be observed.

The most striking observation is that for all laser fluences a distinct decrease in the diffraction efficiency occurs in the first few hundred femtoseconds. For example, for 0.2 J/cm^2 an abrupt drop to approximately 75% of the unperturbed diffraction is measured within 300 fs, followed by a more gradual decrease on a much longer time scale.

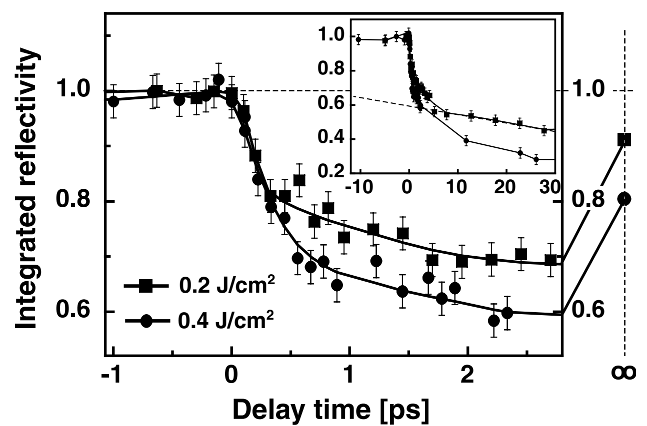

FIG. 1. X-ray diffraction efficiency (integrated reflectivity) versus delay time. Infinity symbol: measurement a few minutes after the pump pulse. Inset: integrated reflectivity for an extended time span. Dashed line: melt-front velocity of 850 m/s for rapid thermal melting.

Ultimately, the diffraction efficiency recovers (data points marked ∞ in Fig. 1), indicating nearly complete restoration of the Ge crystal layer [17]. Qualitatively similar behavior is measured for other laser excitation fluences.

Two principal conclusions can immediately be derived from these data: (i) The observed fast initial decrease in the diffraction signal provides clear evidence that a portion of the Ge crystal undergoes disordering within a few hundred femtoseconds. The measured 25% decrease in the diffraction indicates the development of a molten layer of approximately $L_{\mathrm{liq}} \approx 40$ nm [18]. The subsequent slower decrease over several tens of picoseconds is attributed to rapid thermal melting [19] (see below); (ii) an upper limit on the duration of the x-ray pulses of 300 fs can be given. This is the first experimental evidence of multi-keV x-ray pulses of such short duration. Using a streak camera typical pulse widths of a few picoseconds were previously measured [20].

In Fig. 2 we present examples of time-dependent rocking curves which corroborate our conclusions on ultrafast melting and provide profound insight into the acoustic processes following the structural phase transition.

The dashed lines in Fig. 2 represent the rocking curves of the unperturbed materials, the Ge layer and the Si substrate. The solid line in Fig. 2a (0.8 ps) shows that the shape and the position of the rocking curve remain unchanged; there is only a reduction in the diffraction intensity of Ge to somewhat less than 70%. We believe that an explanation of the decrease in the diffraction in terms of the Debye-Waller effect can be ruled out for the following two reasons: (i) The time needed to establish a thermal energy distribution of the lattice is several picoseconds, which is much longer than the time of the experimentally observed decrease in the diffraction signal; (ii) a lattice temperature over 6700 K would be required to produce the observed reduction in the diffraction. This temperature is about a

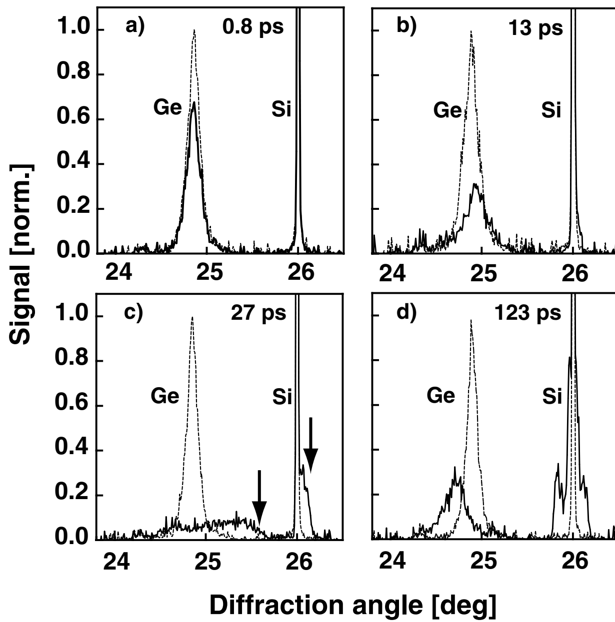

FIG. 2. X-ray diffraction signal versus glancing angle (rocking curves). (a) 0.8 ps; (b) 13 ps; (c) 27 ps; (d) 123 ps. Thin dashed lines: rocking curves in the absence of laser excitation. Arrows: diffraction angles used for estimating stress (see text).

factor of 2 greater than the temperature estimated from the laser energy deposited in the material.

We propose the following scenario to describe the principal processes that take place on a picosecond time scale, after ultrafast melting has occurred and the thermalization of the optical energy has been accomplished. The surface of the sample is covered by a layer of hot, pressurized molten Ge. Below the liquid there is an intact layer of crystalline Ge, also hot and at high pressure. By comparison, the pressure in the underlying Si layer is negligible because at 800 nm the optical absorption in Si and thus the deposited energy is much less than in Ge.

The initial stress/pressure imbalance at the interfaces triggers several acoustic perturbations. It follows from the continuity-of-stress condition that a compressive and an expansive strain wave are launched from each interface into the low pressure and the high pressure side, respectively. Also, a rarefaction wave develops at the surface and travels into the liquid. Figure 3 shows a qualitative picture of the developing strain waves.

The initial pressure is expected to be at its highest in the molten surface layer, because the largest portion of the optical energy is deposited ≈40 to 50 nm beneath the surface. Therefore, the foremost acoustic perturbation in the remaining crystalline Ge should be compressive strain launched from the molten layer.

In addition to the acoustic perturbations, the liquid-to-solid interface (melt front) moves forward into solid Ge. The liquid layer grows at the expense of the crystalline layer, resulting in a continuing overall reduction in the diffraction efficiency. The melt-front velocity can be

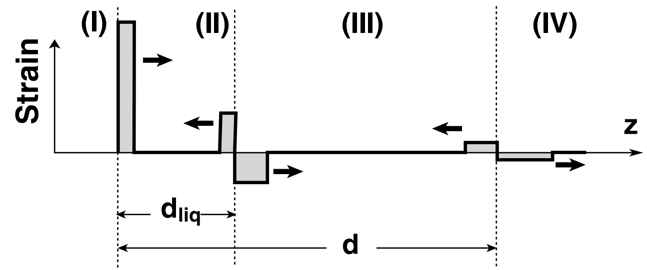

FIG. 3. Different layers of the Ge/Si heterostructure and strain waves developing at the interfaces: (I) vacuum; (II) liquid Ge, (III) crystalline Ge; (IV) Si substrate. z: distance from the surface. Arrows: propagation direction of the acoustic perturbations.

estimated from the slope of the corresponding diffraction curve to be approximately 850 m/s (see Fig. 1 inset). This very fast melt-front velocity suggests highly superheated conditions at the liquid-solid interface [19].

The different acoustic perturbations do not overlap for periods shorter than the travel time between the interfaces (e.g., 23 ps for 130 nm of c-Ge). Later on, however, reflections occur at the various interfaces because of the mismatch of the acoustic impedance. The situation becomes quite complicated until the acoustic transients have finally damped out.

According to this qualitative model, the first acoustic effects to be noticed should be a compression in Ge and, to a lesser extent, also in Si. The rocking curve for 13 ps (Fig. 2b) shows that this is indeed observed. There is a clear shift of the Ge line towards larger diffraction angles and a weak shoulder of the Si curve in the same direction.

The rarefaction wave approaching from the liquid surface is expected to effect the crystalline layer after times $t > L_{\text{liq}}/c_{\text{liq}} \approx 15$ ps, where $c_{\text{liq}} = 2660$ m/s is the sound velocity of liquid Ge [21]. In fact, the Ge rocking curve at 27 ps (Fig. 2c) develops a new side band at lower diffraction angles and exhibits a doubly peaked structure. This shape indicates the presence of both compressed and expanded strata in Ge at this time.

Going one step beyond the simple qualitative interpretation, one can use the data in Fig. 2 to estimate the stress/pressure associated with the acoustic perturbations. For example, consider the positive angular shifts $\Delta\theta$ marked by the arrows in Fig. 2c. They indicate compressive strain $\epsilon = \Delta\theta/\tan\theta_B$ of -0.02 and -0.005 in Ge and Si, respectively. The transient stresses $\sigma = \rho c_{111}^2 \epsilon$ [ρ: density; c_{111}: speed of sound in the (111) direction] obtained from these numbers are 3.3 GPa and 1 GPa, respectively. It can be shown that the initial pressure in liquid Ge must be much higher because the observed net compression in Ge at $\Delta t = 27$ ps represents a superposition of compressive and expansive perturbations.

Finally, the data for 123 ps (Fig. 2d) reveal further points of interest. At this late stage the acoustic perturbations of the Ge layer have damped out leaving the

relaxed, thermally expanded material, as indicated by a shift of the diffraction profile to smaller angles. The shift represents a thermal expansion of $\epsilon_{th} = 0.008$, which would correspond to a temperature of approximately 1100 to 1200 K. This value is close to the melting temperature of Ge, suggesting that liquid and solid Ge have reached an equilibrium near the melting point. Concerning the rocking curve of Si at 123 ps, both expansive and compressive strain can be clearly recognized. This complex structure is presumably attributable to transient bipolar strain superimposed on the thermal expansion profile of Si [7]. However, a more detailed analysis cannot be given here.

In summary, using time-resolved x-ray diffraction we have studied the transition of highly excited Ge to the liquid state. The solid-to-liquid phase transition is accomplished in approximately 300 fs. Our experiments demonstrate subpicosecond time resolution in multi-keV x-ray diffraction. Measurements of time-resolved rocking curves have revealed a rich variety of acoustic processes following ultrafast melting. Several interesting extensions of this work are conceivable. For example, the possibility of studying short-lived states of very high pressure and temperature is likely to have an impact on the study of phase transitions far from the phase equilibrium, and on equation-of-state studies as well as the investigations of ablation and shock waves.

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