Large Acoustic Transients Induced by Nonthermal Melting of InSb

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We have observed large-amplitude strain waves following a rapid change in density of InSb due to non-thermal melting. The strain has been measured in real time via time-resolved x-ray diffraction, with a temporal resolution better than 2 ps. The change from the solid to liquid density of the surface layer launches a high-amplitude strain wave into the crystalline material below. This induces an effective plane rotation in the asymmetrically cut crystal leading to deflection of the diffracted beam. The uniform strain in the layer below the molten layer is $2.0(\pm 0.2)\%$. A strain of this magnitude develops within 5 ps of the incident pulse showing that the liquid has reached the equilibrium density within this time frame. Both the strain amplitude and the depth of the strained material in the solid can be explained by assuming a reduction in the speed of sound in the nonequilibrium liquid compared to measured equilibrium values.

An ultrashort laser pulse can excite a large fraction of the valence band population into the conduction band in a semiconductor. When about 10% of the valence band electrons have been excited, the potential may be softened and disordering may occur [1]. This was first studied using visible radiation [2], and more recently using x-ray radiation [3–5]. The structural information obtained by x-ray studies has shed light on the nature of the disordering process [6,7]. In a recent Letter, Sokolowski-Tinten et al. observed large acoustic transients when melting a Ge film on a Si substrate [8]. This was mainly attributed to expansion of the molten layer due to thermal expansion.

In the present work we observe the acoustic transient originating from the rapid contraction upon melting of InSb in the absence of thermal expansion of the liquid. The temperature here is only about 250 K above the melting temperature whereas the estimated temperature increase giving rise to the expansion observed in Ref. [8] was 3300 K.

In this Letter, we describe a time-resolved x-ray diffraction experiment from which we deduced the acoustic properties of the newly formed liquid in its nonequilibrium state. Our experiment was carried out at a lower fluence than in Ref. [8], so that the experiment could be performed repetitively without large thermal gradients in the liquid. Hence, we observed an acoustic wave with a flat strain profile, which propagated into the crystalline material. Following this expansion wave we observed a compression wave. We have measured the depth profile of the expansion wave together with the molten layer thickness. This ratio gives the speed of sound relative to that in the solid. We deduced the speed of sound in the nonequilibrium liquid to be 1600 m/s, which should be compared to the tabulated value of 2800 m/s for the equilibrium liquid. This shows that novel time-resolved x-ray techniques have enabled the study of nonequilibrium elastic properties in materials.

The experiments were carried out at beam line D611 at MAX-lab in Lund, Sweden, where a femtosecond laser has been synchronized to the MAX II electron storage ring. This allows for visible pump, x-ray probe experiments [9]. The laser operates at a wavelength of 780 nm, and UV beams can be generated at 260 nm. Most of the investigations were carried out using x-ray photon energies near 3.0 keV. The x-ray pulse duration was 400 ps and in order to obtain a temporal resolution better than that, a streak camera was employed. In the present study, the grazing incidence design described by Lowney et al. [10] was used. This design can improve the quantum efficiency and enables convenient in-vacuum motion allowing a range of Bragg angles from 0 to 85°. The streak camera is triggered by the laser via a photoconductive switch. The laser pulse energy was split into three arms: 100 $\mu$J was used to trigger the photoconductive switch and 100 $\mu$J to generate two UV timing fiducials, leaving up to 800 $\mu$J to excite the sample. The size of the laser beam on the sample was $5 \times 0.4$ mm, which is larger than the $3 \times 0.3$ mm footprint of the x-ray beam which was focused to $0.4 \times 0.25$ mm on the photocathode. The laser pulse duration was less than 50 fs so the temporal resolution was limited by the streak camera, to about 2 ps. The mismatch in incidence and exit angles between the x rays and the laser does not influence the time resolution since we are using an imaging detector. The mismatch only gives rise to a tilting of the time axis in the recorded images.

Previous studies of strain pulses using x rays have either used divergent laser-produced plasma sources [11,12] or relied on scanning synchrotron radiation sources [13–15]. In this study we measured the strain in a more direct way via lattice plane rotation of an asymmetrically cut crystal and the use of an imaging detector. The method is explained in Fig. 1. As the strain wave is launched, the crystal expands perpendicular to the surface. This gives rise to...
rotation of the diffracting (111) planes. The InSb sample was cut 30° off the (111) plane (near the 110 plane). The incidence angle of the x rays relative to the crystal surface was 2.3° for the strain measurements and 0.9° for the nonthermal melting measurements. The angles were measured using specular reflection. In both cases the exit angle was around 62°.

The thickness of the molten layer was measured by recording the reduction in diffracted signal (after 10 ps) due to absorption in the liquid. Here an incidence angle of 0.9° was used in order to obtain a long path for the x rays through the molten layer. (The incidence angle was measured by spatial monitoring of the part of the beam reflected from the surface and the direct beam when the sample was lowered out of the beam path.)

Figure 2 shows raw data from the experiment. When the laser irradiates the sample, a strain develops within 5 ps, which creates the plane rotation that deflects the beam along the slit of the streak camera. By subtracting the profile of the unperturbed beam from the data, we can quantify the angular deflection and thus the plane rotation (which is half the deflection angle) at any given time. The relation between plane rotation and strain is

$$\eta = \frac{\tan(\psi + \Delta \psi)}{\tan \psi} - 1,$$

where \(\eta\) denotes strain, \(\psi\) the cut angle relative to the diffracting planes, and \(\Delta \psi\) the plane rotation. In our geometry, and for small deflection angles, the strain is proportional to the plane rotation: \(\eta = \Delta \psi \times 4 \times 10^{-2}\), where \(\Delta \psi\) is the plane rotation in degrees. Thus, expansion will induce an increased exit angle from the sample, and compression a decreased exit angle. However, expansion and compression cannot be observed simultaneously. This is due to the fact that the x-ray energy must be matched in order to achieve efficient Bragg scattering with the modified lattice spacing. Hence, we used an x-ray energy lower than the energy of the Bragg peak of the unperturbed lattice to observe expansion, and a higher x-ray energy to probe for compression. In Figure 2(c) we see raw data from the measurement of the melt depth.

By recording a series of streak images using x-ray energies above and below the Bragg peak, we experimentally observed an expansion followed by a compression. This is the signature of an acoustic wave created by a density increase in the surface layer. The propagation of strain pulses in semiconductors has been studied by Thomsen et al. [16] who presented a model for the resulting strain due to an initial density change in the material. In their study the model was applied to the case of thermal expansion well below the melting temperature. This model can also be applied to expansion due to electronic strain or the density change that occurs at a phase transition.

According to Thomsen and co-workers, the acoustic pulses created mimic the profile of the initial stress but with the opposite sign and half the amplitude. This initial wave is followed by a second half-amplitude replica—this time with the same sign as the initial stress. As we observed expansion before compression, we deduce that the initial stress corresponds to compression. Thermal and electronic strain both induce expansion in InSb, whereas melting corresponds to a large compression. We found the deflection of the diffracted x-rays to be 1.0°. This means that the amplitude of the strain pulse is 2%.

This deflection was evaluated together with the intensity of the deflected beam as a function of laser fluence. Both are shown in Fig. 3, together with the molten layer thickness. It can be seen that the deflected beam intensity shows a threshold behavior at the melting threshold fluence, after which the deflected beam intensity increases linearly with the molten layer thickness. However, the angular deflection...
will be "stretched out." This is given by the relation 
\[ \frac{v_{\text{solid}}}{v_{\text{liquid}}} = \frac{d_{\text{wave}}}{d_{\text{liquid}}} \]
where \( v \) is the speed of sound, \( d_{\text{wave}} \) is the depth of the strain wave and \( d_{\text{liquid}} \) the thickness of the molten layer. Thus, by measuring the thicknesses of the molten layer and the depth of the strain wave, we can deduce the ratio between the speed of sound in the solid and in the liquid. The thickness of the molten layer as a function of laser fluence is plotted in Fig. 3. In order to deduce the thickness of the strain wave we carried out simulations using software described by Sondhaus and Wark [19] and GID_SL by Stepanov [20]. The acoustic wave was modeled as uniformly strained top layers, where the thickness increased with the speed of sound in the solid. The resulting time-resolved rocking curves were convolved with the bandwidth of the monochromator and the time resolution of the streak camera. These simulations show that a 10%–90% rise time of 11 ps corresponds to a layer thickness of 48 nm.

For the benefit of the reader, we mention that the depth of the strain wave can be estimated in a less exact, but more intuitive procedure by multiplying the rise time by the speed of sound in the solid. However, only when the x-ray energy matches the Bragg condition for the expanded lattice, will the whole layer contribute constructively to the diffracted intensity. (The longest rise time will occur for the x-ray photon energy corresponding to the Bragg condition for the expanded lattice.) Therefore, measurements were made for a number of x-ray energies near resonance. Given the relatively thin layer, this resonance is broad. At a fluence of 28 mJ/cm\(^2\) we observed a rise time of 11 ps, independent of x-ray energy near the resonance of the expanded layer, which is 75 eV below the energy of the Bragg peak of the unperturbed crystal. The speed of sound perpendicular to the surface in this InSb wafer is 3770 m/s. Hence the depth of the strain wave in the solid was found to be 42 nm. As can be seen, the intuitive approach yields nearly the same result as the simulation.

We can now determine the speed of sound in the nonequilibrium liquid by using the thickness of the molten layer (21 nm) at the same fluence from Fig. 3. This gives a speed of sound of 3770 \( \times \) 21/48 = 1600 m/s.

In order to verify the results we now analyze the amplitude of the strain wave, using the deduced speed of sound.
The volume of (equilibrium) liquid InSb is 12% smaller than that of the solid. Compression occurs at the speed of sound. Since the lateral dimensions are on the order of 1 mm the initial compression is one-dimensional and perpendicular to the surface. Hence, the amplitude of the static strain represents a 12% contraction. As the molten material contracts it launches an expansion wave into the bulk of the crystal. If the speed of sound in the molten layer and the solid were identical, the Thomsen model predicts a 6% amplitude expansion wave with a depth equal to the thickness of the molten layer. The expansion wave is then followed by a compression wave, as illustrated in Fig. 5.

Since the speed of sound in the liquid is lower than that in the solid we can anticipate a reduction in the amplitude of the propagating wave in the solid. Firstly, there will be reflection at the boundary. The reflection coefficient for the stress of the incident wave is given by 

\[ R = \frac{\nu_{\text{solid}} - \nu_{\text{liquid}}}{\nu_{\text{solid}} + \nu_{\text{liquid}}} \],

Using the values above we obtain a positive reflection of 39%. Since the stress must be the same on both sides of the boundary, the transmitted stress thus becomes 139%.

Secondly, the speed of sound is given by the expression \( v = \sqrt{K/\rho} \Rightarrow K = v^2 \rho \), where \( K \) is the bulk modulus and \( \rho \) is the density. Hence, a factor 2.3 higher speed of sound in the solid corresponds to a factor 2.3^2 = 5.3 higher bulk modulus in the solid. The stress is defined as the product of the strain and the bulk modulus, and thus we obtain a resulting strain of 6% \( \times 1.39/5.3 = 1.6\% \). This excellent agreement in strain amplitude verifies our measurement of the speed of sound in the nonequilibrium liquid 10–15 ps after its formation.

In conclusion, we have investigated the formation of a liquid and probed its properties before the equilibrium structure was reached. We found a significantly reduced speed of sound. We believe the reduction in the speed of sound has two causes. The first is due to the large number of excited electrons leading to fewer bonds and more antibonds, effectively lowering the elastic forces and thus the sonic speed. The second is due to the fact that, for a few percent strain, the harmonic approximation no longer holds and the atoms move out into the flatter parts of the interatomic potentials.

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