Ultrafast Structural Dynamics in InSb Probed by Time-Resolved X-ray Diffraction

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Time-resolved x-ray diffraction is a useful tool for the study of structural dynamics in condensed matter. Until recently, ultrafast atomic motion in solids or molecules has been inferred by observing changes in optical properties [1]. A more direct approach to studying ultrafast structural dynamics is to use x-ray techniques with ultrashort x-ray pulses, as x-rays directly probe atomic core electrons [2,3]. For example, changes in long-range order in crystals may be observed using time-resolved x-ray diffraction. In order to study the ultrafast structural dynamics in laser perturbed InSb, femtosecond time-resolved x-ray diffraction is performed using a novel x-ray source based on 90° Thomson scattering [2,4].

The experiments were carried out in the Center for Beam Physics Beam Test Facility at the Advanced Light Source (ALS). Terawatt laser pulses (~ 100 fs, 800 nm, 100 mJ) are generated using a chirped pulse amplification system based on Ti:Sapphire. These laser pulses Thomson scatter off of relativistic electrons (50 MeV, $\gamma = 98$) produced by the ALS linear accelerator and generate a highly directed (~ 10 mrad divergence) x-ray beam, at a wavelength of 0.4 Å. In the 90° scattering geometry, the x-ray pulse duration (~300 fs) is determined by the transit time of the ultrashort laser pulse across the ~ 90 μm waist of the focused electron beam. The electron beam diameter at the interaction point is measured by imaging optical transition radiation from an aluminum foil placed in the beam path [2,4]. Jitter in the electron beam position (~30 mm sigma) introduces a time uncertainty of ~ 100 fs. The ultrashort x-ray pulses are generated at a 5 Hz repetition rate, limited by the linear accelerator.

Time-resolved x-ray diffraction studies of InSb are performed by using the x-ray pulses along with synchronized femtosecond laser pulses involved in the x-ray generation. The InSb crystal used was cut 3˚ off the (111) orientation to allow x-ray diffraction in the asymmetric Bragg geometry (the x-ray beam is incident ~ 0.4˚ relative to the crystal surface). This geometry provides a better match between the penetration depths of the x-rays (~ 500 nm) and laser (~ 100 nm), measured perpendicular to the surface (note that the optical absorption depth remains ~ 100 nm even for angles of incidence close to 90° from normal incidence, due to the large refractive index of InSb.) The asymmetric Bragg diffraction geometry also increases the x-ray diffraction acceptance bandwidth for x-rays incident at shallow angles.

A fraction (10%) of the laser beam used to generate the x-rays is split off and used for sample excitation. The angle between the sample excitation laser beam and the x-rays (~ 4˚) is kept small in order to reduce the temporal walkoff (~ 500 fs) between the beams. The temporal zero between the x-ray and laser pulses is obtained by sending unamplified laser pulses through the system. A beamsplitter is placed at the electron-laser interaction point to allow part of the laser beam to follow the x-ray beam path, and cross-correlation techniques are used with the two beams. The estimated uncertainty in the zero position is 200 fs, which is within the x-ray pulse duration.

The p-polarized laser beam is focused by a 75 cm focal length lens to a 3 mm diameter spot at the sample, with the sample positioned before the laser focus. The laser beam illuminates an elliptical spot on the sample at a fluence of 20 mJ/cm^2, which is consistent with the laser fluence needed to see signs of disorder in optical experiments [5]. The laser spot on the sample is slightly larger than the x-ray spot. The sample is moved after multiple laser shots (~10,000). While slight surface damage (monitored while collecting data by observing the scattered laser light from the sample) occurs after multiple shots, no significant degradation in the x-ray diffraction signal is observed. The damaged regions were smaller than the laser and x-ray spots on the sample. Inspection of the slightly damaged areas (visible as a white streak) under an optical microscope revealed flat regions mixed in with smaller raised spots, which may indicate recrystallized areas mixed with amorphous regions. Only the reversible changes in the sample are probed in our experiment.

The x-ray beam is apertured to 200 μrad in the diffraction plane to allow for better spectral resolution and to allow the beam to cover a reasonable area on the InSb crystal. The aperturing reduces the number of diffracted x-ray photons to about 1 every 10 x-ray pulses. This allows for pulse-height analysis of the voltage signal from the diffracted x-ray photons detected by LN2 cooled Ge detector (~ 300 eV resolution at 30 keV) to obtain the diffracted photon energy spectrum. The unused portion of the x-ray beam is used to monitor the x-ray flux, via the phosphor detection system [2,4]. A hole is placed in the phosphor to allow the central portion of the x-ray beam to reach the sample.

Representative x-ray diffraction spectra for –20 ps and +100 ps time delays (positive time delays indicate that x-ray pulses arrive after laser pulses on the sample) are shown in Figure 1. The peak of the diffraction spectrum at +100 ps is slightly shifted towards lower energy relative to the diffraction spectrum at –20 ps. This provides evidence that thermally expanded layers are formed near the surface on this time scale. Laser-induced lattice expansion has also been observed in time-resolved x-ray diffraction experiments on Si [6], and more recently in GaAs [7]. Using the thermal expansion coefficient of InSb ($5x10^{-6}$/K) and assuming heating up to the melting temperature (803 K), the maximum spectral shift in diffracted x-rays due to increased lattice spacing is ~ 80 eV, which is on the order of the observed ~ 40 eV shift in the Gaussian fits to the spectra in Figure 1.

The x-ray diffraction spectra integrated over the Bragg peak as a function of time delay is shown in Figure 2. We call attention to two features of the data. First, there is a rise in the integrated counts for long time delays. The rise is evidence of an increase in the diffraction bandwidth caused by the growth of a thermally expanded layer near the surface. Second, a delay (~ 10 ps) in the onset of the rise is observed, due to energy relaxation from the electron-hole plasma to acoustic phonons. The absorbed laser pulse energy is initially deposited into the electron-hole plasma. This dense electron-hole plasma may remain dense for a relatively long time (~ 1 ps) due to ambipolar diffusion and bandgap renormalization, which tend to offset hot carrier transport [8]. Consequently, Auger recombination becomes the dominant recombination mechanism for the carriers, resulting in a lowering of carrier density while maintaining the energy in the carriers. This energy is eventually transferred to the lattice via LO phonons. The time scale for this energy relaxation has been recently observed to be ~ 10 ps in GaAs near the ultrafast melting threshold [9]. Because LO phonons involve relative motion between basis atoms in the zinc-blende structure, these phonons do not induce thermal expansion of the lattice. The relaxation of LO phonons into acoustic phonons and the propagation of these acoustic phonons is the likely cause of the lattice expansion. Since the surface is free to move, and most of the energy is deposited closest to the surface, significant lattice

expansion is likely to occur at the surface first. As more LO phonons relax into acoustic phonons, which then propagate into the sample at the speed of sound, lattice expansion moves deeper into the sample. X-rays diffracting off both an expanded layer and an unperturbed layer result in an increase in the bandwidth of the diffracted x-rays. With our collimated, polychromatic Thomson scattering x-ray source, the result is an increase in the integrated x-ray diffraction signal.

X-ray diffraction from a crystal with a strain profile can be calculated using the method in Ref. 6. A simulation of the rise in x-ray diffraction signal is performed using this method, using the source parameters and assuming an expanded layer at the surface. The expanded layer is assumed to be governed by the thermal expansion coefficient and an exponentially decreasing temperature profile (maximum temperature is assumed to be the melting temperature, 803K). The 1/e depth of the temperature profile is assumed to increase at the speed of sound (5×10^5 cm/s), simulating nonequilibrium acoustic phonon transport. With a 7 ps delay in the onset of expansion, the simulation fits the data well, as shown in the curve in Figure 2.

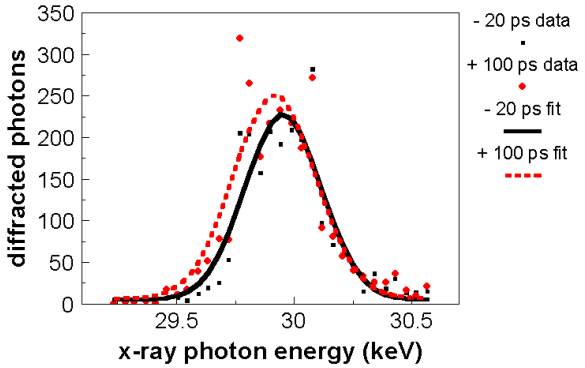

Figure 1. X-ray diffraction spectra at time delays of –20 ps and +100 ps. Solid and dashed lines are Gaussian fits to the data. Note the peak shift and broadening towards lower energy for the +100 ps data, indicating an expansion of the lattice in the volume probed by the x-rays.

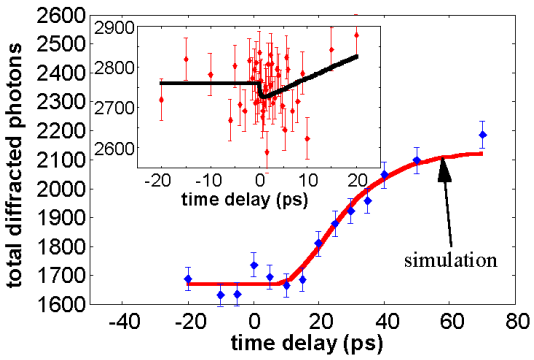

Figure 2. Total diffracted x-ray photons versus time delay. The curve is from a simulation that assumes an expanded layer growing from the surface, with a thickness increasing at the sound velocity. The inset is finer time step data taken around zero time delay. The line is a guide to the eye.

The inset to Figure 2 shows finer time step data taken around zero time delay. The data suggests a very abrupt (< 1 ps) transient reduction in the x-ray diffraction signal, as shown in the fit to the data. A reduction in x-ray diffraction is indicative of disordering. Many optical experiments have been performed on ultrafast disordering in Si [10,11] and GaAs [9,12], all of which indicate that a high electron-hole plasma density induces lattice instability [13,14] as first proposed by Van Vechten [15]. At the laser fluence used in our experiment, a carrier density of ~ 10^{22}/cm^3 is estimated, assuming the linear absorption depth (~ 100 nm) of 800 nm light in InSb. This should be sufficient to induce ultrafast disordering in a thin layer at the surface [5]. This disordered layer does not contribute to the x-ray diffraction signal, but attenuates the number of x-rays entering and diffracting from the sample by photoelectric absorption. The magnitude of the decrease (~ 1.3%) indicates that ultrafast disordering is occurring in a very thin (~ 15 nm) surface layer due to the presence of a dense electron-hole plasma.

In conclusion, time-resolved x-ray diffraction was used to study ultrafast structural dynamics in laser perturbed InSb. A delay in the onset of lattice expansion is observed, due to the time for energy relaxation from electron-hole pairs to acoustic phonons. Lattice expansion is seen to evolve at the speed of sound, as nonequilibrium phonons propagate into the sample. An indication of

subpicosecond disordering of a thin surface layer is also observed. At the laser fluence used, the changes are reversible over multiple laser shots.

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REFERENCES

1. P.F. Barbara, J.G. Fujimoto, W.H. Knox, W. Zinth, Eds., *Ultrafast Phenomena X*, vol. 62 (Springer-Verlag, Berlin Heidelberg New York, 1996).
2. R.W. Schoenlein, et al., Science 274, 236 (1996).
3. C. Rischel, et al., *Nature* **390**, 490 (1997).
4. W.P. Leemans, et al., *Phys. Rev. Lett.* **77**, 4182 (1996).
5. I.L. Shumay, U. Höfer, *Phys. Rev. B* **53**, 15878 (1996).
6. B.C. Larson, J.Z. Tischler, D.M. Mills, *J. Mater. Res.* **1**, 144 (1986).
7. T. Guo, et al., *SPIE Proc.* **3157**, 84 (1997).
8. H.M. van Driel, *Phys. Rev. B* **35**, 8166 (1987).
9. L. Huang, J.P. Callan, E.N. Glezer, E. Mazur, *Phys. Rev. Lett.* **80**, 185 (1998).
10. C.V. Shank, R. Yen, C. Hirlimann, *Phys. Rev. Lett.* **50**, 454 (1983).
11. C.V. Shank, R. Yen, C. Hirlimann, *Phys. Rev. Lett.* **51**, 900 (1983).
12. E.N. Glezer, Y. Siegal, L. Huang, E. Mazur, *Phys. Rev. B* **51**, 9589 (1995).
13. P. Stampfli, K.H. Benneman, *Appl. Phys. A* **60**, 191 (1995).
14. P.L. Silvestrelli, A. Alavi, M. Parrinello, D. Frenkel, *Phys. Rev. B* **56**, 3806 (1997).
15. J.A. Van Vechten, R. Tsu, F.W. Saris, D. Hoonhout, *Phys. Lett.* **74A**, 417 (1979).

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