Time-resolved XAFS Measurements of Laser-heated Germanium Films

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Introduction

Understanding the kinetics of melting and phase transformations is fundamental to progress in the design and manufacture of solid-state devices. The melting of Ge is particularly interesting because of its complex behavior. For example, the density of the liquid is greater (by 4.7%) and has a larger number of nearest neighbors (six versus four). Previous investigations [1-6] have probed the melting kinetics with Bragg diffraction, which is insensitive to changes after long-range order disappears. X-ray absorption fine structure (XAFS) spectroscopy, however, does not require long-range order, and it can therefore monitor local structural changes in the disordered (i.e., liquid) phase directly. With this in mind, we have developed time-resolved XAFS capability on the subnanosecond (sub-ns) time scale for investigating the melting kinetics of Ge by using a femtosecond (fs) laser to melt the Ge. The apparatus is also well-suited for other types of pump-probe experiments, and it utilizes a laser firing at the APS P0 clock rate (~272 kHz), which is about two orders of magnitude higher than typical laser systems used in time-resolved XAFS experiments on this time scale. This allows us to collect data at a rate similar to that of typical non-time-resolved experiments. We have used this apparatus to obtain preliminary data on the dynamics of ultrafast laser heating in both amorphous and crystalline Ge films, with results indicating that lattice heating in amorphous Ge occurs over a time period of ~500 picoseconds (ps) or more after excitation by the laser.

Methods and Materials

The Ti:Sapphire laser produces ~250-fs pulses with ~4 μJ per pulse at an 800-nm wavelength. It is capable of a repetition rate equal to the 272-kHz P0 clock rate at the APS, allowing us to collect data for a given bunch each time around the ring. Synchronization of the laser to the x-rays from the ring is accomplished by phase-locking the mode-locked seed laser (Mira 900F) to an 88-MHz signal derived from the ring rf signal and then triggering the main laser amplifier (RegA 9000) with the P0 signal. X-ray pulses are detected by an avalanche photodiode (APD) (I0) and a plastic detector (sample fluorescence). Pulses from the bunch with the desired timing are selected by passing the detector outputs through analog gates, also triggered by P0. Relative timing is changed by adjusting the phase of the 88-MHz reference signal and/or advancing the RegA trigger to select different seed pulses from the Mira for amplification.

The results shown below were obtained in pulse-counting mode by using fast discriminators for the pulses passing through the gates. The timing resolution is limited by the x-ray bunch width and the accumulated jitter of the electronic components that lock the laser output to the ring timing. The effective timing resolution is estimated to be on the order of 100 to 200 ps. We are currently installing an improved rf timing reference from the synchrotron. It should improve the effective timing resolution to approximately the bunch width, which is ~92 ps full width at half-maximum (FWHM). A block diagram of the electronics and laser system is shown in Fig. 1.

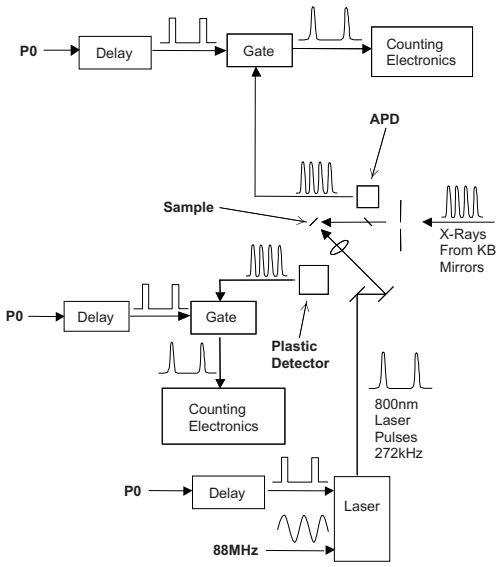

FIG. 1. Schematic of the laser system and timing electronics.

The Ge samples consisted of self-supported 200-nm films, produced by depositing the film on a silicon substrate and etching the substrate from the back of the film. Initially the film was amorphous. The crystalline sample was produced by heating with the laser above the crystallization temperature. The incident x-ray beam was focused with Kirkpatrick-Baez mirrors to a spot on the sample approximately 10 μm in diameter. The laser was focused to a spot on the sample approximately 40 μm in

diameter. The sample was kept in a flowing H_2/He atmosphere to prevent oxidation during heating.

Results

We were able to obtain time-resolved XAFS data from the crystalline Ge sample heated by the laser to approximately 740K, and from the amorphous sample heated to approximately 525K. Temperatures were estimated by analyzing the data to obtain the mean-square relative displacement and by applying the Einstein model, which has been shown to represent the temperature dependence of Ge XAFS quite well [7]. The temperature estimate is also in agreement with a recent experimental study of Ge at high temperatures [8].

Figure 2 shows k^2 Fourier transforms (FTs) of extended XAFS (EXAFS) from the crystalline sample for times within a few nanoseconds of excitation by the laser pulse. The sample cooled to a temperature of only ~500K between pulses. It can be seen from the figure that the temperature rise after arrival of the laser pulse occurred within 2 ns, as the FT peaks at 2 ns and 5 ns are essentially identical.

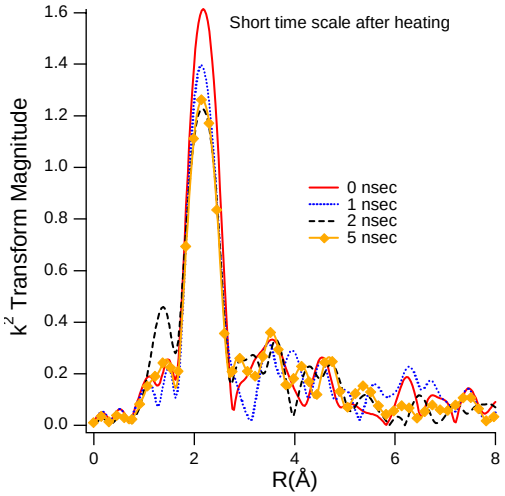

FIG. 2. Fourier transform of crystalline Ge EXAFS at short times after excitation by the laser.

We were able to obtain more detailed time-resolved XAFS data from the amorphous sample. Figure 3 shows the temperature versus time within a few nanoseconds of the excitation by the laser pulse. We determined that the excitation occurred at approximately 3.6 ns in the nominal time units obtained from observing, on an oscilloscope, the x-ray pulses detected by the APD and the laser pulses detected by a fast photodiode. The data were compared to a curve containing an exponential rise (also shown in the figure), and lattice heating was estimated to occur with a rise time of approximately 500 ps. The final temperature was reached at times up to ~1 ns or more after laser excitation. Interestingly, this is quite a bit slower than the lattice heating time determined for a crystalline silicon film in the well-known study by Downer and Shank, who found that the final lattice temperature was reached by ~100 to 200 ps [9]. Future measurements will include a more detailed examination of films produced from the start with a crystalline structure, which are in preparation.

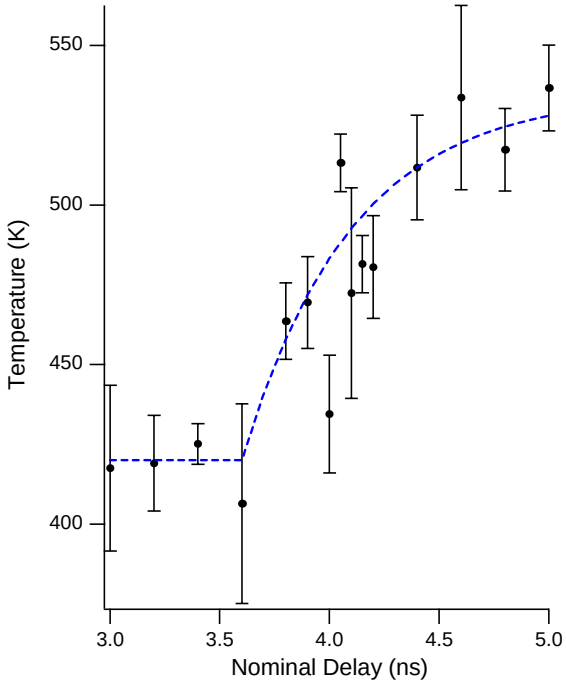

FIG. 3. Temperature versus time within a few nanoseconds of excitation by the laser pulse. Also shown is an exponential curve with a rise time of 500 ps.

Discussion

We developed an apparatus for obtaining time-resolved XAFS with high efficiency, for use in laser pump-probe experiments on a sub-ns time scale, by using a high-repetition-rate laser to increase the effective flux by more than two orders of magnitude over that of typical pulsed laser systems used for time-resolved x-ray experiments. We used the apparatus to obtain preliminary time-resolved XAFS of laser-heated amorphous and crystalline Ge films. We have determined that the process of energy transfer from the laser excitation to the lattice and the subsequent equilibration of the lattice vibrations to reach a final temperature are complete within 2 ns in the crystalline sample. More detailed measurements of the amorphous sample show that the energy transfer and

equilibration occur with a rise time of ~500 ps, with the final temperature reached at times of ~1 ns or more.

Acknowledgments

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