Ultrafast XAFS Measurements on Laser Excited Ge Films

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Abstract. Laser-pump/x-ray-probe measurements were made on Ge films with nominal time-delay steps of 18 ps. The response of the Ge lattice to the excitation of a high efficiency 200 fs pulse laser operating at 800 nm wavelength and at the Advanced Photon Source (APS) ring frequency of 272 kHz is probed by x-ray absorption fine structure (XAFS) measurements which determine the time dependences of the local structure. Initially the lattice response is dominated by a large increase of the RMS nearest neighbor bond disorder that decays within a single delay step. The next nearest neighbor RMS disorder shows an increase delayed by ~ 30 ps, consistent with only optical modes dominating the initial lattice response and other phonons being excited more slowly. The different rate of excitation of optical than the rest of phonons require a different mechanism for exciting the optical phonons. Because the laser excites electrons from binding to anti-binding states, a Franck-Condon like effect is suggested as the cause of this initial response, instead of the standard hot electron-hole coupling to phonons.

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INTRODUCTION

The semiconductor Ge is an interesting material, not only for its electronic but also for its structure properties. Its semiconductor amorphous state is different from its metallic liquid state, not only electronically, but also structurally. Amorphous Ge has almost the same density and nearest neighbor coordination as the crystal, while the liquid is one of the few materials that is denser, with higher coordination. Thus, there has been a lot of interest in understanding its properties, including recently the non-equilibrium dynamics. Many dynamic measurements have been made recently but our timeresolved XAFS capabilities that can probe the local structure from the crystalline through the melting transition will be able to add new important quantitative information about the non-equilibrium dynamics of Ge which should test the accuracy of our present theoretical understanding of the interactions between the initially excited electrons and the resulting non-equilibrium state of the lattice till thermal equilibrium is reached. In this paper we present our time-resolved measurements for lower laser powers where the Ge remains a solid and is heated by converting the initially excited electronhole cloud to a thermal equilibrium of increased temperatures below its melting point.

PROCEDURES

The apparatus used an 800 nm RegA 9000 Ti:Sapphire laser from Coherent Laser Systems producing ~200fs pulses at 272 kHz, which is the repetition frequency of a single bunch at the APS. Thus each occurrence of a single bunch was utilized. The laser system was synchronized to the synchrotron bunch pattern with the ring 352 Mhz RF signal followed by a phase-locked frequency divider providing the 88 MHz signal used as reference for the "Synchrolock" feedback system controlling the Mira 900 seed laser. Relative timing between laser and x-rays was adjusted in the range of interest by delaying the RF reference with electronics designed by engineers at the APS. The nominal delay increment was 18ps in the range where σ^2 changed rapidly. An additional delay ~500ps beyond this range was also used. The actual change in delay resulting from each change in delay setting was measured and used in determining the relative time dependence of σ^2 . Power output from the RegA laser was ~0.9W. During the experiments an ND filter was used to reduce the output power to 50mW.

An avalanche photodiode measuring the fluorescence/scatter from a titanium foil was used to monitor the incident x-ray flux, and a large-area

plastic scintillator was used to measure the germanium fluorescence. Each detector was operated in pulse-counting mode. Filters were used to limit the flux to a range that pulse-pileup effects were correctible using a fit to a polynomial. Future improvements to the apparatus will include use of multi-element APD detectors that will divide the total flux among 64 elements and thus reduce the necessity to limit the flux to avoid pulse pileup.

Kirkpatrick-Baez mirrors were used to focus the x-ray beam to a spot approximately 3µm in diameter. The x-ray beam was incident on the sample at approximately 30deg. from normal. The laser beam was incident on the sample at 15deg. from normal, and focused to a spot ~25µm in diameter vertically by $\sim 32 \mu m$ horizontally, as measured by the 10%/90% points of knife-edge scans. The knife-edge scan results were fit to a gaussian beam profile and the fluence onto the sample was calculated to be 20mJ/cm², also taking into account the transmission of the steering optics and sample chamber window. The actual laser energy absorbed may have been lower, due to reflection from the sample surface. The temperature rise per shot was estimated as 150K using an Einstein model for $\sigma^2(T)$, compared to a predicted temperature rise of 371K using the estimated fluence onto the sample. Thus the effective fluence may have been as low as 8mJ/ cm². The sample did not cool entirely between shots, and the baseline steady-state temperature before each laser pulse was ~532K. The two microbeams were aligned by scanning the sample position while monitoring the transmission of the laser and x-ray beams through the sample opening, and adjusting the laser steering mirrors until both beams were centered on the sample opening at the same sample position. Temperature stability is extremely important in maintaining alignment of two independent microbeams in an experiment lasting several days, and efforts were made to optimize the temperature stability, including a ventilation flow control system installed by the APS, sealing the labyrinth between the experimental "C" hutch and the adjoining "B" hutch, and precision sample stages. Remote control of laser focusing, laser shutter, etc. were very important in avoiding any need to enter the hutch once the experiment was set up. We also used a timescanning strategy in which we collected a single XAFS spectrum at each delay setting, and repeating this sequence many times to improve statistics at each time delay. This helped to average out longterm fluctuations.

EXAFS data was analyzed with Athena and Artemis software, which are part of the Ifeffit analysis package. FEFF7 [1] was used to generate the germanium standard. Fitting was done in R-space and S_0^2 was fixed in the analysis for σ^2 . Seventeen or eighteen scans were acquired at each of 19 delay settings. For the 1st shell each scan at a given delay time was analyzed individually and the results were averaged to obtain the final result. The noise in each scan was limited by the statistics from the about 10^5 effective counts for an energy point. The variation in σ^2 obtained from the individual scans was analyzed using standard statistical methods to determine the uncertainty at each time. For the second shell the variation in σ^2 was determined from the fluctuations of the eight averaged data points below the rise in the response.

The relative time dependence of σ^2 for both the first and second neighbor shells was fit to a simple model consisting of a step-function time response convoluted with a gaussian beam time profile. Note that the true beam profile is not gaussian, but slightly flattened at the leading edge. However, the gaussian gives a convenient means to vary the beam profile in the fit to test for jitter and/or broadening of the sample response from the simple step-function model [2]. Though the step-function model is probably a simplified picture of what must occur as a response to the laser excitation, it is still a useful first model since deviations from it could reveal physical behavior necessary to correct it. Uncertainty in a given fitted parameter was determined by varying it from its best-fit value and refitting the remaining parameters until such point that χ^2 of the fit increased by 1 [3].

The sample was a 200 nm thick polycrystalline Ge film formed by evaporation on a substrate heated to 520° C. The Ge film was coated on its surface facing the laser beam with a ~900nm Si₃N₄ layer and on its back surface with a ~2000 nm Si₃N₄ layer, all of which were supported on a 80 micron² opening produced by an anisotropic etch in a silicon wafer. The effects of the grain boundaries in the sample are expected to be negligible for the ~200nm grain size.

RESULTS

The two figures show fits of the measured time dependence of the EXAFS "Debye-Waller" factor (σ^2) for the first-neighbor shell (Figure 1) and the second-neighbor shell (Figure 2) to the simple step-function model. The gaussian RMS width was varied in the fit for both the first (second) neighbor shells. The best-fit values were 40ps +/- 8ps (14 +/- 5 ps). The value of χ_v^2 for the fit was 1.3 (1.2) for four parameters. The value of RMS width of the first shell obtained in the fit is very close to the known RMS width of the x-ray beam (e.g. 39ps +/-1ps for a recent

run in 24-bunch top-off mode with 100mA), indicating a very fast time response and negligible time delay jitter in the measurements. More evidence of negligible jitter is the similar noise in the data points where σ^2 has a large slope to those where σ^2 has zero slope.



FIGURE 1. First shell σ^2 as a function of relative delay between laser and x-rays. The curve is constructed from the best-fit parameters in the fit to the step-function response model.



FIGURE 2. Second shell σ^2 as a function of relative delay between laser and x-rays. The curve is constructed from the best-fit parameters in the fit to a step-function response model.

The value of the reduced χ_v^2 for both fits was ~1.2 for four parameters. Here v is the degrees of freedom in the fit given by the number of data points minus the number of variables. The parameter t₀ is one measure of the relative time at which the step-function-like response in σ^2 occurs in the two shells.

If one assumes that the response to laser excitation is immediate, t₀ represents the nominal relative time at which the laser pulse (essentially a delta function) and the center of the x-ray pulse coincide in real time. At that time $\frac{1}{2}$ of the x-rays see an unperturbed sample, and $\frac{1}{2}$ see the sample that has been excited by the laser, therefore the change in σ^2 at t₀ is $\frac{1}{2}$ of the final value (for the symmetrical beam time profile assumed in the model). Note that we don't at present have an independent means of establishing the true time at which the laser and x-ray pulses coincide in real time. Thus there could be some delay in sample response before which time there is no measurable change in σ^2 . However, we can certainly make a relative comparison between the first and second neighbors (and in principle, more distant neighbors), and the results of this comparison indicate that t_0 for the first neighbor σ^2 occurs 15 +/-7 ps *before* t_0 for σ^2 of the second neighbors. Therefore it appears that the lattice vibrations dominating the second neighbor σ^2 are not populated until a short time after those dominating σ^2 of the first neighbors.

DISCUSSION

The narrowing of the RMS response function of the 2^{nd} shell to 14 +/- 5 ps relative to that of the first shell of 40 +/- 8 ps is evidence that the step-function model is not correct. If it were then in the thermal equilibrium assumed in the step-function model, both shells should have the same RMS values and similar time dependence. The delay of 15 +/- 7 ps of t_0 of the 2nd shell relative to the 1st shell of Ge, reinforces the lack of thermal equilibrium. Offhand, the narrowing of the RMS of the response function of the 2nd shell is surprising, since even with a step function response of the 2nd shell, the fastest monotonic response to equilibrium that can occur, the measured response would be broadened by the 40 ps RMS of the Gaussian profile of the x-ray pulse. This more rapid rise in the σ^2 response can be explained by a non-monotonic variation to thermal equilibrium. Note that in Fig. 1 the rise in response of the 1st shell occurs after the first 6 data points while for the 2nd shell it occurs after the first 8 points (Fig. 2), a delay of about 40 ps.. If the variation to equilibrium has a delayed non-monotonic response such as a step of triple the height of the equilibrium step-function which then decays to the equilibrium value in a time shorter than the 40 ps RMS of the x-ray pulse, then the initial rate of rise will be about 3 times faster than the step function model and would level off to the equilibrium value explaining the observed smaller RMS. We also investigated the effect of noise

causing fluctuations in point 8. If point 8 is increased from 19.98 to 21.25 (2.4 times its standard deviation), the value it would have on a fitted curved obtained by fixing the RMS to 40 ps, then the fit deteriorates and the value of RMS becomes 28 +/-11 ps, instead of 14 +/- 5 ps. Although noise may be a factor in causing some uncertainty in the RMS of the of the response of the second shell, the fact of the delay of the response of the second shell is robust, though its value may range between 15 - 40 ps.

In the diamond structure of Ge the long wavelength optical modes have the property of the nearest neighbors vibrating in opposite phase with the same amplitude while the second neighbors vibrating in phase with the same amplitude. Thus the relative σ^2 between the first neighbors is finite while that of the second shell is zero. The time scale of the present measurement is commensurate with the results of a Raman scattering study showing a lifetime of 8ps +/- 1ps at 77K and 4ps +/- 1ps at 300K for the populations of both the TO and LO optical phonon modes probed by the measurement [4]. Since our measurement occurred at a higher temperature (T~532K), one might expect even shorter time scales, but the EXAFS provides a complementary measurement, probing phonons to which the Raman measurement is not sensitive.

This Raman measurement shows that the TO and LO response occurs only in the first 18 ps time slice, yet the XAFS measured response lasts much longer. To understand this consider Fig. 3 which shows a schematic of the relation between the x-ray pulse, the laser pulse, and the σ^2 response of the Ge 1st and 2nd shells. The gray histogram indicates the portion of the x-ray pulse added to the signal in three nominal 18 ps steps. Two laser pulses at different times relative to the x-ray pulse are shown by the thicker vertical lines. On the time scale of Fig. 3 the laser pulse has no significant width. The laser pulse on the right arrives after all of the x-ray pulse has already probed the sample and measures data points in Fig. 1 before the laser excitation. Time flows from right to left in the direction of the arrow attached to the x-ray pulse profile. The laser pulse on the left arrives before the x-ray pulse so that all of it probes the response of Ge to laser excitation as per the last five data points of Fig. 1. The light vertical lines indicate the nominal 18 ps time step that the laser makes as it approaches the intermediate regime where a portion of the x-ray pulse to the right of the laser pulse will detect the Ge response due to the laser excitation. The gray histogram indicates the area of each newly added 18 ps slice of the x-ray pulse that detects the response as the laser delay time is stepped to the left of the slice. The response is schematically shown as the white histogram. The clear portion of the white histogram is the first two time delay steps of the first shell response, the first step being the large optical phonons signal, while the hatched third and fourth steps are the overlap of the response of the 1st and 2nd shells, taking into account that the 2nd shell has negligible response in the first two steps.



FIGURE 3. A schematic of the relationship of the timing of pump-laser pulses, the probe-x-ray pulse and the Ge film response to the laser excitation.

As the right laser pulse steps to the left so that the dominant TO and LO response of the 1^{st} shell overlaps the largest section of the gray histogram the response of the 2^{nd} shell just starts overlapping the smallest portion of the gray histogram, still giving an insignificant signal . Only at the next step one might expect a significant signal in the 2^{nd} shell which is delayed relative to the 1^{st} shell. Note that since the x-ray pulse is longer than the time delay steps, the large initial 1^{st} shell response continues to contribute to the increase of the total measured signal till the laser pulse steps to the left of the x-ray profile.

Though the Raman measurement [4] showed the response of the optical modes it could not determine the existence of the delay of excitation of other phonons. Since Ge is a non-polar solid ref. [4] realized it was necessary to explain both why it had a cross section of exciting the optical modes similar to that of a polar solid such as GaAs, and the similarity of the strengths of the TO and LO signals. This was done by assuming that the mechanism of exciting TO and LO phonons is by direct coupling to the excited electrons and holes. However, this mechanism does not explain the delay in the excitation of the other modes since non-equilibrium electrons and holes excite in similar time and with similar cross sections the rest of the phonons [5]. A different mechanism is required to explain the more rapid time response of the long wavelength optical modes.

We suggest that this different mechanism is a Franck-Condon like effect in Ge solid. The laser excites bonding valence electrons into anti-bonding states, destabilizing the lattice, presumable to a larger nearest neighbor distance. Exciting long wavelength optical phonon modes can initially accomplish the task of elongating .the nearest neighbor distances. The diamond structure of Ge consists of two FCC structures displaced along the (111) direction by 1/4 of the cube diagonal. Long wavelength optical phonons vibrate the two essentially rigid sub-lattices relative to one another with the nearest neighbors distance (given by the displacement between the two sub-lattices) changing, while the second neighbor distance (given by a sub-lattice nearest neighbor distance) not changing. Vibrating along the diagonal so as to initially expand the nearest neighbor distance is the response to satisfy the instability. Note that the nearest neighbors are directly covalently bonded, while the second neighbors are not, so the first neighbors are the ones most affected by the Franck-Condon effect.

SUMMARY

Laser-pump/x-ray probe XAFS measurements have found a new effect in the lattice response of Ge under laser excitation; a time delay of about 30 ps in the response of the 2^{nd} shell of Ge atoms from the origin atom in the local structure compared to that of the 1^{st} shell. This behavior is consistent with the initial excitation of optical phonons before other phonons are significantly excited. The time delay is evidence that the mechanism of the excitation of the optical phonons is not by the standard mechanism of excitation by hot electrons and holes, but by a different one which we suggest is a Franck-Condon like effect in solid Ge as the laser destabilizes the lattice by exciting binding electrons into antibinding states.

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