

## Anharmonic Lattice Dynamics in Germanium Measured with Ultrafast X-Ray Diffraction

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Damping of impulsively generated coherent acoustic oscillations in a femtosecond laser-heated thin germanium film is measured as a function of fluence by means of ultrafast x-ray diffraction. By simultaneously measuring picosecond strain dynamics in the film and in the unexcited silicon substrate, we separate anharmonic damping from acoustic transmission through the buried interface. The measured damping rate and its dependence on the calculated temperature of the thermal bath is consistent with estimated four-body, elastic dephasing times ( $T_2$ ) for 7-GHz longitudinal acoustic phonons in germanium.

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In semiconductors, the response to impulsive, interband optical excitation generally proceeds through intraband relaxation of hot carriers via phonon emission, radiative and nonradiative recombination, vibrational acoustic transport into the bulk or across interfaces, and eventual thermalization of the phonon modes via lattice anharmonicity [1]. While the processes involving charge carriers and Raman-active optical phonons have been extensively characterized with optical methods [1], the ultimate steps of transport and thermalization of nonequilibrium acoustic lattice vibrations have remained largely undetected. Moreover, anharmonic lattice effects are of general interest because they are responsible for many other common processes in the solid state, such as thermal expansion, volume-dependent elastic constants, and temperature dependent thermal conductivity in solids [2]. Yet, the measurement of non-Raman-active coherent acoustic phonons is demanding and has been indirectly achieved only at surfaces [3,4]. By combining the temporal resolution of ultrafast laser spectroscopy [5] with the structural sensitivity of x-ray scattering [6], a number of direct studies [7–13] of atomic motion deep within the bulk of matter have been recently achieved. In this paper, we report on ultrafast x-ray measurements of strain oscillations in an impulsively heated germanium film. Excitation-dependent damping times and vibrational transport across a buried interface are simultaneously measured, thereby identifying individual coherent phonon decay mechanisms.

In our experiment, multiterawatt, femtosecond laser pulses [14] were focused onto a moving copper wire to produce ultrafast x-ray bursts [15] at 20 Hz. The emitted

x rays, consisting of spin-orbit split 8-keV (1.54 Å) Cu- $K_{\alpha 1}$  and Cu- $K_{\alpha 2}$  lines, were diffracted by the sample, a 400-nm-thick, crystalline (111) germanium film grown on bulk (111) silicon by surfactant-mediated heteroepitaxy [16]. After symmetric Bragg diffraction, the x rays were recorded with a solid state area detector [x-ray charge-coupled device (CCD)]. The two  $K_{\alpha}$  doublets were diffracted at two distinct Bragg angles (germanium 13.6°, silicon 14.2°) resulting from different lattice constants of the two diamondlike materials (germanium 5.65 Å, silicon 5.43 Å). The area of the sample probed by the x rays was illuminated by an 800-nm wavelength, 30-fs laser pulse with fluence of 40 mJ/cm<sup>2</sup>. By simultaneously probing the film and the substrate, we could measure the strain dynamics in both components of the structure. Multishot degradation at the very surface was avoided by translating the sample after exposure to a few hundred pulses.

Typical x-ray probe lines, diffracted at a pump-probe time delay of 100 ps, are shown in Fig. 1. In the Ge film a full shift of the two nonbroadened lines indicates homogeneous expansion over its entire thickness. As the sample was illuminated with a Gaussian intensity profile, fluence resolved measurements of the time-dependent centroid shifts (averaged over the  $K_{\alpha 1}$  and  $K_{\alpha 2}$  positions) could be easily made and are displayed in Fig. 2 for four regions of the photoexcited region (A–D as indicated in Fig. 1). The displayed experimental points represent the average deviation from the static diffraction angle of the  $K_{\alpha 1}$  and  $K_{\alpha 2}$  for four different fluences [(A) 40 mJ/cm<sup>2</sup>, (B) 32 mJ/cm<sup>2</sup>, (C) 25 mJ/cm<sup>2</sup>, (D) 15 mJ/cm<sup>2</sup>]. Typical values of the peak strain of ~0.05%–0.1% correspond

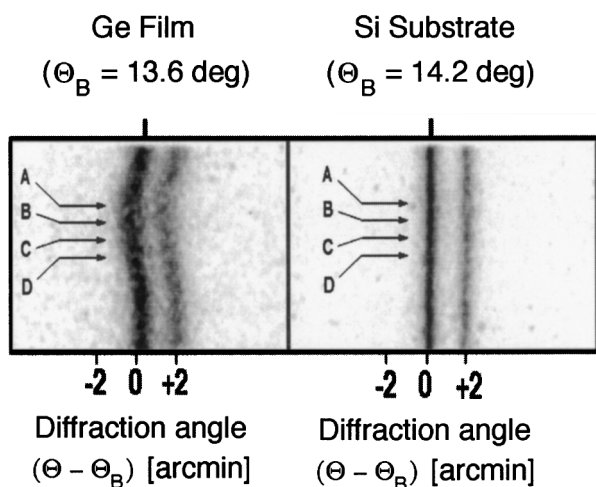


FIG. 1. Experimentally measured diffraction curves from the photopumped germanium film and the silicon substrate for a 100 ps pump-probe delay. The horizontal axis is the diffraction angle and the vertical is the position on the crystal. The regions of the samples labeled as A–D represent the positions where fluence and time resolved centroid positions were measured.

to an increase in the distance between lattice planes of about 150–300 fm and result in shifts of the Bragg angle that range between  $-25$  and  $-50$  arcsec. The peak of the measured compressions, representing a spatial average over  $2.6\text{-}\mu\text{m}$  probed depth in silicon, correspond to 20–40 fm average change in lattice spacing (i.e., by a few nuclear diameters). Because of better crystalline quality of the bulk substrate, the silicon measurement was about  $4\times$  more sensitive than that of the germanium film. Approximately 75 ps after photoexcitation, expansion of the germanium lattice reaches its peak value [Fig. 2(a)]. Damped oscillations were observed at longer time delays, indicative of periodic expansion and compression of the film. Diffraction from the silicon substrate evidenced centroid shifts toward higher angles, indicating compression simultaneous with Ge-film expansion [Fig. 2(b)].

Two fluence dependent effects are immediately apparent in the Ge data. First, we observed a fluence-dependent delay on the onset of expansion, becoming shorter at higher excitation level. Second, fluence-dependent lifetimes of coherent oscillations in germanium were clearly observable.

Recently, a similar effect has been observed under different experimental conditions [10]. In Ref. [10], a reversible, nonthermal phase transition was evidenced from strongly overdamped acoustic oscillations in InSb, with reported strain near the Lindemann criterion ( $\sim 10\%$ ). In our experiment, the equilibrium lattice is coherently strained by as little as 0.1%. Second, unlike the case of ultrafast melting [11], the total diffraction efficiency in the 111 direction (integrated over the whole Ge-rocking curve) oscillates around the static value but never decreases, indicating that no significant loss of order is taking place. Finally, as shown below, after the coherent oscillations are damped, we can quantitatively model our data for all fluences by

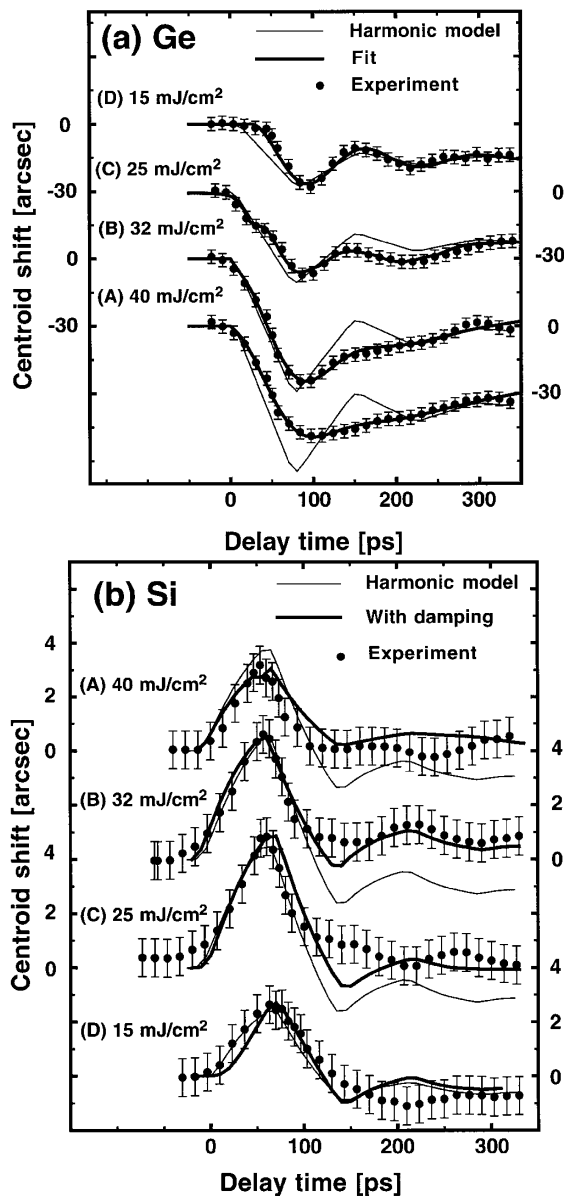


FIG. 2. Time dependent shift of the angular centroid position, for (a) 400-nm germanium film, (b) silicon bulk. Thin lines: theoretically calculated centroid shifts after heating of the germanium film with the calculated strain profile. A fully harmonic model for a perfect crystal and a fluence-independent heating time of 10 ps is assumed. Thick lines: (a) phenomenological fits to the germanium diffraction centroid, yielding total damping times ( $1/\Gamma_{\text{tot}}$ ) of  $44 \pm 20$  ps (A),  $62 \pm 15$  ps (B),  $75 \pm 12$  ps (C),  $109 \pm 10$  ps (D). (b) Expected silicon response using heating and damping times from the germanium data.

assuming a hot crystalline germanium cooling by thermal diffusion into the silicon substrate. Therefore our results cannot be explained with a phase transition.

Our interpretation proceeds along the following lines. The optical pump pulse excites carriers in germanium over its absorption depth (200 nm), with initial peak surface density of  $\sim 10^{21}\text{ cm}^{-3}$ , with negligible photoexcitation of the substrate. The absorption depth is largely independent on the excitation fluence, due to the high density of states

available for interband excitation and to rapid electron-hole thermalization, depleting the optically coupled states already during absorption of the pump pulse. While efficient ambipolar diffusion homogeneously distributes the hot carriers over the entire film within a few picoseconds [17], equilibration with the lattice takes place through a combination of nonradiative Auger recombination and intraband relaxation [18]. The 430-meV potential barrier at the interface between germanium ( $E_g = 0.67$  eV) and silicon ( $E_g = 1.1$  eV) is significantly higher than the quasi-Fermi-levels of the relaxed electrons and holes, confining the carriers at all times and leaving the silicon substrate unexcited. Thus, the diffracted Ge lines shift fully, with virtually no broadening and no significant negative strain is generated in the silicon. The observed delays in the onset of expansion are in good agreement with delayed heating times of 50 ps (*D*), 15 ps (*C*), 5 ps (*B*), and 3 ps (*A*), calculated using available values for germanium Auger recombination rates [19].

Homogeneous impulsive heating starts the coherent film vibration with a period of  $2d/c_L \approx 150$  ps ( $d = 400$  nm  $\pm$  20 nm is the film thickness and  $c_L = 5400$  m/sec is the longitudinal speed of sound in germanium) with the unexcited silicon substrate acting as vibrational energy sink. In a harmonic approximation and assuming a perfect crystal, decay of the coherent vibration results only from transmission of acoustic pulses into the substrate. In a real crystal, however, a variety of additional effects, ranging from defect and surface scattering to phonon-phonon scattering, result in more rapid damping of the coherent oscillations. Importantly, while all the defect-mediated scattering mechanisms are independent of the degree of excitation of the lattice, anharmonic interactions between the normal modes of the crystal depend upon the population of individual phonon modes and thus on the temperature of the solid [20]. Therefore, the observed fluence dependent damping is a direct indication of lattice anharmonicity.

To estimate the relative contributions of the various mechanisms to the measured damping rate ( $\Gamma_{\text{tot}}$ ), we first compare the data to a fully harmonic model for a perfect crystal with no defects and assuming complete acoustic matching between the film and the substrate [Fig. 2]. The initial stress distribution was numerically calculated by solving two differential equations for carrier and lattice temperature [21], taking into account screened Auger recombination [22] and density-dependent carrier diffusion [17]. The one-dimensional elastic equation [23,24] was then numerically solved in the two-layer system starting from the calculated stress distribution. Thermal diffusion, significant at the sharp interface between hot germanium and cold silicon, was included in the model. The expected time-dependent x-ray diffraction pattern was calculated using dynamic diffraction theory [25]. The model predicts fluence-independent damping ( $\Gamma_{\text{harm}}$ ), originating from the transmission of the coherent vibrations into the substrate. The long lived coherent oscillations measured at

the lowest fluence follow the calculated curve very closely, demonstrating that defect and surface scattering play a minor role in our sample, and that only acoustic transmission should be taken into account among the fluence-independent processes. As the laser fluence is increased and anharmonicity becomes significant, the data start to deviate from the model. Total damping rates ( $\Gamma_{\text{tot}}$ ) were fitted to the germanium data using a phenomenological functional form for damped coherent oscillations superimposed on a delayed thermal response. In the substrate, while the harmonic model is in reasonable agreement with the data for low excitation, inclusion of the fitted damping times yields better matching in the higher fluence range. No clear evidence for fluence-dependent delay in the onset of compression can be observed in the data, probably because of the relatively large uncertainty in the measurement.

The damping rate from acoustic transmission (dominant at low fluence) was subtracted from the fitted rates, yielding the fluence-dependent component of the damping ( $\Gamma_{\text{anh}}$ ), displayed in Fig. 3. Two different mechanisms can explain the anharmonic damping of the 7-GHz oscillations: inelastic collisions with thermally populated phonons, causing decay of the population of the coherent mode ( $T_1$  processes) [25] and energy conserving collisions, leading to mutual decoherence between the individual phonons ( $T_2$  processes). Both processes exhibit a linear dependence on temperature for a classical thermal bath [26], consistent with our observation. The former,  $T_1$  process, originates largely from three-body collisions arising from cubic anharmonicity. For a 7-GHz phonon, however,  $T_1$  processes are expected to occur at a rate of  $\sim 10^{-5}$  psec $^{-1}$ , 3 orders of magnitude slower than the measured decay of the oscillations [26]. On the other hand, four-body elastic dephasing ( $T_2$ ) processes [27] can be significantly faster. The origin of pure dephasing lies in quartic anharmonic coupling, modulating the frequency of the 7-GHz mode and causing loss of coherence. This effect can occur on time scales that are much faster than inelastic collisions and energy flow out of this very mode. By introducing reasonable four-body terms for the temperature range of our experiment, we find [27]  $T_2^{-1}$  of order 0.01 psec $^{-1}$ , which is consistent with our measurement.

In conclusion, we have measured ultrafast, acoustic phonon dynamics in a germanium/silicon layered structure, measuring atomic vibrations with 10-fm resolution, using ultrafast x-ray diffraction. The fluence dependence of the oscillations directly yields the temperature-dependent decoherence rates resulting from anharmonic lattice dynamics within the germanium film. We attribute the observed damping to  $T_2$  processes, which originate largely from four-body interactions that cause decoherence in the evolution of the mode. Ultrafast x-ray diffraction allows direct measurement of coherent acoustic excitations before their thermalization with the environment, thereby making experiments of nonequilibrium ballistic

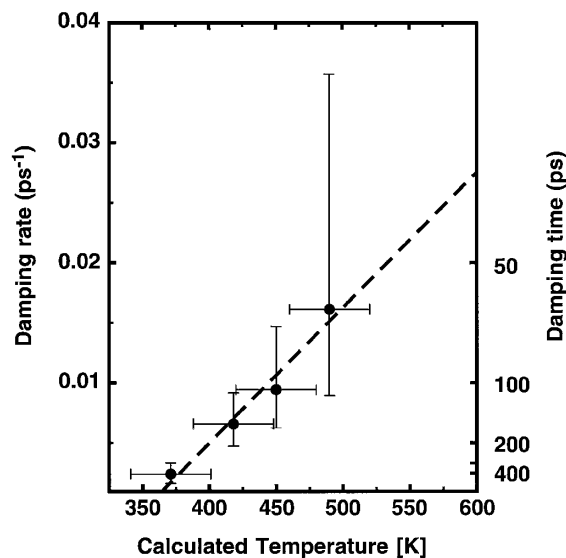


FIG. 3. Anharmonic damping rates as a function of calculated temperature in germanium. The anharmonic damping rates are calculated by subtracting the low fluence, harmonic damping rates from the total damping rates. The vertical error bars have been determined from the uncertainty on the fitted value. The error bars on the calculated temperature of the crystal (horizontal) originate from the uncertainty on the optical constants of the sample during irradiation, on laser fluence variations, and on the thermalization time of the thermal bath. Dashed line: linear fit to the data.

heat transport possible. Anharmonic effects of strongly driven or shocked crystals and of solids close to phase transitions and critical points could also be examined, with both fundamental and technological ramifications.

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- [27]  $T_2^{-1} \approx \pi/16\hbar^2 \sum_i \varphi_{11ii}^2 n_i (n_i + 1)/\gamma_i$  (Ref. [28]), where  $\varphi_{11ii}$  is the quartic coupling coefficient between the 7-GHz mode (mode 1) and bath mode  $i$ ,  $n_i$  is the average number of phonons in mode  $i$ , and  $\gamma_i$  is  $T_1^{-1}$  of mode  $i$ , which we take to be of the order of  $10^{-3}$  psec $^{-1}$  [Ref. (26)]. To estimate  $\varphi_{11ii}$ , we take the result for a one-dimensional chain, where  $\varphi_{11ii} \sim \pi \hbar^2 \omega_1 \omega_i / (ka^2)$ , where  $k$  is the spring constant and  $a$  is the lattice spacing [29], for temperatures around 500 K. We find  $T_2^{-1}$  to be  $\sim 10^{-2}$  psec $^{-1}$ . Note that, for experimentally relevant temperatures, since  $n_i$  and  $\gamma_i$  vary linearly with temperature, so does  $T_2^{-1}$ .
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