Ultrafast x-ray measurement of laser heating in semiconductors: Parameters determining the melting threshold

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The pulse-width dependence of thermal melting and ablation thresholds in germanium and gallium arsenide is correlated to direct, ultrafast x-ray measurements of laser-heated depths. The heating dynamics, determined by the interplay of nonlinear optical absorption, delayed Auger heating, and high-density carrier diffusion, explain the scaling laws of thermal melting thresholds in different semiconductors.

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Short-pulse laser structuring of solids is a key component in modern materials science and technology, with applications ranging from optical recording[1] to pulsed laser deposition of thin films,[2] and femtosecond micromachining.[3] In particular, ablation in semiconductors and metals follows a physical pathway that is *strictly thermal*, with melting,[4,5] and phase explosion[6–8] determining the early steps of material removal. This behavior is in contrast with what occurs in transparent materials, where damage and ablation are driven by optical breakdown and plasma formation.[9] The parameters determining length and time scales of lattice heating are therefore crucial for the understanding of the processing of absorbing materials. Yet, since thermalization dynamics after laser irradiation cannot be exhaustively monitored using ultrafast optical probes, precise control of laser modifications is still largely achieved on empirical grounds.

In this paper, ultrafast x-ray diffraction[10] measurements of thermally generated strain profiles[11,12] are performed close to the thermal melting threshold in laser-excited Ge and GaAs. By modeling the measured thermal/elastic response of the solids, a precise estimate of the laser-heated depth and of the critical parameters determining the characteristic scales of energy thermalization is achieved. Delayed Auger heating,[13] two-photon absorption,[14,15] and high-density carrier diffusion[16] are found to be key processes regulating the heating dynamics. The different pulse-width dependence observed in the thermal melting threshold for Ge and GaAs are in this way understood. Importantly, while it is sometimes claimed that femtosecond processing of materials is characterized by energy localization after laser deposition, we find this effect to be not generally true for semiconductors.[17]

Figure 1 shows single-shot thermal melting and ablation thresholds of Ge(111) and GaAs(111) for 800-nm wavelength irradiation, measured for different pulse durations (50–500 fs) with time-resolved optical microscopy.[18] A p-polarized optical pump pulse, impinging at an angle of 60° was used to induce the phase transformations in the semiconductor crystals, while a variably delayed probe pulse provided snapshots of the evolving surface, imaged with an optical microscope objective onto a charge-coupled device (CCD) camera. By measuring the molten and ablated areas 200 ps after optical excitation, we could precisely assess the respective thresholds[19] with significantly smaller uncertainties than a postexcitation analysis of the craters. Surprisingly, while both the thermal melting and ablation thresholds in GaAs increase by about a factor of 3 across the measured pulse-width range, those in Ge are found to be approximately constant. The absolute fluence values are also difficult to reconcile with respective linear absorption depths for 800-nm light ($1/\alpha_{Ge}=200$ nm and $1/\alpha_{GaAs}=900$ nm) and known physical parameters for the two semiconductors.[20]

In Ref. 11, we reported ultrafast x-ray diffraction measurements of picosecond acoustic pulses propagating into the bulk of GaAs and showed that the scale length of surface strain could be accurately retrieved. In this paper, we utilize this same method to assess the respective heating dynamics of the two materials, GaAs(111) and Ge(111) (Fig. 2). X-ray bursts of spin-orbit split 8-keV (1.54-Å) Cu $K\alpha_1$ and Cu $K\alpha_2$ line radiation at 20 Hz were generated by focusing terawatt femtosecond laser pulses onto a moving copper wire. The experiments were conducted by measuring symmetric Bragg diffraction from the (111) lattice spacing (d_{111}

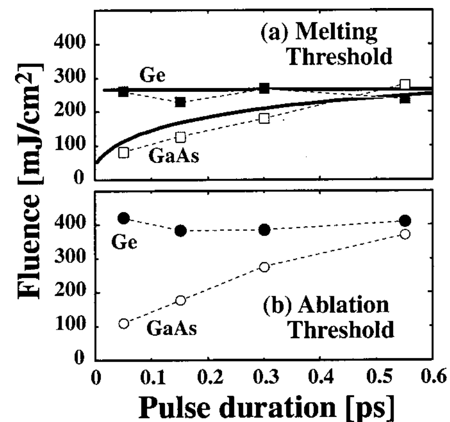

FIG. 1. (a) Thermal melting thresholds of Ge (solid symbols) and GaAs (hollow symbols) as measured using time-resolved microscopy. Solid lines are the results of model calculations obtained using tabulated parameters for the two materials and the heating behavior from the x-ray measurements. (b) Ablation thresholds of Ge and GaAs. Error bars for both figures are smaller than the symbol size.

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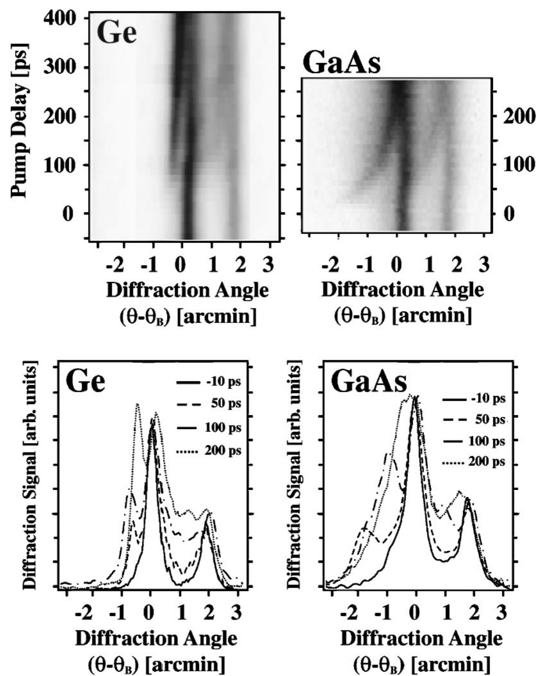

FIG. 2. Ultrafast x-ray diffraction measurement on Ge and GaAs, pumped with 800-nm, 30-fs laser pulses at 100 and 50 mJ/cm^2 fluence. Horizontal axes represent angular deviation from the Bragg angle for Cu $K\alpha_1$ radiation. For GaAs, $\theta_B = 13.6523°$, while for Ge $\theta_B = 13.6420°$. The absolute angle of diffraction could not be measured. Top figures plot the time-resolved rocking curves on a gray-scale map, while the lower figures present line scans at four representative time delays.

$= 3.2639$ Å for GaAs and 3.2663 Å for Ge), which for both diamondlike materials resulted in a Bragg angle θ_B of approximately 13.6°. The area probed by the x rays was excited by 800-nm, 30-fs laser-pulses at different pump-probe time delays with fluences slightly below the thermal melting threshold (Ge, 100 mJ/cm^2; GaAs, 50 mJ/cm^2). To avoid multishot surface degradation, the samples were translated at each time delay. At positive pump-probe time delays, we observed in both materials a new diffraction line at lower angles, indicative of expansive strain. The onset of the strain-induced shift of the shoulder was observed to be significantly slower in Ge (>100 ps) than in GaAs (few tens of ps). At the initial Bragg angle a largely unperturbed diffraction line originated from the unstrained parts of the crystal beneath the expanded volume. At later times the new lines decreased in width and merged asymptotically with the broadened and shifted main lines. Both materials showed qualitatively similar behaviors, differing in the magnitude of shifts (Ge, ≈ -1 arcmin, corresponding to -1.8×10^{-7} Å^{-1} in reciprocal space; GaAs, ≈ -2 arcmin) and in the decay time (Ge, ≈ 400 ps; GaAs, ≈ 250 ps).

After absorption of the optical energy by interband excitation, thermalization between the hot carriers and the lattice occurs through a cascade of scattering processes, involving intraband decay and emission of longitudinal optical phonons that later decay into acoustic phonons. The heating rate is ultimately limited by delayed Auger processes, which reduce carrier density while increasing their temperature and generating hot electron-hole pairs for several tens of picoseconds. During the delayed heating process, carrier diffusion[16] can play a significant role in determining the depth ζ over which the energy is thermalized. As discussed in detail in previously published work,[12,21,22] heating is generally significantly faster than thermal expansion of the solid, leading to quasi-isocoric generation of a nonuniform stress distribution. Expansion of the surface and propagation of a strain pulse into the bulk follow the heating process. The onset of surface strain occurs in a characteristic time scaling as the heated depth ζ divided by the longitudinal speed of sound c_L. Anharmonic lattice interactions eventually cause a transition to diffusive thermal transport within 100–500 ps,[19] while reshaping of the strain profile due to dispersion effects is not important on this time scale.[23] While excitation of optical phonons results only in small modulations of the diffracted intensity, dynamic strain formation causes the observed reshaping of the diffraction curve. Importantly, the profile of the acoustic pulse launched into the bulk of the solid is critically determined by the initial thermal stress profile, which can be retrieved over a depth of several microns by diffraction measurements of the thermoelastic response.[11]

The results displayed in Fig. 2 were compared to model calculations, in which the heat equation was solved in the two-temperature approximation,[24] starting from linear and two-photon optical absorption and including intraband and delayed Auger relaxation, carrier diffusion into the bulk, and cooling of the lattice via heat diffusion. The heat equation was coupled to a one-dimensional elastic equation and x-ray rocking curves were calculated using standard dynamic diffraction theory using literature values for the linewidths.[11] The simulations were performed using low-density electron-phonon scattering rates[25] and experimental Auger recombination rates.[26,27] Two-photon absorption and density-dependent diffusion coefficients, not precisely known in these conditions, were left as free parameters.

Calculations were first performed neglecting two-photon optical absorption and carrier diffusion, i.e., assuming that heating occurs primarily over the linear absorption depth ($1/\alpha_{Ge} = 200$ nm and $1/\alpha_{GaAs} = 900$ nm). Nowhere within the uncertainties of the parameters used did this assumption provide a satisfactory prediction of the x-ray results. Excellent agreement could be found, however, when the heating depth ζ was additionally adjusted to account for two-photon absorption and fast carrier diffusion. The best agreement was found for $\zeta_{Ge} = 1$ μm in Ge and $\zeta_{GaAs} = 275$ nm in GaAs (Fig. 3).

The observation of heating depths significantly larger than expected by the linear absorption coefficient is surprising. However, ambipolar diffusion is a highly nonlinear function of carrier density,[16] and diffusion coefficients of 100 cm^2/s can be expected at 10^{20} cm^{-3}.

In Ge, then, the combination of efficient high-density carrier diffusion[6] ($D > 100$ cm^2/s) and slower Auger heating[14,15] ($\gamma_{Auger} = 1.1\times10^{-31}$ cm^6/s) allows redistribution of the absorbed energy deep into the bulk of the solid.[28] Slow Auger recombination rates and significant heated volumes cause the observed long strain formation time, approxi-

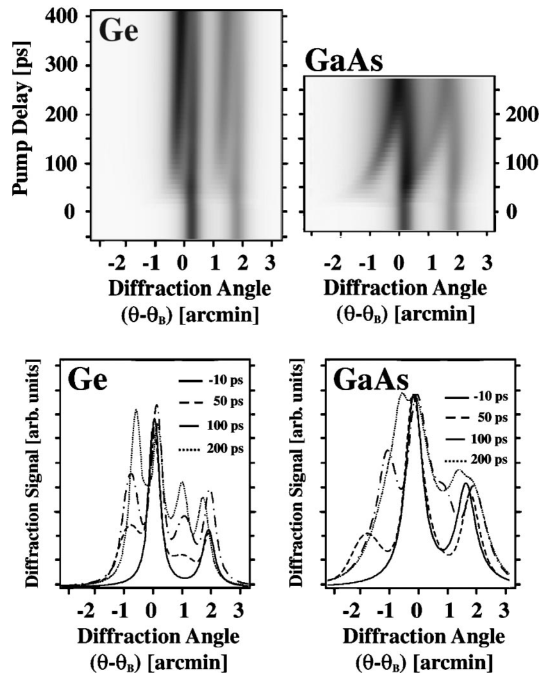

FIG. 3. Calculated rocking curves corresponding to Fig. 2. Heating depths of $\zeta = 275$ nm and $\zeta = 1$ μm for GaAs and Ge are used, respectively.

mately determined by $\zeta_{\mathrm{Ge}}/c_{L\mathrm{Ge}}$ (>100 ps), with $c_{L\mathrm{Ge}}$ being the longitudinal speed of sound in Ge.

To confirm the role of hot electron diffusion in the heating of Ge, we repeated the measurement of strain dynamics using x-ray diffraction, this time using crystalline Ge(111) films of 150-nm, 400-nm, and 900-nm thicknesses.[29] The 430-meV potential barrier at the interface between Ge (with a band gap $E_g = 0.67$ eV) and Si ($E_g = 1.1$ 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. For all films (Fig. 4 presents data and calculations for the 900-nm film), homogeneous heating over the entire thickness was conclusively evidenced by shifts of the nonbroadened diffraction lines toward smaller diffraction angles, with no splitting of the lines seen. Importantly, no expansive strain of the Si lattice was observed, confirming that no laser heating occurred in the substrate beneath the Ge film, and thus ruling out the possibility that bleaching of the interband optical transition may cause enhanced heating depths. Thus, this set of observations further supported our conclusions: rapid electronic transport in Ge is responsible for redistribution of the energy contained in the not-yet-thermalized, hot electrons from the initial 200-nm-deep absorption profile to micrometer-scale depths.

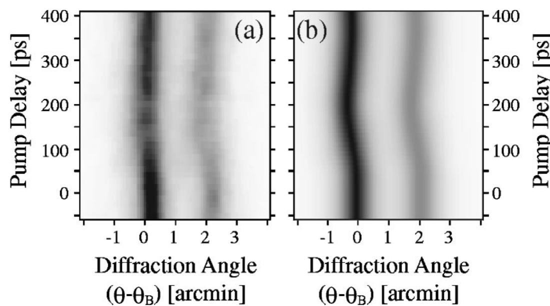

FIG. 4. (a) Measured time-resolved x-ray rocking curves for a 900-nm Ge(111) film on a Si(111) substrate. (b) Calculated rocking curves for the conditions of (a).

In the case of GaAs, the x-ray measurements indicated an energy-deposition scale length shorter than the linear absorption depth. Nonlinear absorption, neglibible in the case of Ge, is expected to contribute significantly to absorption in GaAs,[14,15] while delayed Auger heating[13] ($\gamma_{\mathrm{Auger}} = 7\times10^{-30}$ cm^6/s) will rapidly transfer the hot-carrier energy to the GaAs lattice before significant ambipolar diffusion. Inclusion of both these effects in our model accurately accounts for the decrease in the heating depth to about 275 nm. A two-photon absorption coefficient $\beta \sim 15$ cm/GW was obtained by fitting the diffraction data. This is in excellent agreement, after extrapolation to 800 nm, with literature values.[14,15]

The heating dynamics concluded from the x-ray measurements readily explain the pulse-width dependence of the thermal melting and ablation thresholds. In Ge the energy is rapidly redistributed by hot-carrier diffusion, with melting and ablation being determined, at least in this range of pulse-widths, only by the total absorbed energy and independent on the duration of the laser pulse. Conversely, the heated depth in GaAs decreases for shorter pulses because of two-photon absorption, with the energy remaining localized due to fast Auger recombination. This results in more efficient heating of a smaller volume and a decrease in the thresholds for thermal transformations.

In Fig. 1, we show the predicted thermal melting threshold for different pulse widths as calculated by using the measured heating depths in Ge and using the extracted two-photon absorption coefficient in GaAs. Although no temperature dependence of the heat capacity was taken into account, the predicted results match well the overall behavior of the thermal melting threshold. No attempt was made to predict the ablation threshold, as the parameters determining its precise value are still the subject of active research and debate.[6]

In conclusion, we directly measured the bulk heating volumes of Ge(111) and GaAs(111) using ultrafast x-ray diffraction, which can be applied to study transport and heating processes that are not accessible with other techniques. Our experiments clarify the controversial dependence on laser-pulse duration of semiconductor thresholds for thermal transformations, primarily determined by the interplay of nonlinear optical absorption, high-density carrier diffusion and delayed Auger heating. We find spatial and temporal scales for the phase transformation to depend on the details of a complicated energy thermalization pathway, where nonequilibrium diffusion can play an important role.

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