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We have observed an ultrarapid electronic phase transformation to a centrosymmetric electronic state during laser excitation of GaAs with intense femtosecond pulses. Reflection second-harmonic intensity from the upper 90 atomic layers vanishes within 100 fs; reflectivity rises within 0.5 ps to a steady value characteristic of a metallic molten phase, long before phonon emission can heat the lattice to the melting temperature.

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Several years ago, Van Vechten, Tsu, and Saris suggested that semiconducting materials with a diamond lattice structure could be disordered by direct excitation of the electronic system while the lattice modes remain vibrationally cold [1]. The diamond structure is stabilized by bond charges in the tetrahedral sp^3 bonds. Absorption of photons creates a free-carrier plasma by removing electrons from bonding to antibonding orbitals. It was suggested that a sufficiently dense photoexcited plasma could weaken the lattice, giving atoms enhanced mobility without significantly increasing their thermal energy. This mechanism was called "plasma annealing."

Several groups undertook experiments with pulses lasting 20 ps and longer to determine whether annealing could take place without heating the lattice above the melting threshold [2]. In disagreement with the plasma annealing picture, it was found that a thermal model could account for observed changes in the reflectivity of laser-excited Si, Ge, and GaAs. The thermal model assumes that the excess energy of photoexcited electrons relaxes rapidly to the lattice vibrational modes predominantly by the emission of longitudinal optical (LO) phonons [3,4]. When sufficient energy is absorbed to heat the lattice to the melting temperature and to supply the latent heat of fusion, the material melts. Kash, Tsang, and Hvam measured the rate of LO phonon emission in GaAs, finding that the time required for a hot electron to emit a single LO phonon is 165 fs [5]. Consequently, phonon emission was determined to cool the carriers and heat the lattice in 2 ps [5], and melting proceeds with a hot lattice.

Intense femtosecond laser pulses, however, deposit energy in the carrier system in a pulse shorter than the phonon emission time. With femtosecond excitation it may be possible for the ions of the lattice to be driven to disorder directly by the electronic excitation, before phonon emission can heat the vibrational modes appreciably. Shank, Yen, and Hirlimann reported melting of silicon after a 90-fs pump pulse as evidenced by reflectivity and second-harmonic generation [6,7]. In a refinement of the second-harmonic generation experiment, Tom, Aumiller, and Brito-Cruz reported a loss of cubic order in crystalline Si only 150 fs after a 100-fs pulse [8].

In this Letter, we report time-resolved reflection second-harmonic and reflectivity measurements on GaAs showing a 100-fs decay time for the second-harmonic intensity and a 200-fs rise time for the reflectivity. Second-harmonic generation in crystalline GaAs is dipole allowed in the bulk of the crystal; it arises from the asymmetry in the bond between adjacent gallium and arsenic atoms. Consequently, valence electrons are primarily responsible for second-harmonic generation; core and conduction electrons contribute very little [9,10]. The strong second-harmonic signal that we detect monitors the $\bar{4}3m$ symmetry of the electronic state in roughly the upper 90 atomic layers (13 nm), which is the absorption depth of light at the second-harmonic frequency in GaAs. The 230-nm penetration depth in crystalline GaAs at 620 nm assures that pumping is uniform over the absorption depth of the second harmonic. Surface second-harmonic generation, which arises from the broken symmetry at the upper atomic layer, is at least 3 orders of magnitude weaker than the contribution from the bulk, and therefore negligible. We observe a 100-fs drop in reflection second-harmonic intensity that implies a transformation to a centrosymmetric electronic state of the upper 90 atomic layers within 100 fs. The reflectivity rises to a steady value characteristic of a metallic molten phase within 0.5 ps, well before the vibrational excitation of the atoms can reach the melting temperature, based on lattice heating rates from phonon emission [5].

Pulses for the experiment are produced by amplifying the output of a colliding-pulse mode-locked laser at 10 Hz in a five-stage dye amplifier. The amplifier uses prism dye cells and relay imaging to produce 1-mJ pulses with uniform spatial profile [11]. A grating pair compensates the dispersion of the amplifier, yielding pulses with a Gaussian $1/e$ width of 100 fs centered at 620 nm (2.00 eV). The sample is a (110) GaAs wafer (Cr doped, $\rho > 7\times10^7$ Ω cm) in air, with the in-plane [001] axis and sample normal oriented horizontally. The amplified output beam is divided into pump and probe beams with an energy ratio of 300:1. The pump beam is incident along the normal to the sample with its electric field parallel to the [001] axis. This orientation prevents the pump from generating second-harmonic radiation. After an adjustable delay the s-polarized probe beam strikes the sample at an incidence angle of 45°. It is focused down to probe

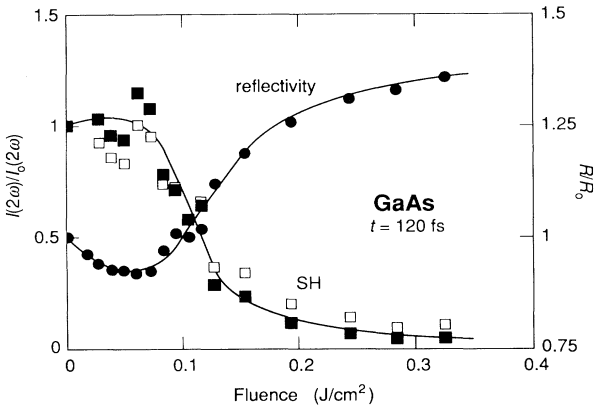

FIG. 1. Fluence dependence of the relative reflected second-harmonic intensity (■) and reflectivity (●) of a (110) GaAs surface. The data were taken at 120-fs delay with 100-fs pulses of 620-nm wavelength at an incident angle of 45°. The open squares are the second-harmonic data divided by $[(1-R)/(1-R_0)]^2$ to correct for changes in reflectivity.

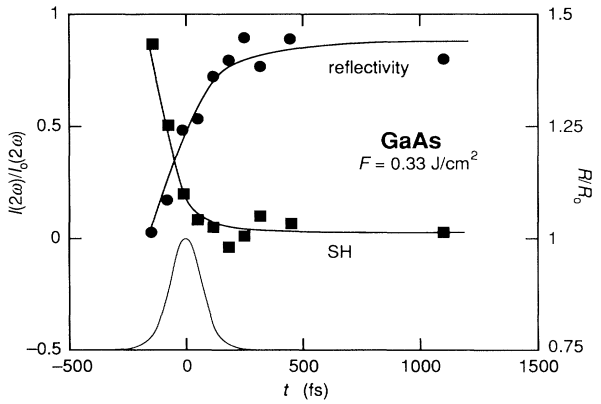

FIG. 2. Time dependence of the relative second-harmonic intensity (■) and reflectivity (●) signals at a fluence of 0.33 J/cm^2. The curves are fits by exponentials yielding $1/e$ times of 90 fs for the second-harmonic decay and 170 fs for the reflectivity rise. The peak at $t=0$ shows the duration of the laser pulse.

only the central 10% of the pumped area. The orthogonal polarization of the two beams eliminates the "coherent artifact" seen in several pump-probe experiments where parallel polarization was used [12,13]. The sample is translated between shots to avoid cumulative damage effects. For each shot a computer records the intensity of the incident pump and probe and the reflected fundamental and second harmonic. The signals are averaged and normalized relative to the reflectivity and second-harmonic intensity of unpumped crystalline material. Data were collected at fixed time delays of the probe pulse with respect to the pump pulse over an incident fluence range of 0.05–0.35 J/cm^2.

Figure 1 shows the normalized reflectivity and second-harmonic signals as functions of laser fluence at 120-fs delay. Because the second-harmonic signal depends on the probe intensity penetrating the interface, the second-harmonic data are corrected for the observed change in reflectivity (open squares). The second-harmonic intensity begins to drop at a threshold fluence of 0.1 J/cm^2. At fluences above 0.2 J/cm^2 the second-harmonic intensity vanishes, even at this short time delay. The reflectivity data show two interesting features. For fluences less than 0.1 J/cm^2, the reflectivity drops below the unpumped crystalline value. This dip can be attributed to a dense free-carrier plasma created by the excitation pulse, which reduces the real part of the index of refraction [6]. At the highest fluence the reflectivity rise approaches 40%, which agrees with the high level of ionization characteristic of molten GaAs.

In Fig. 2 the second-harmonic and reflectivity signals are shown as functions of time for a fluence of 0.33 J/cm^2. The data are fitted with exponential functions of the form

$$\Delta A(t) = (A_f - A_i)\{1 - \exp[(t_0 - t)/\tau_A]\},$$

where A_i and A_f represent the initial and final values of reflectivity or second-harmonic intensity, and τ_A is the $1/e$ time of the response. The fits give response times of 90 and 170 fs for the second-harmonic decay and reflectivity rise, respectively. Note that the fit function has not been convolved with the temporal profile of the probe pulse; *the actual response times are likely to be significantly shorter.* The results of performing exponential fits to the data at different fluences are summarized in Fig. 3, which displays response times as functions of fluence. Above approximately 0.15 J/cm^2, the second-harmonic decay time is constant at 100 fs. Similarly, above 0.25 J/cm^2 the reflectivity rise time is constant at 200 fs.

To what must we attribute this extremely rapid decay in second-harmonic generation? Let us first consider whether changes in the linear dielectric response of the

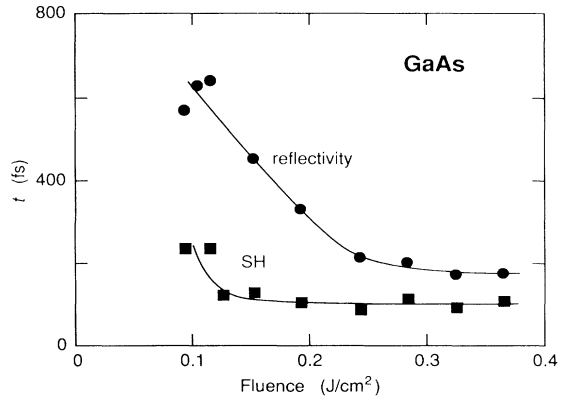

FIG. 3. Fluence dependence of the $1/e$ response time of second-harmonic decay (■) and the reflectivity rise (●). Each data point corresponds to a fit to a full time trace, as in Fig. 2.

material can account for the observed drop. Pump light at 2.0 eV excites valence electrons from the light-hole, heavy-hole, and split-off valence bands to the conduction band. These interband transitions are the dominant absorption mechanism for 2.0-eV photons. Based on the band structure and density of states of the valence band [14], the maximum attainable carrier density one can excite by linear absorption is less than 5% of the valence band, or 8×10^{21} cm^{-3}. An incident fluence of 0.1 J/cm^2 is sufficient to produce this carrier density, assuming the crystalline linear absorption constant. The presence of such a plasma affects the linear dielectric response of the material in two ways: through depopulation of the valence states and through the dielectric response of the plasma itself.

Valence-band depopulation acts directly to lower the observed second-harmonic intensity by removing electrons from the states responsible for the strong dipole signal. Depopulation effects would produce smooth, gradual changes with increasing fluence. However, the fluence dependence of the data (see, e.g., Fig. 1) shows that the second-harmonic response displays a threshold of 0.1 J/cm^2 above which the second-harmonic intensity vanishes rapidly with fluence.

At very high plasma density the plasma response dominates the crystalline dipolar response, driving the real part of the dielectric constant negative and causing an increase in reflectivity. Even when the second-harmonic intensity at 120 fs is corrected for the decrease due to increased reflection, it drops more than 90% above 0.2 J/cm^2 (see Fig. 2). Consequently, the observed drop cannot be accounted for by changes in the linear dielectric response of the highly excited material and must be attributed to a transformation of the electronic state from the noncentrosymmetric crystalline state to a centrosymmetric one in which second-harmonic generation is dipole forbidden.

Changes in the reflectivity further clarify the nature of this transformation. Within 0.5 ps the reflectivity rises by 40% to a steady value that persists for more than 5 ps. Similar reflectivity rises have been observed in nanosecond and picosecond melting experiments on GaAs and other semiconductors as the material assumes the metallic character of the molten phase [9,15]. Using a Drude model and the measured value of conductivity for molten GaAs [16], we estimate that at least 50% ionization of the valence electrons is necessary to produce the observed reflectivity rise (electron densities of order 10^{23} cm^{-3}). Our previous reflectivity measurements with a p-polarized probe on a (100) GaAs surface [17] also rise to a steady value consistent with a molten phase. Apparently, above a threshold carrier density of $\sim8\times10^{21}$ cm^{-3}, the electronic system becomes ionized to a much higher degree than the 5% expected from linear absorption.

Interestingly, the 200-fs $1/e$ time required for this transformation is an order of magnitude lower than the 2 ps necessary for the photoexcited carriers to transfer their excess kinetic energy to the lattice via LO phonon emission [5,18]. A crude estimate of the energy transfer rate from carriers to the lattice, assuming the low-carrier-density emission rate and a carrier density of 8×10^{21} cm^{-3}, gives 150 K/ps. This is more than an order of magnitude too low to bring the material to the melting temperature of 1511 K in the 0.5 ps it takes the electronic response to stabilize (see Fig. 2).

At the threshold fluence of 0.1 J/cm^2 the energy density deposited in the electronic system near the surface is 2.6 kJ/cm^3. This should be compared to the latent heat of melting $Q_m=2.83$ kJ/cm^3, which gives an upper limit for the free-energy change of the electronic configuration. We conclude that at threshold sufficient energy has been deposited for the electronic structural transition to take place. At higher fluence, free-carrier absorption increases the absorbed energy density above the threshold for melting. However, in the first 0.5 ps the ions cannot acquire much energy by either phonon emission or electron-ion collisions. It is likely that the high level of electronic excitation severely weakens the interatomic bonds by depleting the bond charges so that lattice disordering can proceed under the impetus of room-temperature thermal motion of the ions.

The ions in the lattice can move far enough during 0.5 ps to get from a $\bar{4}3m$ to an amorphous configuration in space. At room temperature, the nuclear thermal velocity is roughly 300 m/s. If the high electronic excitation were suddenly to remove the restoring forces on the ions, they would move on average 0.15 nm in 0.5 ps, which is greater than half the original bond length. Actually, the ions will move over larger distances, because they are pulled by the plasma excitations in an ambipolar diffusion process. It is possible, then, for the cold crystal lattice to disorder in 0.5 ps, even though the kinetic energy of the ions remains close to its room-temperature value. Further evidence of the rapid disordering of the crystal lattice could be obtained from time-resolved x-ray-diffraction experiments.

In conclusion, we have observed a sudden electronic phase transformation in GaAs 100 fs after excitation with an intense femtosecond pulse of fluence $F\geq0.1$ J/cm^2. The strong dipole-allowed reflection second-harmonic signal generated in a 13-nm-thick layer near the surface vanishes on this time scale. This drop, which cannot be explained by pump-induced changes in the linear dielectric response of the material, reflects a transformation to a centrosymmetric, and most likely isotropic, electronic state. The optical reflectivity rises with a 200-fs $1/e$ time to a value that agrees with more than 50% ionization of valence electrons in a metallic molten phase. At the transformation threshold of 0.1 J/cm^2, the energy absorbed by the electronic system is approximately equal to the latent heat of melting of crystalline GaAs. Furthermore, the transformation proceeds long before phonon

emission can raise the lattice to the melting temperature. These results suggest that the crystal lattice is driven to disorder directly by the high electronic excitation and that atomic disorder occurs while the lattice is still cold.

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