Subpicosecond Time-Resolved Raman Spectroscopy of LO Phonons in GaAs

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Time-dependent spontaneous Raman spectra of optically pumped GaAs have been measured with subpicosecond time resolution. When the optically injected carrier density is less than 10^{17} cm^{-3}, we temporally resolve the growth of the optically induced nonequilibrium LO-phonon population and deduce an average electron-phonon scattering time of about 165 fs. For higher injected carrier densities, substantial time-dependent changes are observed in the spectra which result from screening of the LO phonons by the free carriers and the relaxation of the free carriers to the band edges.

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The initial relaxation of optically excited carriers in polar semiconductors is dominated by the emission of small-wave-vector LO phonons via the Fröhlich interaction.[1] Many recent time-resolved studies of carrier relaxation in GaAs have focused on the temporal dependence of the optical constants near the absorption edge and the hot luminescence from the excited carriers.[2-4] These studies have been unable to resolve in real time the LO-phonon cascade which dominates the energy-relaxation process.[5] In this Letter, we directly detect phonons in the cascade by measuring the time dependence of the LO-phonon population in the presence of a nonequilibrium carrier population. We observe for the first time spontaneous Raman scattering with subpicosecond time resolution from phonons in a semiconductor. These results provide a unique view of the process by which energy is transferred from the electronic to the lattice system in GaAs. They show that for optical excitation energies near 2.0 eV, the excess population of Raman-active phonons with wave vectors near 8×10^5 cm^{-1} requires 2 ps to reach its maximum value. In addition, given our subpicosecond time-resolved Raman *spectra,* we study for the first time the temporal evolution of the free-carrier screening of LO phonons as the optically excited carriers relax over the first several picoseconds from a monoenergetic distribution to a quasiequilibrium distribution at the band edges.[5]

Von der Linde, Kuhl, and Klingenburg,[6] using a temporal resolution of 3 ps, were able to show that the lifetime of these optically generated nonequilibrium phonons in GaAs is 7 ps at 77 K. Collins and Yu[7] demonstrated that optically created carriers at high densities in quasiequilibrium screen the LO phonon exactly as carriers introduced by doping.[8] But these workers have not directly studied the dynamics of how optically injected nonequilibrium carriers *create* nonequilibrium phonons, nor have they addressed the problem of the dynamics of screening by *nonequilibrium* carriers.

In order to observe directly the electron–LO-phonon dynamics, we have performed pump-probe Raman scattering experiments on GaAs with 600-fs laser pulses. The photoexcited carriers and Raman spectra were excited by compressed[9] pulses from a synchronously pumped rhodamine-6G dye laser usually operating at 588 nm. The compressed pulses had an autocorrelation full width at half maximum of 900 fs, average power of about 20 mW at a repetition rate of 80 MHz, and a spectral full width at half maximum of about 40 cm^{-1}. There was also detectable optical emission in the form of broad tails in the spectral distribution. These tails, which would have otherwise obscured the weak Raman signals, were eliminated by placement of a slit in front of the diffraction grating of the grating compressor. The slits reduced the spectral width to 35 cm^{-1} and greatly reduced the strength of the broad tails, but did not measurably increase the temporal width of the compressed pulses.

In this paper, we present results obtained from undoped GaAs layers grown by molecular-beam epitaxy. The sample surfaces studied were GaAs (100), where only the LO-phonon scattering is allowed.[10] Most of the data reported here were obtained in air at room temperature. Low-temperature data were obtained by mounting the samples on a liquid-helium–cooled cold finger. The backscattering light from the GaAs surface was collected by an $f/1.2$ lens, analyzed by a triple monochromator, and detected by a microchannel-plate photomultiplier with a position-sensitive resistive anode.[11] This multichannel detector allowed us to observe the Raman spectrum of GaAs even when the probe power level was less than 1 mW and the excitation linewidth was in excess of 30 cm^{-1}.

The detector response time is greater than 5 ns. To perform subpicosecond time-resolved measurements, we divided each compressed laser pulse into a pump pulse and a weak (10%–20%), orthogonally polarized, delayed probe pulse, which were recombined on the sample. Zero delay at the sample was determined to within ±250 fs by observance of the interference which occurred when pump and probe were temporally and spatially overlapped. Because the polarizations of the pump and probe were perpendicular, the LO-

phonon Raman scattering excited by the pump and the probe beams was also orthogonal.[6] Thus, a prism polarizer placed before the entrance slits prevented the detection of Raman scattering excited by the pump and only Raman scattering from the probe was observed. The pump beam also produced broadband, unpolarized emission from our samples. In order to discriminate against both this background and the usual Raman scattering from thermally excited phonons, difference spectra were measured. Spectra were measured for the delay time of interest and also for a negative delay time (i.e., probe preceding pump) where we verified that the pump beam did not affect the probe signal. By subtracting the second, or background, spectrum from the first, we observe only the probe Raman signal induced by the pump beam.

Figure 1(a) shows room-temperature anti-Stokes Raman spectra of GaAs measured in our pump-probe configuration. The LO-phonon frequency of 290 cm^{-1} is at the center of the 35-cm^{-1}-wide bands. The width and unusual shape of the Raman peak is almost completely due to the width and shape of the excitation.[9] The dashed curve is the background, obtained with the probe preceding the pump by 20 ps. For the solid curve, the probe followed the pump by 1 ps. The probe-delayed Raman peak is larger than the dashed curve because of the nonequilibrium phonon population generated by the pump. Figure 1(b) shows the anti-Stokes Raman difference spectra, obtained by subtraction of the dashed curve from the solid curve. Difference spectra for other probe delay times are shown in Figs. 1(c) and 1(d). These spectra, which are linear in pump-laser intensity for optically injected carrier concentrations below 2×10^{17} cm^{-3}, show clearly both the rise and the decay of the nonequilibrium phonon population. Within the noise, the shape of the difference spectra for ≥ 2 ps is the same as the thermal phonon spectrum. The shape change seen in Fig. 1(b), however, is reproducible. This change is discussed below.

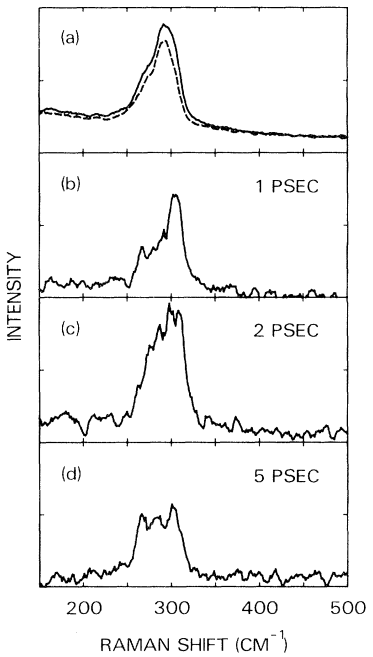

FIG. 1. (a) Time-resolved anti-Stokes Raman spectrum for room-temperature GaAs. The instantaneous carrier concentration induced by the pump laser was about 5×10^{16} cm^{-3}. The solid curve is for a probe delay of 1 ps; for the dashed curve the probe *preceded* the pump by 20 ps. (b)–(d) Difference spectra at 1, 2, and 5 ps, obtained by subtraction of Raman spectra like (a). The full-scale count rate is 0.5 count/s in (a) and 0.125 count/s for the difference spectra.

The nonequilibrium LO-phonon population versus probe delay, taken from the integrated weight of Raman difference spectra like Figs. 1(b)–1(d), is displayed in Fig. 2 for both room temperature and low temperature. (The cold-finger temperature was 20 K and we could not observe any thermal phonons in the cw anti-Stokes spectrum. Including sample heating by the laser, the sample temperature was less than 80 K.) Given the photon energy of 2.11 eV used in these experiments, each optically excited electron creates about sixteen (fourteen at low temperatures) LO phonons in a cascade before reaching the band edge.[12] Carrier-carrier scattering, which would complicate this simple cascade model, theoretically is not important for carrier concentrations below 10^{17} cm^{-3}.[1] Our experimental observation that the nonequilibrium phonon population is linear with induced carrier concentration up to 2×10^{17} cm^{-3} also supports the dominant role of the cascade in the initial energy-loss process. Since we use a backscattering geometry, only LO phonons with wave vector $k \approx 8.4\times10^{5}$ cm^{-1} are detected by the probe. For a parabolic conduction band with an

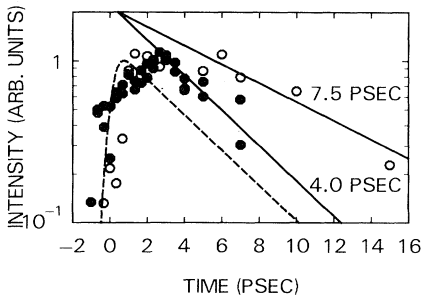

FIG. 2. Integrated weight of Raman difference peaks as in Figs. 1(b)–(d) vs probe delay. The solid points are room-temperature data, while the open circles are low-temperature data. The solid lines correspond to exponential decays of 4 and 7.5 ps. The dashed curve shows the system resolution, calculated by the assumption that the nonequilibrium phonon population is created instantaneously and decays in 4 ps.

effective mass of $0.067m_e$, the dispersion near the band minimum means that we only detect phonons emitted during cascade steps occurring more than 100 meV above the conduction-band minimum, i.e., the first twelve steps at room temperature. The phonon and electron density of states and the $1/k$ dependence of the Fröhlich matrix element favor the emission of small-k-vector LO phonons versus large-k-vector phonons. Therefore, a substantial fraction of the Raman-active phonons that we detect are emitted during the later steps in the cascade process where the relaxing electrons are in states within 100–200 meV of the conduction-band minimum. The small contributions from the phonons generated by the light-hole absorption and from the earlier steps in the electron cascade greatly complicate the quantitative calculation of the temporal dependence of the rise of the optically generated phonon population.[5] However, these corrections do not change the basic fact that the optically induced Raman signal will peak when the electrons have decayed to within 100 meV of the conduction-band minimum or after twelve phonons have been emitted at room temperature. Since the electron-phonon scattering rate is nearly independent of electron energy[13] over the 0.5 eV involved in this cascade, we deduce that the electron-phonon scattering time is about one-twelfth of our observed maximum, i.e., 165 fs. This time is consistent with earlier estimates[1] of the scattering rate which range between 100 and 200 fs. Finally, note that while the phonon emission process does not depend on temperature, the decay of the nonequilibrium phonon population decreases with temperature. This decrease is not surprising, since the LO phonons decay into acoustic phonons through anharmonic terms in the Hamiltonian which become less important at low temperatures.

We have observed that for low pump power densities, the only effect of increasing pump intensity is to increase the nonequilibrium LO-phonon population. However, more substantial changes in the pump-induced Raman spectra are observed at power densities where the optically injected carrier concentration approaches or exceeds 10^{18} cm^3. At these high power densities the qualitative changes that we observe are shown in the difference spectra in Fig. 3, which should be compared to those obtained at low powers in Fig. 1. At the shortest delays, the spectrum is dominated by a broad continuum. The intensity of the continuum varies in a superlinear fashion with pump power and makes the identification of the phonon bands of GaAs difficult. Superimposed on the continuum is weak structure in the spectral region defined by the LO- and TO-phonon energies of GaAs. After 3 or 4 ps, we observe a well-defined dip in the pump-induced spectrum at the LO-phonon energy. The continuum which dominated the spectrum at shorter times is still present but considerably reduced in intensity. For times greater than 6 ps, the continuum disappears and the dip becomes a negative-going peak. This negative-going structure, which remains essentially unchanged for delays from 10 to at least 30 ps, represents a real reduction in the strength of the allowed LO-phonon scattering.

The spectroscopic results in Fig. 3 can be correlated with the relaxation of the optically induced carrier population. Shank and co-workers[2] have shown that for times greater than 3 or 4 ps, the optically injected carriers are relaxed to the band edges and are almost in thermal equilibrium with the lattice. For carrier concentrations $\gtrsim 10^{18}$ cm^{-3}, the plasmon due to these relaxed carriers couples with and screens the LO phonon. Because of the inhomogeneous nature of our laser excitation, we do not expect to resolve the coupled modes produced by this mixing since we have many different carrier densities. We can, however, observe the loss of phonon oscillator strength at the unscreened phonon frequency. Thus the screening causes the negative difference spectrum observed at long times and high carrier concentrations. The screening will persist until the carriers diffuse into the crystal. Our results are therefore similar to those observed in a quasisteady state by Collins and Yu.[7] For delays less than 2 ps, we do not find the dip. The failure to observe this dip at short times can be most simply explained if we assume that the carrier-induced screening of LO phonons does not fully develop until the carriers reach quasiequilibrium.

The broad continuum which dominates the top curve of Fig. 3 appears to be similar to the continuum reported by Pinczuk, Shah, and Wolff,[14] who attributed it to LO-phonon–plasmon coupled modes modified by inter-valence-band transitions of photoexcited holes. Our results suggest that only the nonequilibrium carriers contribute to the continuum, since after 3 to 4 ps, the band disappears. Because of the inhomogeneous nature of the laser excitation, however, we are unable to determine whether both the broadband and the beginning of the negative-going LO-phonon structure would coexist in the scattering from a homogeneously excited sample. It may be that the continuum and the LO-phonon effects occur simultaneously in separate regions of the sample.

We now return to the spectral shape changes seen at the shortest times in the low-power spectra, Figs. 1(b)–1(d). Since our measured electron–LO-phonon scattering time is nearly as short as the phonon oscillation period of 115 fs, we can expect that the phonon will not oscillate at its natural frequency until the transients associated with the short scattering time have damped out. Our time-resolved Raman spectra measure the instantaneous phonon frequency, which apparently is higher than the natural frequency during

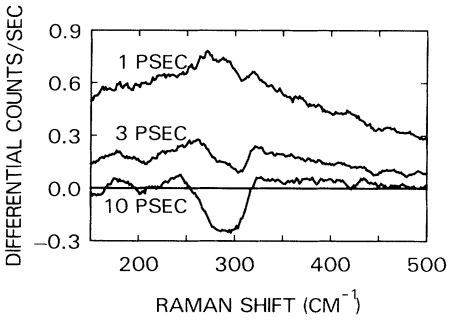

FIG. 3. Raman difference spectra at room temperature for probe delays of 1, 3, and 10 ps. The instantaneous carrier concentration for all curves is $\sim 3\times 10^{18}$ cm^{-3}.

the first picosecond. Because these spectra are *difference* spectra, a small shift would appear as a derivative-like structure. This feature can, as observed, be on the high-energy side of the Raman peak and be narrower than the probe bandwidth. The negative part of the derivative structure will be obscured by the increase in phonon population.

In conclusion, we have measured LO-phonon Raman spectra with subpicosecond resolution, and have measured both the creation and the decay times for the nonequilibrium phonons. Since for the first time we report the complete Raman spectrum, as opposed to the peak intensity, we are able to observe the dynamics of the phonon-plasmon coupling and the transients of the nonequilibrium phonon creation. Spontaneous Raman scattering techniques have not been widely used in picosecond experiments, but the added sensitivity of multichannel detection now makes this a powerful technique for the exploration and understanding of semiconductor dynamics.

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[12]The excitation energy of 2.11 eV used in this experiment is just above the threshold where carriers excited into the Γ conduction band can scatter to the L-point conduction-band minimum. We have repeated our measurements at 2.0 eV, where Collins and Yu have shown that this process is negligible and found that it does not significantly perturb our results. The experimental results at the two different excitation energies are identical with respect to both the rise and decay times. We also ignore the $\sim 20\%$ absorption of the light-hole band which creates a cascade from both electrons and light holes of ten and eight phonons at room temperature.

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