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Nonequilibrium phonon spectroscopy: A new technique for studying intervalley scattering in semiconductors

Charles L. Collins and Peter Y. Yu
Department of Physics, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
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We present a new technique for studying intervalley scattering of hot carriers by phonons in direct-band-gap semiconductors. This technique utilizes the nonequilibrium optical-phonon population generated by the relaxation of photoexcited hot carriers as an internal probe of intervalley scattering of hot carriers. As an illustration of this technique the deformation potentials of intervalley electron-phonon interactions in GaAs have been deduced. Our results are in good agreement with values measured by other methods.

The ideas behind the generation of nonequilibrium optical phonons by photoexcitation are fairly well known.[1] Electron-hole pairs can be created in a direct-band-gap semiconductor by photons of energy, $\hbar\omega_l$, larger than the band gap E_g. If the kinetic energy of these photexcited carriers are much larger than the thermal energy k_BT (k_B being the Boltzmann constant and T being the lattice temperature) the carriers are known as hot carriers. Hot carriers typically relax to the band extrema by emission of optical phonons. In many polar semiconductors, such as GaAs, this relaxation proceeds via emission of longitudinal optical (LO) phonons in a very short time, typically $\sim 10^{-12}$ sec (picosecond or psec).[2] The LO phonons, on the other hand, have lifetimes of the order of 10 psec.[3] If one excites the hot carriers with a picosecond laser pulse, the LO phonon population will rise temporarily above the thermal equilibrium value. This transient nonthermal equilibrium population of phonons has been called "hot phonons" in the literature.[4,5] There are several ways to detect this nonequilibrium phonon population. The simplest technique is to use the same excitation photons to probe the phonons by Raman scattering. It is well known that σ_{AS}, the cross section for the anti-Stokes Raman mode, is proportional to the phonon population N_q while Stokes Raman cross section σ_S is proportional to $1+N_q$. The phonon population is given simply by $\sigma_{AS}(\sigma_S-\sigma_{AS})^{-1}$. The advantage of this technique is that precise absolute measurements of Raman cross sections are not necessary since N_q depends only on the ratio σ_{AS}/σ_S. The limitation of this technique is that Raman scattering probes the zone-center phonons only. Hot phonons in several semiconductors have been studied in this way using both cw and pulsed lasers.[4,5] The lifetime of such optically excited hot phonons in GaAs has recently been measured by von der Linde *et al.*[3]

In this Communication we propose to utilize the nonequilibrium phonon population as an internal probe of any *inter*valley electron-phonon scatterings which may compete with the *intra*valley scattering processes responsible for the hot phonon generation.

Figure 1 shows schematically the band structure of a direct-band-gap semiconductor like GaAs. We notice that the conduction band contains higher-energy minima at X and L points of the Brillouin zone. The simple picture presented above is valid only when the kinetic energy of the photoexcited hot electrons is below these higher minima. When the electron energy is larger than these higher-energy minima the hot electrons can be scattered into the X and L minima by emission of zone-edge phonons.[6] These intervalley scattering processes (indicated by arrows labeled 2 and 3 in Fig. 1) are often stronger than the intravalley scattering processes (indicated by arrow 1) because of the larger density of final states. For exam-

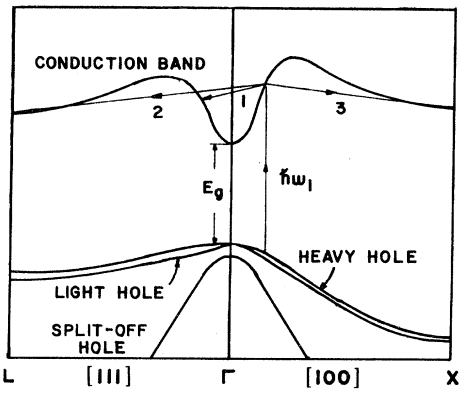

FIG. 1. Schematic band structure of GaAs. Arrows 1, 2, and 3 represent, respectively, intravalley scattering of electrons by LO phonons, intervalley scattering of electrons by zone-edge phonons to the L and X conduction minima.

ple, transfer of hot electrons from the Γ valley to the X valley in GaAs is responsible for the Gunn effect.[2] Since intervalley scattering reduces the amount of hot carriers generating the hot phonons one should observe a decrease in N_q when the photon energy $\hbar\omega_l$ is larger than the indirect band gaps Γ-L and Γ-X as shown in Fig. 1. Thus by monitoring N_q as a function of $\hbar\omega_l$ one can determine, in principle, the direct band gaps and also intervalley electron-phonon interactions. In the rest of this paper we demonstrate the feasibility of this idea in GaAs.

Our experimental setup is shown schematically in Fig. 2. The sample is a high purity ($N_D, N_A \lesssim 10^{14}$ cm^{-3}), 4-μm-thick layer of GaAs grown by liquid phase epitaxy. The sample surface orientation is (100) and excited by a mode-locked dye laser beam polarized along the [010] direction. The dye laser consists of a train of $\lesssim$ 4-psec-long pulses separated from each other by $\sim$ 12 nsec. The dyes used were R6G and DCM[7] allowing the excitation photon energy to be tuned continuously from 1.75 to 2.15 eV. The laser pulse lengths are monitored continuously by an autocorrelation setup to ensure that pulse lengths do not vary with photon energy and time. The photoexcited LO phonon population is determined by Raman backscattering with the same dye laser beam. From Raman selection rules[8] the radiation scattered by the LO phonon is polarized along the [001] direction. The scattered photons are analyzed with a double monochromator and photon counting electronics. A microcomputer calculates N_q from the Stokes and anti-Stokes Raman intensities after correction for spectral response of the system and the variations in the penetration depth of the incident and scattered radiations.

The average power of the dye laser incident on the sample is typically $\lesssim$ 80 mW. The laser is not very tightly focused on the sample to minimize heating up the sample which is cooled to $\sim$ 10 K by helium exchange gas. the density of photoexcited carriers is estimated to be between 10^{16} to 10^{17} cm^{-3}. At higher excitation densities the Raman spectra are complicated by appearance of a strong luminescence background and screening of the LO phonon by photoexcited carriers.[9,10] The lattice temperature as deduced from the photoluminescence spectra and the frequency of the LO phonons is $\lesssim$ 15 K. At this temperature the thermally excited LO phonon population is completely negligible. However, due to optical pumping by the dye laser pulses we have observed N_q as large as 0.4. We have convinced ourselves that this large LO phonon population is not due to heating or other antifacts of the system by repeating the experiments with the dye laser running cw and by measuring the population of the TO phonons which do not couple to electrons as strongly as the LO phonons.[2] In both cases no hot phonons were detectable, consistent with the fact that heating of the sample by the laser is minimal.

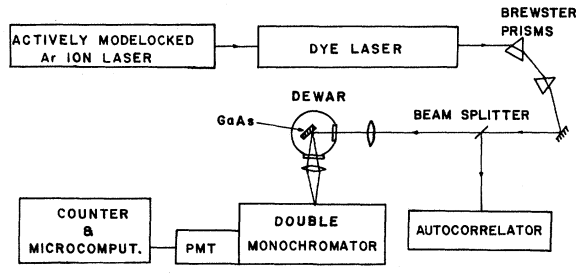

FIG. 2. Experimental setup for observing nonequilibrium optical phonons in GaAs. The Brewster angle prisms are used to filter the fluorescence from the dye laser.

In Fig. 3 we plot the measured values of N_q as a function of the excitation photon energy $\hbar\omega_l$ (solid circles). As expected, there is a sudden drop in N_q for $\hbar\omega_l \gtrsim 2.10$ eV when the photoexcited electrons have sufficient energy to be scattered into the X valleys. However, no decrease in N_q was detectable within experimental accuracy at $\hbar\omega_l \gtrsim 1.90$ eV, where intervalley scattering into the L valleys is expected to occur.

To understand our results quantitatively we have performed a model calculation based on Fig. 1 under these assumptions: (1) Optical transitions from the light- and split-off-hole bands are neglected compared to transitions from the heavy-hole band. (2) Hot phonons emitted by the hot holes are negligible by comparison to those emitted by hot electrons. (3) Only spontaneous emissions of LO phonons by the hot carriers are included in the model. With these assumptions the LO phonon population can be obtained by solving the following rate equations[11]:

$$\frac{df_k}{dt} = \left(\frac{\partial f_k}{\partial t}\right)_g - \left(\frac{\partial f_k}{\partial t}\right)_{e\text{-ph}} - \frac{f_K}{\tau_k} , \tag{1}$$

$$\frac{dN_q}{dt} = \left(\frac{\partial N_q}{\partial t}\right)_{e\text{-ph}} - \frac{N_q}{\tau_q} , \tag{2}$$

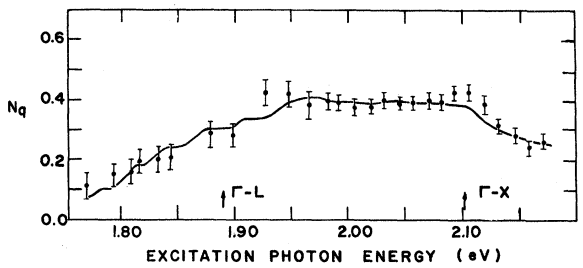

FIG. 3. LO phonon population N_q in GaAs plotted as a function of excitation photon energy. The solid circles are experimental points while the solid curve is the result of a model calculation discussed in the text. The arrows labeled as Γ-L and Γ-X represent, respectively, the photon energies for the onset of Γ to L and Γ to X intervalley scatterings according to pseudopotential band-structure calculation.

where f_k is the distribution function of the electron with wave vector k. $(\partial f_k/\partial t)_g$ stands for the optical generation rate of electrons while $(\partial f_k/\partial t)_{e\text{-ph}}$ is the rate at which electrons are scattered out of the state k due to LO phonons. $(\partial N_q/\partial t)_{e\text{-ph}}$ is the LO phonon generation rate due to the hot-electron relaxation. τ_q is the LO phonon lifetime. τ_k^{-1} is the rate of decay of electrons in state k due to any process *not* involving the LO phonons. For electrons not energetic enough to undergo intervalley scattering, τ_k is of the order of nanoseconds due to radiative recombination so f_k/τ_k is negligible compared to $(\partial f_k/\partial t)_{e\text{-ph}}$. When the electron is energetic enough to scatter into the X and L valleys, τ_k is determined by the intervalley scattering rates which can be calculated from the intervalley deformation potentials $D_{\Gamma\text{-}X}$ and $D_{\Gamma\text{-}L}$.

The solid curve in Fig. 3 has been obtained by numerical intergration of Eqs. (1) and (2) using the band structure of GaAs obtained by empirical pseudopotential calculation.[12] There are two adjustable parameters in achieving the good agreement between theory and experiment. The photoexcited carrier density is adjusted to fit the experimental values of N_q at $\hbar\omega_i \sim 2.0$ eV. The carrier density of 3×10^{16} cm^{-3} deduced is close to what we estimate from the laser intensity and absorption coefficient of GaAs. The value of the deformation potential $D_{\Gamma\text{-}X}$ is adjusted to 1.1×10^9 eV/cm to fit the decrease in N_q around 2.10 eV. This value of $D_{\Gamma\text{-}X}$ is in excellent agreement with the value deduced by Vinson *et al.*[13] The fact that the theory reproduces the photon energy at which this drop occurs to within ~ 10 meV is a tribute to the accuracy of empirical pseudopotential band-structure calculations. Since we did not observe a drop in N_q due to the Γ-L intervalley scattering we have placed an upper limit of $\sim 1.4 \times 10^8$ eV/cm on $D_{\Gamma\text{-}L}$ in GaAs. Although this value of $D_{\Gamma\text{-}L}$ is smaller than the Gunn effect measurement, it is consistent with the value of $\sim 1.5 \times 10^8$ eV/cm recently deduced by Koch *et al.*[14] from laser action in optically pumped GaAs.

In conclusion, we have shown that optically generated nonequilibrium phonons can be used to study intervalley electron-phonon scatterings which are important in devices such as Gunn oscillators and as a spectroscopic technique for determining indirect energy gaps in direct band-gap semiconductors. For these reasons we have labeled this new technique: nonequilibrium phonon spectroscopy. As a spectroscopic technique it can be regarded as an optical-phonon analog of the well-established photoacoustic spectroscopy.[15]

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[1]See, for example, J. Shah, Solid-State Electron. 21, 43 (1978).

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[6]See Ref. 2, p. 248.

[7]R6G and DCM stand, respectively, for Rhodamine 6G and 4-dicyanomethylene-2-methyl-6-*p*-dimethylamniostyryl-4H-pyran.

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[15]See, for example, *Optoacoustic Spectroscopy and Detection,* edited by Y. H. Pao (Academic, New York, 1977).