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TIME RESOLVED PHONON SPECTROSCOPY IN SEMICONDUCTORS

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A novel technique of nonlinear spectroscopy providing Raman spectra with a picosecond time resolution has been used for studying the generation and the decay of nonthermal LO-phonons in GaAs and InP. The relaxation time of the non-equilibrium phonon population has been measured to be $\tau' = 7 \pm 1$ ps for GaAs and $\tau' = 5 \pm 1.5$ ps for InP. This time resolved Raman spectroscopy can be readily employed to investigate the fast dynamics of other elementary excitations in solids such as photoexcited electrons or plasmons.

Information about the relaxation of optical phonons in semiconductors has been obtained in the past mainly from the analysis of the linewidth of infrared and Raman spectra. Direct investigations of the fast dynamics occurring on a picosecond time scale by means of picosecond spectroscopy [1] have provided a detailed picture of the dephasing of molecular vibrations [2] and the decay of coherent optical phonons [3], however. In a recent paper [4] we reported the first direct observation of the time revolution of non-equilibrium incoherent optical phonons in GaAs achieved by a novel technique of time resolved Raman spectroscopy. The experiment is based on a variant of the excite-and-probe-scheme [1]. The sample is irradiated by two successive pulses of picosecond duration with the same frequency and intensity but with orthogonal polarization. The experimental difficulties inherent to most excite-and-probe-experiments are strongly reduced because the excite-and probe pulses can be derived from the same laser source. The high average power level, necessary to record the weak Raman spectra is detrimental, however.

The output of a synchronously pumped cw Rhodamine 6G dye laser operating at $\lambda = 575$ nm (photon energy $\hbar\omega = 2.16$ eV, pulse duration 2.5 ps, average power 80 mW, pulse repetition rate 80.6 MHz) is split into two pulse trains which are then polarized perpendicular to each other, sent through an optical delay line providing continuous variation of the time delay Δt and finally are recombined on the surface of the samples, grown by molecular beam expitaxy (Fig.1). The short laser pulses of photon energy significantly larger than the bandgap photoexcite hot carriers. The Fröhlich type interaction of these hot electrons and holes with the lattice which is predominant in polar semiconductors results in the emission of LO-phonons when the carriers are cascading to the bottom or top of the conduction and valence band, respectively. The non-equilibrium population of the LO-lattice modes can be detected with a conventional photon counting Raman spectrometer by measuring the LO-phonon anti-Stokes Raman line intensity, which is directly proportional to the number of generated phonons

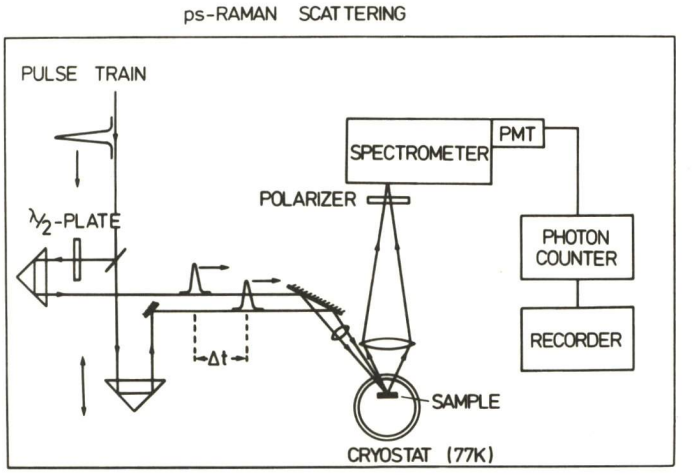

Fig. 1 Experimental arrangement

if the sample is cooled to liquid nitrogen temperature. For materials of T_d-point group symmetry like GaAs and InP light scattered backward by the LO-phonon from a (100)-surface is polarized perpendicular to the incident beam. Thus the Raman light generated by one of the pulses (pump pulse) can be suppressed by a suitably oriented polarization analyzer in front of the detector. The second pulse (probe pulse) serves ror excitation and probing simultaneously. When the signal is recorded as a function of the delay time Δt the phonon generation by the pump pulse and the relaxation of this excitation is displayed. The contribution due to excitation by the probe pulse itself is independent of Δt and leads to a constant background. The trace presented in Fig.2 has been obtained for excitation conditions corresponding to 10^{17} e-h pairs per cm^3 in GaAs at a lattice temperature of 77 K.

From the exponential decay of the signal to the background level the relaxation time of the non-equilibrium LO-phonon population at 77 K in GaAs and InP are found to be 7±1 ps and 5±1.5 ps, respectively. The phonon occupation number N calculated from the intensity ratio of the Stokes (S) and anti-Stokes line (A) $N = (S/A - 1)^{-1}$ are N = 0.7 (GaAs) and N = 0.2 (InP). These values considerably exceed the equilibrium population of $3.8 \cdot 10^{-3}$ (GaAs) or $1.4 \cdot 10^{-3}$ (InP) corresponding to the crystal temperature of 77 K. The phonon emission or the relaxation process of the photoexcited electrons can be evaluated from the rise time of the anti-Stokes signal. At present the pulse length of our dye laser system is too long to resolve details of these extremely fast processes.

Applications of our technique to the examination of phonons in the non-polar semiconductors Si and Ge have failed because no detectable deviation of the phonon population near the center of the Brillouin zone which is probed by Raman scattering from the thermal equilibrium value could be measured. With respect to the different band structure it is possible that all phonons emitted during the relaxation of hot carriers in these materials have wave vectors much larger

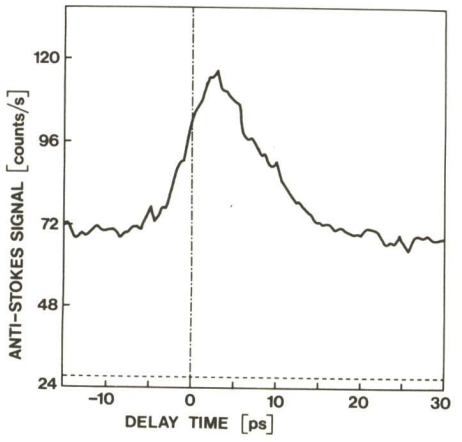

Fig. 2 Anti-Stokes Raman signal vs delay time Δt for the LO-phonon mode of GaAs at 77 K: The zero of the time scale is given by the maximum of the excitation pulse. The dashed horizontal line marks the background counting rate due to residual laser light and dark current of the detector

than two times the wave vector of the photons of the probe beam. Otherwise we have to suggest that owing to the inefficiency of the electron-phonon coupling by the lattice deformation potential the phonon generation rate is too small compared to the fast phonon decay to build up a nonthermal population of the lattice vibration modes. In contrast to our results generation of such non-equilibrium phonons in Si with tightly focussed cw Ar^+laser excitation has been reported [5]. This discrepancy may be explained by strong lattice heating in the case of cw irradiation with power densities up to 10^4 W/cm^2. In our experiments the average power density was less than 70 mW/cm^2. Measurement of the ratio S/A for LO- and TO-phonons in GaAs at 77 K in a configuration which permits both LO and TO Raman scattering confirm that heating of the sample can be neglected. No anti-Stokes scattering from TO phonons was detectable whereas the ratio S/A for the LO phonon amounted to about 2.5 under the same conditions.

The described light scattering technique can be readily extended to time resolved spectroscopy of photoexcited single electrons and collective electronic excitations (plasmons). In Ge, GaAs and InP we have measured strong Raman scattering from the photoexcited electrons and holes. The time resolved spectra indicate very rapid changes of the velocity distribution of the electron-hole gas. Detailed analysis of the electron-phonon coupling is currently under investigation.

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