(1973).

 $¹¹M$, R. Phillpot and J. M. Turlet, J. Chem. Phys. 64,</sup> 3852 (1976). '

 12 C. S. Fadley, R. J. Baird, W. Siekhaus, T. Novakov, and S. Å. L. Bergström, J. Electron. Spectrosc. 4, 93 (1974).

 13 The energy resolution was determined by differentiating the $UPS(s)$ spectrum of gold at the Au Fermi edge. The full width at half-maximum of the resultant peak is a convolution of thermal broadening (0.025 eV at 300'K) and the net instrumental resolution, which then is found

to be about 0.1 eV.

¹⁵P. Nielsen, Xerox Webster Research Center, private communication.

 16 D. T. Clark and H. R. Thomas, to be published.

¹⁷P. Nielsen, D. J. Sandman, and A. J. Epstein, Solid State Commun. 17, 1067 (1975).

 ^{18}P , Gosar and S. Choi, Phys. Rev. 150, 529 (1966). ¹⁹R. W. G. Wyckoff, Crystal Structures (Interscience

New York, 1971), Vol. 6, Part II, p. 454.

Direct Observation of Phonons Generated During Nonradiative Capture in GaAs p -n Junctions

V. Narayanamurti, R. A. Logan, and M. A. Chin Bell Laboratories, Murray Hill, New Jersey 07974 (Received 7 September 1977)

Phonon generation by GaAs epilayers and $p - n$ junctions is studied by means of a superconducting bolometer and time-of-flight techniques. The polarization of the emitted radiation is found to be sensitive to doping in agreement with theoretical selection rules. The relative strength of the radiative and nonradiative processes is shown to depend on defect density and bias and demonstrates the energy transfer processes in $p - n$ junctions.

The phenomena of carrier-capture and energytransfer processes in semiconductor $p-n$ junctions is of considerable fundamental and technical importance. The luminous output of semiconductor LED's (light-emitting diodes) and lasers, for example, depends on the relative strength of radiative (photon) and nonradiative (phonon or Auger) processes. Nonradiative capture can take place at shallow acceptors and donors by means of single-phonon emission involving a cascade process¹ and/or by multiphonon emission (MPE) at deep levels.² Experimental evidence for MPE has recently been obtained by Henry and Lang' through the temperature dependence of earriercapture cross sections. Heinke and Queisser' have shown the decrease of photoluminescence output due to the presence of dislocations in GaAs. In this Letter, we report the first, direct observation of nonradiative (phonon) capture processes' in semiconductor $p-n$ junctions.

The phonons were generated by the application of short current pulses to thin n and p layers and $p-n$ junctions epitaxially grown on one side of insulating GaAs substrates of thickness \sim 2 mm. After a ballistic time of flight, the phonons were detected at the opposite side by means of a thinfilm superconducting bolometer⁵ at $T \approx 1.5$ K. These measurements shed light on the energy transport mechanisms in $p-n$ junctions and also

serve as a direct method of determining symmetry of defect levels in GaAs epilayers through the anisotropy of their phonon emission. This is made possible by the high speed and high sensitivity of the superconducting bolometer detector.

All the layers used in this study were grown by liquid-phase epitaxy (LPE) .⁶ The *n* layers were doped with Sn donors whose concentration ranged from 2×10^{17} to 5×10^{15} cm⁻³. The *p* layers were Ge doped and had a typical concentration of 2 \times 10¹⁸ cm⁻³. p-n junctions were formed on the semi-insulating substrates by first growing an n layer over the entire face and then a smallarea p layer. In some experiments, the first n layer was grown from two adjacent melts so that the doping in each half of the layer was separately controlled. The junctions were defined near the edge of the p layer by conventional photolithographic masking and etching, The junction areas were typically 0.1 mm^2 , with RC time constants ≤ 10 ns and with Ohmic contact to each side made by alloying small In pellets at 400'C for 3 min in a $H₂$ ambient. The $I-V$ characteristics were strongly temperature dependent with a reverse breakdown voltage at low temperatures of \sim 10 V. Appreciable forward-bias injection occurred at voltages of \sim 1.5 V and currents of approximately several milliamperes. The thickness of the layers was varied from 10 to 60 μ m. The majority

 14 J. J. Ritsko, A. J. Epstein, W. R. Salaneck, and D. J. Sandman, to be published.

of measurements were made on semi-insulating $(\rho \sim 10^8 \Omega \text{ cm})$, high-quality oxygen-doped GaAs substrates grown by Monsanto Chemical Co., St. Louis, Mo. and these were found to be excellent in their phonon transmitting properties, Some measurements were also made on Cr-doped substrates but these were found to attenuate the phonon beam. Several different orientations were studied. For the sake of clarity, only data on (100) substrates will be reported in this paper.

The superconducting bolometer was a granular Al film biased at its resistive transition by means of a current. The bolometer signals were amplified and signal averaged either by means of a PAR 160 boxcar integrator or a Tektronix WP221 transient digitizer. The time resolution in all cases was better than 10 ns,

Figure 1 shows some typical data of ballistic phonons observed when current pulses were applied to long etched mesas formed in the epitaxial n and p layers with alloyed In contacts at each end. The n -layer carrier concentration here was $-5-8\times10^{15}$ cm⁻³ and showed evidence of carrier

FIG, 1. Bolometer signal as a function of time, $T = 1.5$ K. Trace a, n layer; trace b, p layer. The p and n layers were grown simultaneously using two different melts. Long mesas 0.5 mm \times 3 mm were etched and contacted as described in text for formation of $p - n$ junctions. A schematic of the generated phonon spectrum is shown on the right-hand corner. The value of ω_{max} depends on the electron temperature T_e and in the low-field region is considerably smaller than the resonant phonon energy $(\sim 4 \text{ meV})$. See text.

freezeout. Here we observe a strong longitudinal (L) pulse and a weaker transverse (T) pulse. In the case of p layers, we observe a strong T pulse and an extremely weak L pulse.

The data shown in Fig, 1 can be qualitatively explained as follows. Under the action of the electric field $\frac{2 V}{cm}$ or greater) the donors are impact ionized. The excited carriers relax first to the bottom of the conduction band, emitting a continuum of phonons with a maximum frequency' $_{ax} \sim (2v/\hbar)(2m_e kT_e)^{1/2}$, where m_e is the electron mass, T_e is the electron temperature, and v is the sound velocity. The value of T_e ranges from 6 K to about 30 K for fields' in the range 2-25 V/cm. The carriers at the bottom of the band then relax via single-phonon emission with an energy of -4 meV during capture by a shallow donor. A schematic of the generated phonon spectrum is shown in the top corner of Fig. 1. The polarization selection rules are governed by the relative strength of the piezoelectric and deformation coupling constants.⁹ Because of the spherical symmetry of the conduction band, in the effectivemass approximation, deformation-potential coupling is isotropic and involves only L phonons. The piezoelectric coupling is orientation- and concentration-dependent (as a result of screening), ¹⁰ and involves both L and T phonons. The T mode seen in trace a is a measure of the strength of this coupling in GaAs. In contrast, to donors, however, holes can relax via predominant p -wave (T-mode) coupling even in the absence of piezoelectric coupling due to the existence of the valence-band degeneracy^{9, 10} in GaAs. Thus the data provide strong evidence for the preservation of the expected polarization selection rules in our epilayers. Preliminary measurements replacing the bolometer detector with a low-concentration n -layer detector (which acts like a quantum detector because of the presence of a discrete donor level) show that significant amounts of the donor signal is resonant in character. These data, along with the orientation and electric-field dependence of the phonon signals which confirm the above interpretation, will be presented elsewhere

We now turn to data obtained with $p-n$ junctions. Under forward-bias conditions one might, at low temperatures, expect to see contributions characteristic of donors, acceptors, and phonons generated during nonradiative recombination at deep states in the depletion region of the junction and/or at the surfaces of the junction. Figures ² and 3 iltustrate some of these features. In Fig.

FIG. 2. Bolometer signal as a function of time, $T = 1.5$ K, $p-n$ junction generator. Trace a, $n \sim 2 \times 10^{17}$ cm⁻³; trace b, $n \sim 8 \times 10^{15}$ cm⁻³. Generator current, 10 mA.

2, for example, we show phonon signals from two $p-n$ junctions with different *n*-layer dopant concentrations. It is clear from this figure that the ratio L/T increases with donor concentration. The strong dependence of the L-mode intensity on donor concentration shows that significant amounts of the emission from the junction occurs through carrier capture associated with the Γ conduction band. The T mode seen in Fig. 2 is due to both acceptor states and the increase in the piezoelectric scattering (over deformationpotential scattering), due to the reduced carrier screening in the depletion region of the junctions.¹⁰ Orientation-dependence studies confirm the above
interpretation.¹¹ interpretation.

In Fig. 3 we show data for two $p-n$ junctions with different concentrations of nonradiative centers. The nonradiative centers, here, were intentionally produced by adding GaP to the growth melt. The lattice mismatch of the epitaxial layer to the substrate at the growth temperature (850'C) produces an array of misfit dislocations with a density in the range $10^6 - 10^8$ cm⁻² depending on density in the range $10^6 - 10^8$ cm⁻² depending on
the phosphorus concentration.¹² From Fig. 3, it is clear that the dislocated junction shows considerably enhanced phonon emission particularly at the T mode. Note that these data are on junctions grown simultaneously on the same sub-

FIG. 3. Bolometer signal as a function of time for two $p-n$ junctions. In case b, approximately 10⁷ misfit dislocations/cm2 were introduced during the growth process. This results in enhanced phonon generation due to nonradiative recombination. See text.

strate, forming a "control" and "dislocated" junction side by side on the same sample. Such behavior has been seen in five different junctions and in different samples.

We believe that these data provide strong, direct evidence for nonradiative recombination in semiconductor $p-n$ junctions via phonon emission. The increased emission of T phonons in Fig. 3(b) is presumably due to the combined effects of (1) preferential coupling of the slow transverse phonons to dislocations,¹³ and of (2) the expected longer lifetime¹⁴ of high-energy T phonons, during multiphonon emission, because of the bottleneck in the decay process. This bottleneck arises because the primary coupling to deep states' is assumed to involve a large number of high-energy optic and acoustic phonons (in the range 10-30 meV). Such high-energy phonons are expected to decay into acoustic phonons of lower energy. Since the TA (transverse acoustic) phonons form the lowest branch of the acoustic spectrum they
are expected to have the longest lifetime.¹⁴ are expected to have the longest lifetime.¹⁴

In Fig. 4 we show that amplitude of the phonon signals as a function of generator current at low currents¹⁵ for the $p-n$ junctions of Fig. 3. Also shown for comparison are data on the total light output under identical pulsed conditions, as measured by a photomultiplier. It is clear that the

FIG. 4. Bias dependence of phonon and light emission for junctions of Fig. 3.

phonon output anticorrelates with the radiative (light) output. In addition, saturation of the phonon signals at a relatively modest current is observed, with the saturation occurring particularly rapidly for the L modes. We believe this phenomena is consistent with the lower n -layer dopings and suggests a saturation of the nonradiative centers, the subtle competition between the radiative and nonradiative energy-transfer processes in such junctions being determined by doping and defect density. This figure, then, provides further quantitative confirmation of the importance of nonradiative processes occurring in the depletion region of the $p-n$ junction.

In summary, we have directly observed phonon emission in semiconductor epitaxial layers and $p - n$ junctions by means of a novel superconductingbolometer technique. The use of low temperatures, when propagation of ballistic phonons can be observed, allows for a fundamental understanding of nonradiative capture processes and their tures, when propagation of ballistic phonons can
be observed, allows for a fundamental understand-
ing of nonradiative capture processes and their
importance in determining energy transfer in p -n
intions through the *po* junctions through the polarization and bias dependence of the emitted phonon radiation. Further experiments involving controlled photoexcitation of carriers and energy selective detectors¹⁶ should yield even more detailed information on the energy-transfer processes.

We would like to thank M. Lax, D. V. Lang, C. H. Henry, and D. C. Tsui for helpful discussions. We would also like to thank H. G. White

and A. J. Williams for their excellent technical assistance with the epilayer growth and contacting of the samples.

 1 M. Lax, Phys. Rev. 119, 1502 (1960).

 2 D. V. Lang and C. H. Henry, Phys. Rev. Lett. 35, 1525 (1974); C. H. Henry and D. V. Lang, Phys. Bev. 8 15, 989 (1977), and references cited therein. See also D, V. Lang and B, A. Logan, Phys. Rev. Lett. 39, 635 (1977).

 3 W. Heinke and H. J. Queisser, Phys. Rev. Lett. 33. 1082 (1974), and references cited therein.

 4 The effect of dc fields to study the electron-phonon interaction in semiconductor epilayers has been reviewed by R. W. Keyes, Comments Solid State Phys. 6, 63 (1975); see also R. S. Crandall, Solid State Commun. 7, 1109 (1968). See also the work of A. Zylbersztejn [Phys. Bev. Lett. 19, 838 (1967)] who studied phonon emission by hot electrons in Ge. No data, however, exist in the important area of nonradiative capture in $p - n$ junctions.

 ${}^{5}R$. J. von Gutfeld, in *Physical Acoustics*, edited by %. P. Mason (Academic, New York, 1968), Vol. V.

 ${}^{6}R$. A. Logan and F. K. Reinhart, IEEE J. Quantum Electron. 11, 461 (1975).

 7 T. M. Gasymov and L. E. Gurevich, Fiz. Tverd. Tela 11, 2946 (1969) [Sov. Phys. Solid State 11, 2386 (1970) .

 3L . P. Zverev, G. M. Min'kov, and N. K. Sumin, Fiz. Tekh. Poluprovodn. 9, 767 (1975) [Sov. Phys. Semicond. 9, 503 (1975)].

 ${}^{9}C$. Herring and E. Vogt, Phys. Rev. 101, 944 (1956). 10 M. Lax (private communication) has calculated the orientation dependence of the piezoelectric scattering in GaAs. Our data are in good qualitative agreement with Lax's calculations.

 11 V. Narayanamurti, R. A. Logan, and M. A. Chin, to be published.

 12 G. A. Rozgonyi, P. M. Petroff, and M. B. Panish J, Cryst. Growth 27, 106 (1974).

 13 K. Ohashi, J. Phys. Soc. Jpn. 24, 437 (1968).

¹⁴R. Orbach and L. A. Vredevoe, Physics (Long Island City, N.Y.) $1, 91 (1964)$.

 15 Data at high currents are not of interest here because of excessive carrier heating, and diffusive heat pulses are observed which will be described elsewhere. 16 See, for example, W. Eisenmenger and A. H. Dayem Phys. Rev. Lett. 18, 125 (1967); R. C. Dynes and

V. Narayanamurti, Phys. Rev. B 6, 143 (1972).