Oscillatory Photoconductivity of Epitaxial GaAs

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Oscillation due to interaction of photoexcited electrons and optical phonons has been observed in the intrinsic photoconductivity spectrum of epitaxial GaAs at 2°K. From the spacing of the minima of the oscillation, values have been obtained for the energy gap (1.520 eV) and for the effective-mass ratio for heavy holes and electrons (m_h/m_e)=6.2.

OSCILLATION due to interaction of photoexcited electrons and optical phonons has been observed for the first time in the intrinsic photoconductivity spectrum of GaAs. The oscillation was found at 2°K in a pure epitaxial layer ($n\simeq 5\times 10^{14}$ cm^{-3}; $\mu\simeq 50\,000$ cm^2/V sec at 77°K). The present results, which are shown in Fig. 1, show two sharp peaks at 1.5135 and 1.5164 eV followed by a rise and then the oscillation. The minima of the oscillation are separated by 43×10^{-3} eV, which is slightly larger than the energy ($\hbar\omega_l$) of longitudinal optical phonons at $k\simeq 0$.

The epitaxial GaAs was grown from the vapor phase on an n-doped GaAs substrate by K. L. Lawley at Bell Telephone Laboratories. Magnetoresistance and Schottky barrier techniques were used to obtain values for the mobility and carrier concentration, respectively. Photoconductivity was obtained by shining chopped, monochromatic light on the sample which was in a series circuit with a bias battery and a resistor. Contacts were on the sample face and masked from the light. The change in voltage across the resistor was monitored at the chopping frequency as the wavelength of the light was varied. Since the layer was about 69 μ thick, the light in the spectral region of interest did not penetrate sufficiently deeply to reach the substrate.

The oscillation is similar to that observed recently in various other semiconductors, including InSb,[1-4] GaSb,[1] and ZnTe,[5] where the periods of oscillation were all found to be somewhat larger than $\hbar\omega_l(k\approx 0)$. The oscillation arises because photoexcited electrons interact strongly with LO phonons but relatively weakly with acoustical phonons according to the condition[1] $\tau_a > \tau > \tau_{op}$. Here τ is the lifetime of photoexcited electrons; τ_a and τ_{op} are characteristic times for loss of carrier energy to acoustical and optical phonons, respectively. Thus, electrons are removed from the conduction band before losing appreciable energy through emission of acoustical phonons. If the energy ϵ of photoexcited electrons relative to the conduction band edge is greater than $\hbar\omega_l$, then LO phonons are very quickly emitted so that electrons cascade down and spend most of their lifetime in the conduction band at energies $0<\epsilon<\hbar\omega_l$ according to the relation

$$\epsilon=(h\nu-E_g)/(1+m_e/m_h)-n\hbar\omega_l.$$

E_g is the energy gap between parabolic bands with electron and hole masses m_e and m_h, and n is the largest integer such that ϵ is positive. Within this framework, oscillation in photoconductivity with increasing $h\nu$ can arise because of an energy-dependent free-carrier mobility[1] or lifetime.[2] Also, preferential momentum loss[3] from the injected electron distribution due to LO phonon emission can give periodic structure. It is difficult to distinguish these different mechanisms on the basis of photoconductivity spectra alone. It should be noted that several other semiconductors[6] have shown oscillation in the intrinsic photoconductivity spectrum, but, unlike GaAs and the other materials mentioned above, the period of the oscillation was very closely equal to $\hbar\omega_l(k\simeq 0)$. To explain recent results in two of these, CdTe[7] and CuCl,[8] explanations have been advanced based on dissociation[7] or competition[8] of excitons created by photons with phonon participation. Since these models predict a period of oscillation equal to $\hbar\omega_l$, they can be ruled out in the case of GaAs.

For the present data, consistent with the equation above, a plot of the order numbers n assigned to the minima of the oscillation versus energy of the minima is a straight line, as shown in Fig. 1. The period of the oscillation (energy spacing of the minima) is 0.043 eV according to the slope of this line. Using this and $\hbar\omega_l=0.0368$ eV,[9] we calculate from the above relation that $m_h/m_e=6.2\pm 0.7$. From the magnitude of this ratio it is concluded that m_h refers to heavy holes. The ratio m_h/m_e obtained is somewhat larger than the value

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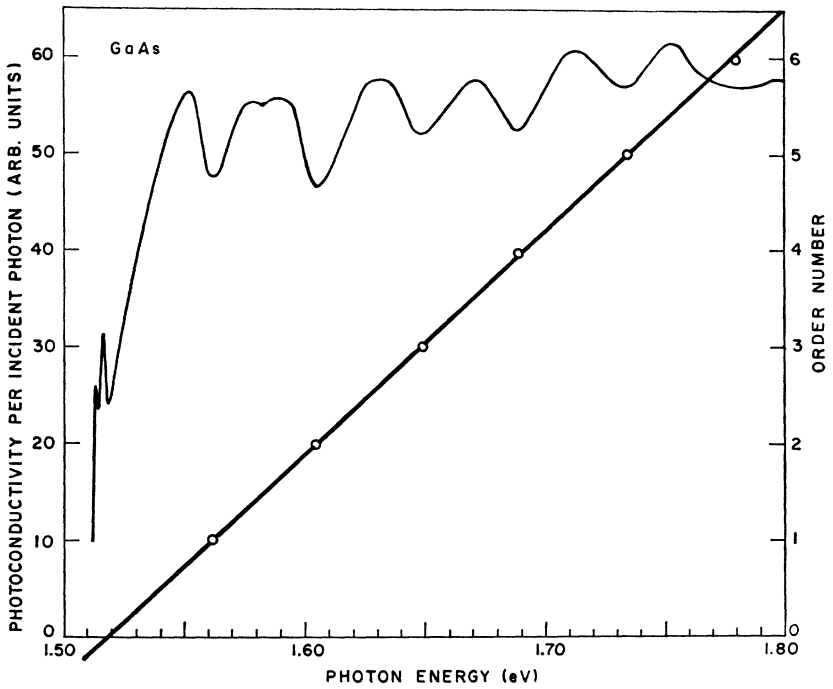

FIG. 1. Photoconductivity spectrum of a GaAs epitaxial layer at 2°K. The straight line is a plot of order number versus photon energy for the minima of the oscillation. Spectrometer resolution was ≈1 meV.

$m_h/m_e \simeq 5$ reported by Bailey, Gilleo, and Hill[10] for epitaxial layers and is somewhat smaller than the value $m_h/m_e = 9.7$ calculated from values obtained by various workers (as listed by Cardona[11]) for bulk-grown GaAs. Using the electron mass[11] $m_e = 0.07\ m_0$, we get $m_h \simeq 0.43\ m_0$ from the present measurements.

The straight line in Fig. 1 intersects the energy scale at $n=0$ at an energy 1.520 ± 0.002 eV, which corresponds to the published energy gap in accord with the above interpretation. From absorption measurements, Sturge[12] obtained 1.521 ± 0.0015 eV for the energy gap, and from photoluminescence Bailey *et al.*[10] obtained 1.5202 ± 0.0003 eV, both consistent with the energy obtained above. This energy is located in the photoconductivity spectrum at the sharp dip on the high-energy side of the two sharp peaks. Thus the rise above this dip corresponds to the threshold of intrinsic photoconductivity. No other related minima were found at lower photon energies. It was found that the rise-time of the photoconductivity when light was turned on underwent a change at this photon energy, 1.5193 ± 0.0008 eV. This was readily observed by noting a change in phase of the output of a lock-in amplifier as the energy of incident chopped light was swept through the above value. The change, which was reproducible and independent of the direction of drive of photon energy, evidently indicates the onset of band-to-band transitions, the presence of which alter the recombination and trapping processes.

The two sharp peaks shown in Fig. 1, which occur at photon energies of 1.5164 ± 0.0002 eV and 1.5135 ± 0.0002 eV, are thus below the energy gap. The higher-energy peak lies at the energy of free excitons, which has been reported at 1.5155 (Ref. 10) and 1.516 eV (Ref. 13) by different authors according to photoluminescence in epitaxial layers and at 1.5176 ± 0.015 eV (Ref. 12) according to the absorption spectrum of bulk-grown semi-insulating GaAs. Dissociation of free excitons could be responsible for the photoconductivity peak at the exciton energy. Two other peaks in the photoconductivity spectrum, not shown in Fig. 1, were observed in the present work at lower energies at 1.510 and 1.488 eV in epitaxial GaAs. These peaks, as well as that at 1.5135 eV, are apparently related to excitation of conducting carriers from impurities. Further discussion of these photoconductivity peaks below the energy gap will be given in a future paper.[14]

The small dip between the $n=1$ and $n=2$ minima at 1.583 eV in Fig. 1 is reproducible. It may be a weak minimum of oscillation involving excitation from the light-hole valence band. Similar weak minima at higher photon energies could not be found, however, Assuming the weak dip to be the first minimum for transitions originating at the light-hole band, an effective mass

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ratio of $m_e/m_{lh}\simeq 0.7$ is obtained which is reasonable for electrons and light holes. This value is somewhat larger than the ratio $m_e/m_{lh}\simeq 0.58$ calculated from the values listed by Cardona.[11]

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Optical Third-Order Mixing in GaAs, Ge, Si, and InAs*

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Nonlinear optical difference mixing of CO_2 laser radiation is studied in the semiconductors GaAs, Ge, Si, and InAs. The fourth-rank electric susceptibility tensor receives independent contributions from the bound or valence electrons, χ^b, and, in n-type material, from the conduction electrons, χ^n. These two contributions are separated and measured in GaAs. χ^b is found to be anisotropic and χ^n to be isotropic for carrier concentrations $n\leqslant 5\times 10^{16}$/cc. The relative signs of the susceptibilities are determined. χ^b in Ge and GaAs and χ^n in GaAs and InAs all have the same sign for the particular frequency combination studied. Theoretical and experimental evidence indicate that this sign is positive. At room temperature, χ^n in GaAs is a linear function of n for $n\leqslant 5\times 10^{16}$/cc. The value of the slope $\partial\chi^n/\partial n$ is a direct measure of the nonparabolicity of the conduction band in GaAs. It is shown to be inconsistent with Kane's model for small direct-band-gap semiconductors, and in agreement with Cardona's indirect measurements of the nonparabolicity in GaAs.

I. INTRODUCTION

THE existence of a nonvanishing electric polarization cubic in electric field strength offers the possibility of studying optical nonlinearities in centrosymmetric crystals. In noncentrosymmetric crystals the effects of a polarization cubic in the field are usually much smaller than quadratic polarization effects, but the cubic effects may be singled out for study. Several workers have studied polarizations third order in electric field. Maker and Terhune[1] studied materials transparent in the visible using a pulsed ruby laser. More recently, the CO_2 laser has been used[2–4] to study semiconductors which are not transparent in the visible.

Jha and Bloembergen[5] (JB) have shown that, for n-type semiconductors of group IV and the III-V type, the nonlinear susceptibility may be separated into two independent contributions, the bound or valence electron contribution χ^b and the conduction-electron contribution χ^n. Wynne and Boyd[4] (WB) measured the effect of the valence electrons χ^b in Ge and Si, and JB calculated χ^b for Ge, Si, GaAs, InAs, InSb, and GaSb using stationary state perturbation theory to derive nonlinear susceptibilities in terms of multipole moments in a tetrahedral-bonding orbital ground state. The agreement in magnitude to within the experimental error is encouraging, but, as shall be seen, there are still serious discrepancies.

Wolff and Pearson[6] (WP) made a simple one-band calculation of the conduction-electron contribution χ^n based on Kane's[7] band structure for InSb. Their results are in good agreement with the experimental results of Patel, Slusher, and Fleury[2] for InAs and InSb. JB have shown that the WP results for χ^n need a correction when the photon energies are not very small compared to the energy gap between conduction and valence bands.

The experimental work has been extended to measure both χ^b and χ^n in GaAs for varying carrier concentration. In addition the anisotropy and the relative signs of χ^b and χ^n have been determined in Ge, GaAs, and InAs ($n\approx 2.6\times 10^{16}$/cc) using an interference technique. In Sec. II, the experimental method of determining χ is discussed. All measurements were made relative to the absolute determination of χ in Ge by WB. The basic experimental uncertainty of $\pm 50\%$ in the magnitude of χ(Ge) carries over to all measured χ, but the relative measurements are more accurate. In Sec. III, the experimental results are presented and compared with theory in terms of magnitude and sign.

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