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Photoreflectance Line Shape at the Fundamental Edge in Ultrapure GaAs

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Reflectance modulation produced by an intense secondary light beam (photoreflectance) has been studied for wavelengths near the fundamental edge in ultrapure epitaxial layers of GaAs as a function of doping, temperature, and intensity of the modulating light beam. As the doping increases, the built-in electric field at the surface increases and the photoreflectance line shape stretches, in qualitative agreement with the predictions of the Franz-Keldysh theory. These results show directly that the photoreflectance is due to the modulation of the electric field in the Schottky surface barrier by photoexcited carriers. Since the line shape is much narrower than earlier electroreflectance measurements, we arrive at a more accurate value for the band gap of 1.420 eV at 300 °K. As the temperature is lowered, the spacing in energy between adjacent peaks in the photoreflectance spectrum decreases, indicating that the electric field at the surface is decreasing. This temperature dependence is explained by a simple model for the surface consisting of a large density of electron traps located a fixed energy below the conduction-band edge. For all but the purest sample, the line shape is independent of the intensity of the modulating beam, consistent with the model that the secondary light beam is only slightly modifying the surface electric field. However, in the purest sample available ($n_e = 1.65 \times 10^{13}$ cm^{-3}), a new effect is observed at the highest intensities of the modulating beam (~ 0.1 W/cm^2). The qualitative features of the new line shape agree with the predictions for both the Burstein effect and exciton screening by free carriers. Since the discrete exciton is thermally quenched at 300 °K, the new line shape may result from the Burstein effect.

I. INTRODUCTION AND CONCLUSIONS

Photoreflectance is the modulation of a crystal's reflectance by a coincident secondary light beam. Several authors[1-5] have recently shown that photoreflectance (PR) can result from a modulation of the built-in electric field near the surface of a crystal. Other workers have suggested that PR can result from a change in the population of the conduction and valence bands[6] (a Burstein effect), from temperature modulation[7] (thermoreflectance), or from a screening of excitons by free carriers.[8] The importance of the surface electric field in photoreflectance was first demonstrated by the observation[1,9] of the "Λ" transitions in GaAs, since for these transitions the Burstein effect is not possible. On the other hand, the evidence that the photoreflectance structure near the fundamental band gap in GaAs was also an electric field effect was only circumstantial. In the present work, we show directly that the PR structure at the fundamental edge in GaAs results from a modulation of the electric field in the Schottky surface barrier by the photoexcited carriers. To do this, we study the changes in PR line shape accompanying changes in the bulk doping.

In our purest epitaxial layer we observe, in addition to the usual PR line shape, another structure which may be due to the Burstein effect.[6] We show in a later section that the amplitude of the built-in surface field decreases as the donor concentration decreases. Hence, in sufficiently pure material the electric field mechanism just described becomes weak and other mechanisms such as the Burstein effect,[6] exciton screening,[8] or electric field quenching of the exciton should dominate. Exciton screening or exciton quenching probably cannot be observed at 300 °K since the discrete exciton[10] is thermally quenched.

As the temperature is decreased from room temperature to 77 °K, the spacing in energy between adjacent peaks in the PR spectrum decreases by about a factor of 2, indicating that the surface electric field is decreasing. This temperature dependence is explained by a simple model for the surface consisting of a large density of electron traps located a fixed energy below the conduction-band edge. Either a low density of electron traps at a fixed energy or a continuous energy distribution of surface states would predict the opposite temperature dependence. These results give an indication of the potential of photoreflectance experiments for studying surface properties.

II. EXPERIMENTAL

The experimental arrangement[1,5,9] used to measure photoreflectance is shown schematically in Fig. 1. A tungsten quartz-iodine lamp and a $\frac{1}{2}$-m Bausch and Lomb spectrometer with a 600-lines/mm grating blazed at 1 μ produce the monochromatic radiation reflected from the crystal surface. For low-temperature spectra, the sample is immersed in the liquid refrigerant in a Janis stainless steel Dewar. The reflected light is focused onto an EGG SGD-444 silicon photodiode biased in the photoconductive mode. A 30-mW He-Ne laser (6328 Å) is focused onto the same spot on the sample as is the monochromator light. Typical spot sizes were 10 mm×1.0 mm. By chopping the laser beam at 510 Hz, the crystal's reflectivity is modulated periodically, and the light reaching the silicon detector has a 510-Hz component. Measurements of the voltage waveform using a boxcar integrator indicated that the reflectance modulation was essentially instantaneous with a response time less than 100 μsec. A 2-64 Corning filter placed in front of the detector prevents the scattered laser light from reaching the detector. The dc voltage level at the detector (proportional to the dark reflectivity) is measured by an electrometer and the 510-Hz component is synchronously detected with a lock-in amplifier. The outputs of the lock-in amplifier and the electrometer are simultaneously recorded on a chart recorder or are electrically divided and their ratio, proportional to $\Delta R/R$, is recorded. With this apparatus, modulation depths as small as 5×10^{-7} can be measured with a 3-sec time constant.

The samples used in the present work were epitaxial layers grown by K. L. Lawley at Bell Telephone Laboratories and others grown by several commercial manufacturers. The layers were *n* type, not intentionally doped, and had electron concentrations at 300 °K ranging from 1.65×10^{13} to 5.0×10^{15} cm^{-3}. Typically, the layers were about 75 μ thick.

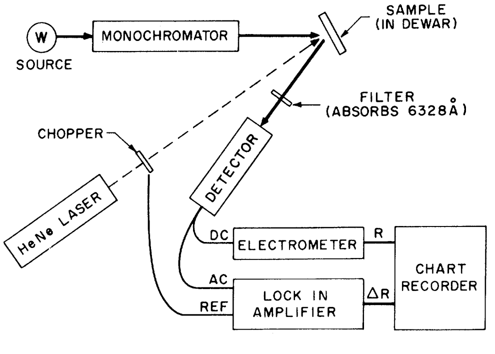

FIG. 1. Schematic diagram of the experimental apparatus for measuring photoreflectance.

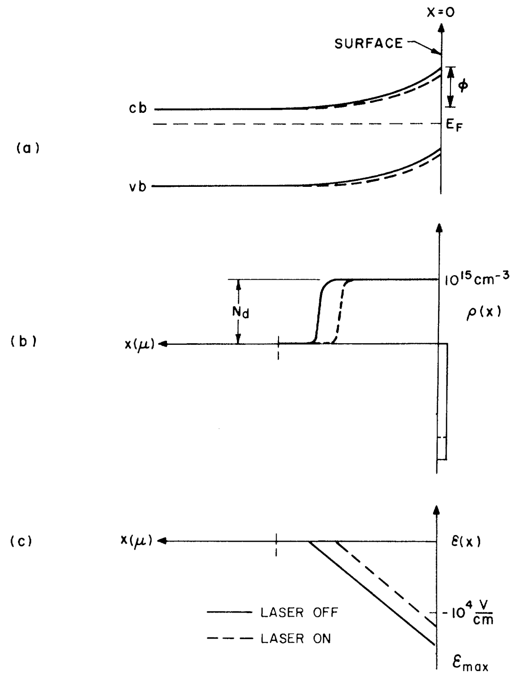

FIG. 2. Schottky barrier depletion region at a semiconductor surface. (a) The energy bands, (b) the charge density, and (c) the macroscopic electric field are shown as a function of depth into the crystal. The changes produced in these quantities by an intense absorbed light beam are shown by the dashed curves.

III. SURFACE SCHOTTKY BARRIER

In this section, we briefly describe the depletion region Schottky barrier at the surface of an extrinsic semiconductor.[11] Of all the possible potential distributions near the surface,[11,12] we choose to discuss this one because (i) there is independent evidence[12–14] that it applies to *n*-type GaAs and (ii) it predicts the essential features of the experimental data to be presented later.

Figure 2 shows the bending of the energy bands, the charge density, and the electric field in the depletion region near the surface of an *n*-type semiconductor. The dashed curves show the changes caused by the free carriers produced by the modulating light beam. The photoexcited electrons and holes find themselves in a strong electric field, and separate in a manner so as to reduce the built-in field.

In the dark, the electric field varies linearly with distance from a maximum value $\mathcal{E}_{\max}$ at the surface to zero at a depth d below the surface. These quantities are given by[11]

$$\mathcal{E}_{\max}=(2eN_d\varphi/\epsilon)^{1/2}, \tag{1}$$

$$d=(2\epsilon\varphi/eN_d)^{1/2}, \tag{2}$$

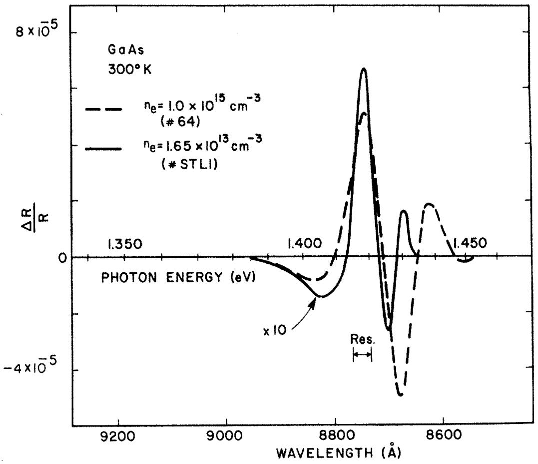

FIG. 3. Photoreflectance spectra near the band gap of GaAs for two epitaxial layers of significantly different electron concentrations n_e. Positive $\Delta R/R$ indicates an increase in reflected intensity when the laser is turned on. For both curves the intensity of the modulating light beam was $\sim 10^{-3}$ W/cm^2.

where N_d is the doping density, ϵ is the dielectric constant, and the potential difference φ is the total amount of band bending. Using a dielectric constant of 12.5 appropriate to GaAs, a band bending of 0.5 V, and a doping density of 10^{15} cm^{-3}, we estimate that $d \approx 0.8\ \mu$ and $\mathcal{E}_{\max} \approx 1.2 \times 10^4$ V/cm.

In Fig. 2, we have assumed that the photoexcited holes are pulled towards the surface and go into surface states. If, in fact, the holes do not go into surface states but are merely pinned against the surface, then the dashed curves in Fig. 2 are incorrect in principle. By Gauss's law, the field just inside the surface is not changed by the laser. This is of no practical importance, however, since the hole diffusion length[15] against the strong field is $\sim 0.01\ \mu$, a distance short on the scale of Fig. 2.

IV. RESULTS

The photoreflectance line shape near the fundamental band gap of GaAs is shown in Fig. 3 for two samples with greatly different electron concentrations. The PR spectra resemble electroreflectance spectra[13,16,17] except that the PR spectra are much narrower, consisting of several oscillations in the vicinity of the band gap usually quoted as 1.43 eV at 300 °K. The PR spectrum in the more impure sample is about 1.7 times wider and 10 times stronger than the spectrum for the purer sample. We notice the interesting result that any thermal broadening of the spectra is much less than kT which is 26 meV at 300 °K.

The effect of temperature upon the PR line shape is shown in Fig. 4. The two spectra have the same general features although the 77 °K spectrum is about twice as narrow as the 300 °K spectrum and displays a pronounced peak B. These data were previously published,[1] but the origin of the B peak was not identified nor was an adequate explanation given for the narrowing of the line shape as the temperature is lowered.

With a single exception, the PR line shape does not change as the amplitude of the modulating beam is changed, whereas the amplitude increases approximately as the cube root of the laser intensity.[1] Representative data are shown in Fig. 5. On the contrary, in the purest sample available, the line shape showed a strong dependence upon laser intensity as shown in Fig. 6. At intermediate intensities, the PR spectrum is a superposition of the low- and high-intensity line shapes. At low intensities the PR line shape is independent of laser intensity and the amplitude varies as the cube root of the laser intensity; at high intensities, the new line shape is also independent of laser intensity but its amplitude varies linearly with laser intensity. The superposition at intermediate intensities implies that the two line shapes arise from quite different mechanisms.

V. DISCUSSION

A. Doping Dependence

The change in the PR line shape shown in Fig. 3 as the donor density is changed demonstrates directly that the Schottky barrier model of Fig. 2 is essentially correct. Since the spacing of peaks in the Franz-Keldysh line shape[18] is proportional to $\mathcal{E}^{2/3}$, where $\mathcal{E}$ is the electric field, and since Eq. (1) predicts that the maximum field increases

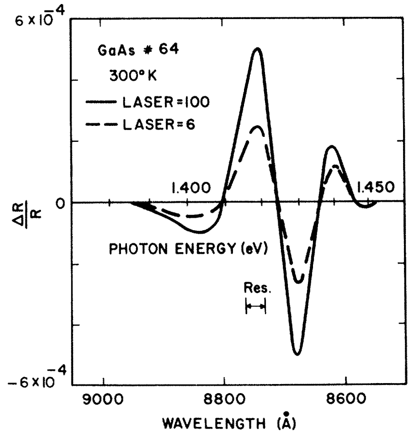

FIG. 5. Dependence of the photoreflectance spectrum upon the intensity of the modulating beam. These data are typical of all crystals except STL-1, the purest sample studied.

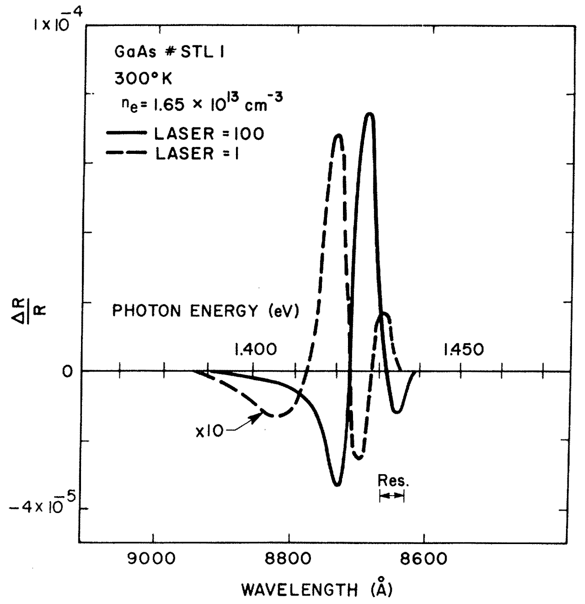

FIG. 6. Dependence of the photoreflectance spectrum upon the intensity of the modulating beam for the purest crystal studied.

as $N_d^{1/2}$, the spacing of peaks in the PR line shape should vary as $N_d^{1/3}$. Hence, the PR spectrum should stretch by a factor of 3.9 between the two impurity concentrations in Fig. 3; the experimentally measured value is 1.7. This discrepancy is not surprising since the impurity concentration in sample STL-1 is probably considerably larger than the free-electron concentration n_e. Neutral donors or compensated acceptors below the Fermi level in the bulk can contribute to the effective N_d in Eqs. (1) and (2) even though they do not contribute free carriers in the bulk. The difference between the curves in Fig. 1 would be consistent with an effective N_d of 2×10^{14} cm^{-3} for sample STL-1. Hence the effective N_d differs by a factor of ~ 5 for the samples in Fig. 3. This ratio is consistent with the low-temperature mobility ratio of ~ 6 due to ionized impurity scattering.

In addition to the variation of the surface field with doping described by Eq. (1), the change in the position of the bulk Fermi level can have a slight effect on the PR line shape. For the two electron concentrations shown in Fig. 3, the Fermi level in the bulk lies 150 and 270 meV below the conduction band for the 10^{15}- and 1.65×10^{13}-cm^{-3} samples, respectively. Therefore, the total band bending φ is about 0.12 eV (~ 20%) smaller in the purer sample. Since the spacing of peaks in the Franz-Keldysh line shape varies as $\mathcal{E}^{2/3}$ and hence as $\varphi^{1/3}$, the change in bulk Fermi level can have at most a 7% effect on the PR line shape.

Since the solid curve in Fig. 3 is about 5 times narrower than earlier electroreflectance line shapes,[13,16,17] we are able to determine a more accurate value for the band gap at 300 °K. Since Franz-Keldysh theory[18] predicts that an increase in the electric field causes structure both below and above the band gap to "move away" from the band gap, we find that the band gap at 300 °K is near the lowest-energy positive peak at 1.420 eV. Our value is significantly smaller than the values of 1.435 quoted by Sturge[10] and of 1.428 quoted by Vrehen.[19] Although our spectrometer resolution introduces an experimental uncertainty of only 2 meV, our value for the band gap may be low by as much as 5 meV due to the uncertainty in the theory for the PR line shape. It is conceivable that the resonant energy ("band gap") for the PR line shape may in fact be the energy of the exciton which lies ~ 5 meV below the thermal band gap.

B. Temperature Dependence

The temperature dependence of the PR line shape shown in Fig. 4 can be explained by a very simple model for the energy levels at the surface consisting of a large density of electron traps located a fixed energy below the conduction-band edge. The decrease in spacing between adjacent peaks in the PR spectrum as the temperature is lowered implies that the surface electric field is decreasing. Referring to Fig. 2(a), this means that the band bending φ decreases as the temperature is lowered. This could not occur for a continuous energy distribution of surface states. The Fermi level would then be pinned relative to the conduction-band edge at the surface, and the band bending φ would increase as the Fermi level in the bulk moved towards the conduction band with decreasing temperature. A careful consideration of the effects of temperature on the balance between the charge in the surface traps and the charge in the depletion region leads us to conclude that the energy of the surface trap must be above the energy of the conduction band in the bulk to explain the observed behavior of the PR line shape. We therefore conclude that the density of surface states is large since, loosely speaking, the trap was raised far above the Fermi level to reduce the amount of charge trapped at equilibrium. With this model we estimate that the density of electron traps at the surface is at least 2.2×10^{13} cm^{-2}. A detailed study of the temperature dependence of the PR line shapes should allow one to determine both the density and the energy of the surface traps. Such studies are underway and will be reported at a later date.

We attribute the B peak at 1.507 eV in Fig. 4 to the free exciton. This suggestion is supported by Vrehen's observation[19] of the free exciton in electroabsorption at 1.508 eV. We have only observed this exciton line shape in samples No. 174 and No. STL-1 in which the line shape consists of a negative peak followed by a positive peak at higher energies. The amplitude of this PR structure is essentially independent of laser intensity. The line shape is consistent with the theory for exciton screening[8] by free carriers, but the intensity dependence is not understood.

C. Intensity Dependence

The lack of any variation of the dominant PR line shape as the laser intensity is varied (Fig. 5) is consistent with the model sketched in Fig. 2; the built-in field is only slightly altered by the modulating light beam. The weakness of the PR relative to electroreflectance[13,16,17] is also consistent with this model.

In our purest sample a new line shape appears in the PR spectrum at high laser intensities (Fig. 6). If one subtracts off the contribution to the solid curve due to the low intensity line shape, the new line shape consists essentially of a negative peak followed by a positive peak at higher energies, with both peaks having approximately the same amplitudes. These general features are consistent with both the theories for the photoreflectance by the Burstein effect[6] and by exciton screening[8] by free carriers. Since the discrete exciton[10] is thermally quenched at 300 °K, the new PR line shape may result from the Burstein effect. The new experimental results cannot be directly compared with the theory of Gay and Klauder[6] since they considered the case of vanishing electron-hole interaction. In fact, the Coulombic attraction drastically modifies the density of states[20] and transforms a square root threshold into a constant density of states independent of energy near the band gap. Nonetheless, a calculation of the Burstein effect photoreflectance using the constant density of states might only sharpen the positive high-energy peak as we observe experimentally.

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