

Room-temperature photoreflectance and photoluminescence of heavily Si-doped GaAs

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Room-temperature photoreflectance (PR) and photoluminescence (PL) spectra in heavily n -doped GaAs were compared. It was found that for highly degenerate semiconductors the critical energy measured by the PR equals to the peak energy of the PL spectrum. When Fermi level lies below the conduction-band minimum, the PR spectra revealed the band-gap energy as well as the energy E_{\max} at which the electron concentration per unit energy in the donor band becomes maximum, and this maximum was observed to merge in the conduction-band at about $3 \times 10^{17} \text{ cm}^{-3}$ electron concentration. © 1995 American Institute of Physics.

Photoreflectance (PR) spectroscopy is proved to be a valuable characterization technique for compound semiconductors and multiple quantum wells.¹ The critical energy E_0 in PR spectra of nondegenerate semiconductors has been known to be the band-gap energy.² It is obvious, however, that the PR cannot determine the band-gap energy of degenerate semiconductors because of the band filling by electrons. Here we use the term degenerate semiconductor meaning that its Fermi level lies in the conduction band. It is known that the PR response depends on the doping concentrations N_d . Peters *et al.*,³ for example, have shown that E_0 depends linearly on N_d in the range of 1×10^{16} – $6 \times 10^{17} \text{ cm}^{-3}$, but they could not clarify the reason for this linear dependence and only attributed it to the many-body effects. Badakhshan *et al.*⁴ have also demonstrated that the line broadening of the E_1 response ($\sim 2.9 \text{ eV}$) varies linearly on $\log(N_d)$ in the range of 1×10^{17} – $4 \times 10^{18} \text{ cm}^{-3}$, and they attributed this phenomenon to the dependence of surface electric field on the dopant concentration. But, in this case E_1 does not correspond to the principal band-gap energy. We therefore believe that the correct answer to the dependence of E_0 on N_d is not given as yet.

Photoluminescence (PL) spectroscopy, on the other hand, has been considered a direct way to measure the band-gap energy of nondegenerate semiconductors. If we consider degenerate semiconductors, the peak energy of PL spectra cannot be easily identified with physically meaningful energy such as band-gap energy or Fermi energy. We can only obtain these energies from detailed line-shape analysis of PL spectra^{5,6} or from the energy of the short-wavelength edge of PL spectra at its half-maximum $E_{1/2}$ at low temperature.⁷ In this communication we, therefore, compare the PR with the PL in order to get a physical insight into the energy values that the PR determines.

Samples were prepared by molecular-beam epitaxy

(MBE). An intrinsic GaAs buffer layer of $1 \mu\text{m}$ thickness was grown on the substrate of Cr-doped GaAs and then followed by a Si-doped layer of $1 \mu\text{m}$ thickness. The electron concentration n of the samples was determined by Hall measurements at room temperature, and ranged from 1.00×10^{17} to $3.70 \times 10^{18} \text{ cm}^{-3}$.

The experimental arrangement for PR measurements was a standard one. The reflectance modulation was achieved by the photoexcitation with an Ar-ion laser (488 nm line) chopped at 139 Hz. The power of the modulating beam was fixed at about 0.4 W/cm^2 to ensure the low-field limit and consequently to avoid any saturation effects. The probe light from a 300 W tungsten-halogen lamp dispersed by a 25 cm monochromator was incident on the sample. The modulated signal ΔR was obtained by a lock-in amplifier, and then the PR signal $\Delta R/R$, by a ratiometer.

The PR spectra were analyzed using the well-known third derivative functional form,⁸

$$\Delta R/R = \text{Re}[C e^{i\theta} (E - E_0 + i\Gamma)^{-m}], \quad (1)$$

where C and θ are the amplitude and phase factors of the line shapes. E_0 and Γ are the critical energy and the broadening parameter, respectively. Here, we assumed the three-dimensional ($m = 5/2$) simple parabolic critical point model. The PR spectra are fitted with Eq. (1) by adjusting the parameter C , θ , E_0 , and Γ . The results are shown in Fig. 1 as a function of electron concentration and the triangles indicate the position of the critical energies E_0 . The accuracy in the evaluation of the critical energies and broadening parameters was within 5 meV, except for the two samples of larger electron concentration. We should note from Fig. 1 that the signals of the three less-doped samples consist of two critical energies, one of which is obviously the band-gap energy of GaAs ($E_g = 1.425 \text{ eV}$). The other is the transition energy from the top of the valence band to the energy E_{\max} at which the electron concentration per unit energy in the donor band becomes maximum. E_{\max} increases with increasing electron

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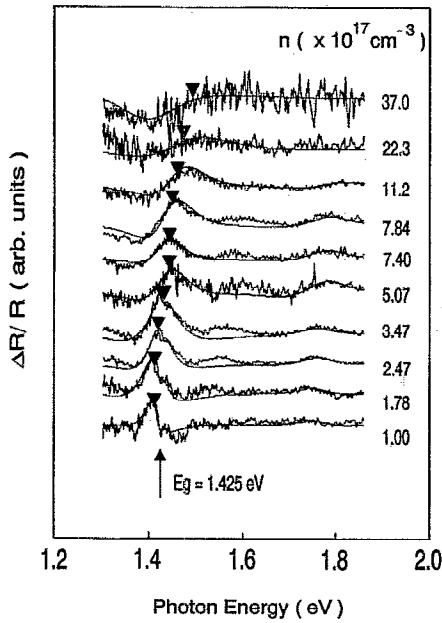


FIG. 1. Photoreflectance spectra of MBE-grown GaAs:Si at room temperature as a function of electron concentration and fitted curves with Eq. (1). The triangles denote the critical energies E_0 determined by PR. Note that two peaks appear in the spectra of the four less-doped samples.

concentration, so that at about $n=3 \times 10^{17} \text{ cm}^{-3}$, the maximum of the electron distribution in the donor band merges in the conduction band and the donor band eventually becomes the conduction-band tail, in which there is no relative maximum. In other words, the donor band may form the conduction-band tail with a relative maximum so that this maximum is measured by PR, and then it becomes the tail without the relative maximum as the electron concentration increases. This donor-band maximum was not observed for the sample of $n=1.00 \times 10^{16} \text{ cm}^{-3}$ (not shown here). We further note that both the band-gap energy and the energy at which the conduction electron concentration becomes maximum were detected for the sample with $n=3.47 \times 10^{17} \text{ cm}^{-3}$. When n is larger, the maximum electron concentration in the conduction band is only seen in the PR spectra. We discuss this point of view later.

For the PL measurements the samples were excited by the 488 nm line of an Ar-ion laser with an intensity of 0.4 W/cm^2 at room temperature. The luminescent light was collected and dispersed by a 75 cm monochromator (Spex 750M). The signals were detected by a cooled photomultiplier. The measured PL spectra are shown in Fig. 2 as a function of the electron concentration. The triangles indicate the position of the critical energies measured from the PR spectra. We plot again, in Fig. 3, the critical energies of the PR and the peak energies of the PL as a function of the electron concentration n , so that their quantitative behavior can be seen more clearly.

We can estimate the electron concentration at which samples start to be degenerate. Assuming parabolic density of states in the conduction band, the electron concentration can be written as follows:⁹

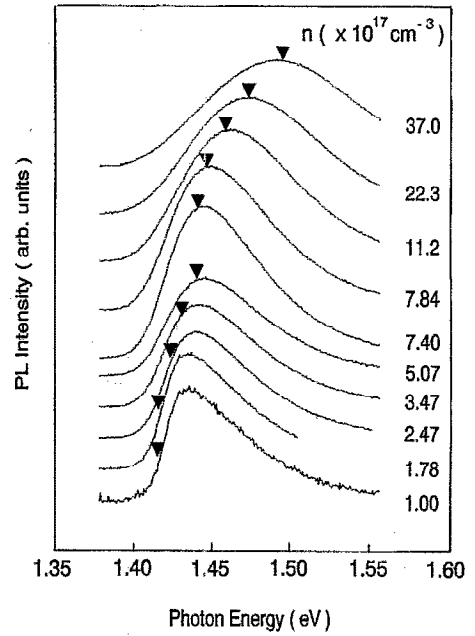


FIG. 2. PL spectra as a function of electron concentration. The critical energies determined from the PR spectra are also indicated by the triangles for comparison.

$$n = N_c(T) F_{1/2}[(E_f - E_c)/kT], \quad (2)$$

where $N_c(T)$ is the effective density of states in the conduction band and $F_{1/2}(\eta_f)$ is the Fermi-Dirac integral. If we evaluate Eq. (2) at $E_f = E_c$ and at room temperature, the minimum electron concentration for degenerate semiconductors can be obtained, and it is about $3.2 \times 10^{17} \text{ cm}^{-3}$ for GaAs. It may, therefore, be concluded from Fig. 3 that the critical energy determined from the PR spectra equals the peak energy of the PL spectra for the electron concentrations where the samples become degenerate. We further note in Figs. 1 and 3 that the degeneracy of the samples starts from about $n=3 \times 10^{17} \text{ cm}^{-3}$, which agrees remarkably well with the values estimated theoretically.

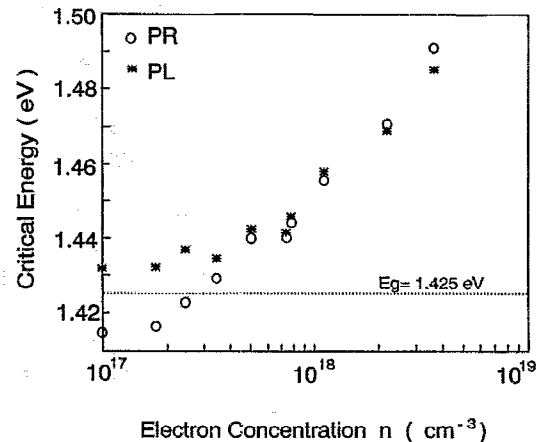


FIG. 3. The critical energies measured by the PR and the peak energies of the PL spectra as a function of electron concentration.

Since the k -nonconserving band-to-band or band-to-acceptorlike states luminescence is dominant in heavily doped n -type GaAs,⁵ the spectral line shape of PL can be written as

$$I(E) \sim D(E)F(E)|M_{if}|^2, \quad (3)$$

where $D(E)$ is the density of states in the conduction band and $F(E)$ the Fermi-Dirac distribution function. M_{if} is the transition matrix for an electron. Since we are dealing with the energy range of about 100 meV, we may consider the transition matrix to be constant in energy. Then $I(E) \sim D(E)F(E)$, so that the electron concentration per unit energy becomes maximum at the peak energy of PL spectra. We can, thus, say that the PR should result from a change in the electron distribution of the conduction band of degenerate semiconductors, so that it determines the energy at which the electron concentration per unit energy becomes maximum. This type of mechanism for PR was shown to determine the band-gap energy for nondegenerate semiconductors.¹⁰ We can also apply the same argument to the donor band. The linear dependence of the critical energy on the donor concentration for $1 \times 10^{16} \leq N_d \leq 8 \times 10^{17} \text{ cm}^{-3}$, reported by Peters *et al.*,³ may be true for the relatively small range of N_d variation as compared to our result, $E_0 \sim \log(n)$, shown in Fig. 3, but the slope of the relation between the critical energy E_0 and the electron concentration n is approximately 40 meV/decade in both cases. They have also suggested that the upward shift of the critical energy from the linear dependence for the sample of $N_d = 8 \times 10^{17} \text{ cm}^{-3}$ would be caused by the band-filling effects. On the other

hand, we are very familiar with the fact that PR can result from a modulation of the built-in electric field near the surface of nondegenerate semiconductors.¹¹

In conclusion, the PR measurement can determine the energy of the maximum electron concentration per unit energy in the conduction band of degenerate semiconductors, and, for nondegenerate semiconductors, it can measure the band-gap energy and the transition energy from the top of the valence band to the maximum electron concentration in the donor band, which merges in the conduction band at about $n = 3 \times 10^{17} \text{ cm}^{-3}$.

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