

## Photoluminescence study of confined donors in GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As quantum wells

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The photoluminescence from doped GaAs quantum wells in GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As multiple-quantum-well structures has been studied at very low laser excitation intensity. Under these conditions, new impurity-associated features appear at energies both below and above that of the impurity-related transition reported in earlier work. The new feature at lower energy is attributed to transitions between electrons on neutral Si donors at the centers of the wells and confined heavy holes, while the feature reported in earlier work is attributed to confined ionized donor bound excitons and the new high-energy feature to confined neutral donor bound excitons. With this assignment, binding energies for Si donors at the centers of the wells agree with values deduced from far-infrared experiments.

Confined impurity states in GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As quantum wells have attracted considerable recent attention. The binding energies of donors<sup>1,2</sup> and acceptors<sup>3</sup> have been calculated as functions of well width and impurity position. Photoluminescence<sup>4-8</sup> Raman scattering<sup>9,10</sup> and far-infrared (FIR) magnetoabsorption<sup>11,12</sup> spectroscopies have been used for the study of donors and acceptors in these structures. Photoluminescence associated with Si donors in *n*-type GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As quantum wells was first reported by Shanabrook and Comas.<sup>5,6</sup> In this work, a donor-impurity-associated feature below the ground-state heavy-hole exciton was observed and attributed to transitions between electrons on Si donors at the centers of the wells and heavy holes in the topmost valence-band confinement state [Si(c) → VB]. This interpretation yielded donor binding energies significantly lower than those inferred from FIR measurements on samples with similar characteristics, as well as with calculated values that are in good agreement with the FIR data.

In this paper we present a systematic photoluminescence study of high-quality, Si-doped multiple-quantum-well samples, carried out under experimental conditions that reveal *two new features* at energies slightly below and slightly above the line previously reported. The *lowest-energy* feature is ascribed to the Si(c) → VB transition; the previously reported photoluminescence feature is identified as the confined ionized donor bound exciton, and the new *high-energy* feature as due to the confined neutral donor bound exciton. Comparison of the spectra from quantum wells doped at the center with those from edge-doped structures having the same dimensions supports this interpretation. The experimental values for the binding energies of donors at the center of the wells deduced from our photoluminescence data are in good agreement with those determined from FIR magnetospectroscopy on the *same samples*, and the theory of Refs. 1 and 2.<sup>13</sup> In addition, the binding energies of excitons on donor impurities are in good agreement with recent calcu-

lations.<sup>14</sup>

Several molecular-beam-epitaxy-grown GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As multiple-quantum-well structures were used in this study; well widths varied from 375 to 80 Å. The samples were doped with Si donors ( $1 \times 10^{16} \text{ cm}^{-3}$ ) either in the central one-third of the GaAs layers, or in the bottom or top one-third of the wells. "Bottom" and "top" are defined as regions of the GaAs wells grown immediately after the Al<sub>x</sub>Ga<sub>1-x</sub>As barrier and immediately before the Al<sub>x</sub>Ga<sub>1-x</sub>As barrier, respectively. All samples had barrier widths of 125 Å. Relevant sample characteristics are shown in Table I. The samples were situated on a copper mounting block in a variable temperature optical cryostat, and the photoluminescence spectra were excited with the 6328-Å line of a helium-neon laser, the 4880-Å line of an argon-ion laser, and the 3250-Å line of a helium-cadmium laser. The emitted light was analyzed by a double monochromator equipped with a cooled photomultiplier tube and standard photon-counting electronics. Laser powers smaller than 0.5 mW were used in these experiments, and the exciting laser beam was focused to a spot of diameter  $\approx 400 \mu\text{m}$ .

Under these conditions new impurity-associated features appeared in the photoluminescence spectra. The various features were better resolved at shorter laser

TABLE I. Sample characteristics.

Sample	Well width (Å)	Doping	$E_{\text{BD}}$ (meV)	$E_{\text{x-Si}}$ (meV)
1	375	Bottom $\frac{1}{3}$		1.1
2	210	Center $\frac{1}{3}$	10.3	1.3
3	210	Center $\frac{1}{3}$	10.3	1.3
4	210	Bottom $\frac{1}{3}$	5.6	
5	210	Top $\frac{1}{3}$		
6	140	Center $\frac{1}{3}$	12.1	1.5
7	80	Center $\frac{1}{3}$	13.0	1.9

wavelengths. This effect was attributed to the shorter penetration depth of the shorter-wavelength light which samples fewer quantum wells, resulting in a correspondingly smaller inhomogeneously broadened linewidth due to small fluctuations in well width versus depth.

In Fig. 1(a) the photoluminescence spectrum from sample 2, excited with 0.1 mW of the 4880-Å line of an argon-ion laser is shown. The various features are numbered for convenience in the discussion. Feature (i) at 1525.0 meV is the ground-state heavy-hole exciton (hhX). Feature (iii) at 1523.2 meV is the dominant donor impurity-related feature observed for laser powers above 5 mW; this was previously reported<sup>5,6</sup> and attributed to Si(c)→VB transitions. Features (iv) at 1522.3 and (ii) at 1523.7 meV appear well resolved only at low laser-power levels (below 0.5 mW). Under the previous interpretation, the donor binding energy measured with respect to the lowest conduction-band confinement state, which is given by the equation  $E_{BD} = E_{hhX} + E_{BX} - E_{Si \rightarrow VB}$ , yielded values consistently lower than those obtained from FIR magnetoabsorption experiments on the *same* samples. (Here  $E_{hhX}$ ,  $E_{BX}$ , and  $E_{Si \rightarrow VB}$  are the energies of the heavy-hole exciton, the binding energy of the heavy-hole exciton, and the Si(c)→VB transition energy, respectively.)

We provide a new interpretation for the photoluminescence spectra. Feature (iv) is attributed to transitions between electrons on donors at the centers of the wells and the higher valence-band confinement state [Si(c)→VB]. Features (ii) and (iii) are interpreted as the confined neutral donor-bound exciton (Si-X) and the confined ionized donor bound exciton (Si<sup>+</sup>-X), respectively. In the photoluminescence study of *n*-type GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As quantum wells of Ref. 7, features (ii) and (iii) were not resolved, and the unresolved combination was identified as due to bound excitons; no Si(c)→VB transition was re-

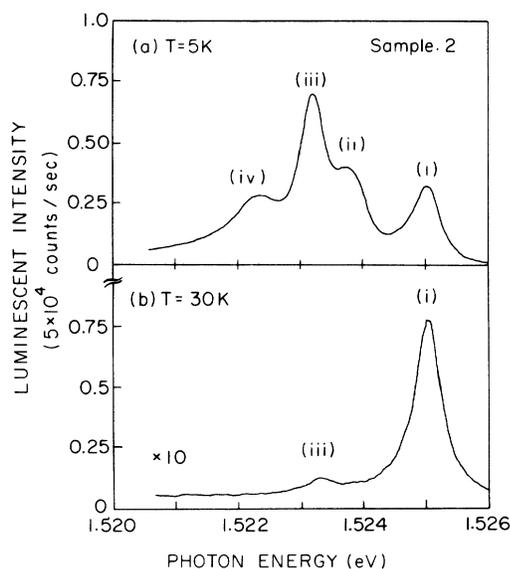


FIG. 1. Photoluminescence spectra from sample 2 excited with the 4880 Å of an argon-ion laser; (a)  $T=5$  K; (b)  $T=30$  K.

ported. A feature identified as this transition was reported in a study of not intentionally doped wells.<sup>8</sup> For sample 2, with the exciton binding energy of Ref. 15, which takes into account the valence-band nonparabolicity,  $E_{BD} = 10.3$  meV for Si donors at the centers of the wells. The binding energies obtained in this study for confined donors in four center-doped samples are plotted, as a function of well width in Fig. 2(a) (solid circles). The triangles represent values for  $E_{BD}$  obtained with the assumption that feature (iii) is the Si(c)→VB transition. The solid line represents the theoretical values of Ref. 1. The agreement between the photoluminescence results with the present interpretation and the theoretical values of Refs. 1 and 2 is quite good.<sup>13</sup>

The binding energy of the exciton on a neutral donor is given by the energy difference between features (i) and (ii) in Fig. 1(a). For sample 2, this energy is equal to 1.3 meV. The experimental values for the exciton binding energy on a confined neutral donor are plotted in Fig. 2(b) as a function of well width. The solid line represents calculated values.<sup>14</sup> The agreement between theoretical and experimental values is in this case also rather good. Thus this assignment provides good agreement with theory for both the confined donor binding energy (and also with the FIR experiments) as well as the binding energy of the confined neutral donor bound exciton.

In order to test the validity of this interpretation further, we have studied the temperature dependence of the photoluminescence spectra. As the temperature of sample 2 was raised, features (ii) and (iv) gradually lost intensity compared with feature (iii) and disappeared in the vicinity of 30 K. At this temperature feature (iii) is still observable, but its intensity with respect to that of the heavy-hole exciton is greatly reduced, as is shown in Fig. 1(b). The temperature dependence of the data can be understood as follows. At  $T=30$  K, almost 50% of the donors are thermally ionized. As a consequence the Si-X feature becomes very weak. On the other hand the binding energy of the Si<sup>+</sup>-X is larger and thus this feature persists up to  $\sim 50$  K. In contrast to Si-X and Si<sup>+</sup>-X which are sharp distinct features, the Si(c)→VB feature is a discrete→continuum transition. As a consequence, its

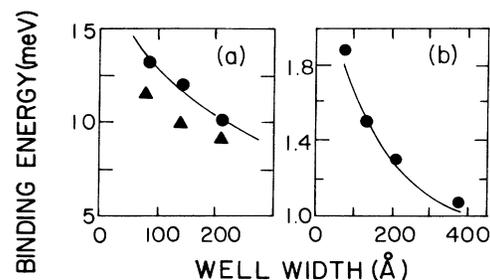


FIG. 2. (a) Binding energies of donors at the centers of the GaAs wells vs well width. Circles: experimental values with feature (iv) in Fig. 1(a) assigned to the Si(c)→VB transition. Triangles: values obtained with feature (iii) in Fig. 1(a) assigned to the Si(c)→VB transition. Curve: Ref. 1. (b) Binding energies of excitons on neutral donors vs well width. Circles: experimental values. Curve: Ref. 13.

linewidth depends strongly on the energy distribution of photogenerated holes. The width of the hole distribution at  $T=30$  K is six times larger than that at  $T=5$  K, assuming Boltzmann statistics. Thus it is no surprise that at  $T=30$  K the Si(c)  $\rightarrow$  VB feature is too broad to be observed. The effects of increased lattice temperature appear to be similar to those caused by laser excitation power levels  $\geq 5$  mW, i.e., only features (i) and (iii) appear clearly in the luminescence spectra. This fact suggests that such laser power levels increase the electron temperature above 30 K and thus simulate the effects of elevated lattice temperature.

We have also studied the photoluminescence spectra from three different multiple-quantum-well samples with identical well and barrier dimensions, but with the donors placed in different positions inside the GaAs wells during growth. The linewidth of the free heavy-hole exciton for all three samples is approximately the same ( $\approx 0.5$  meV), indicating the high quality of the samples, as shown in Fig. 3. Slightly different laser power levels (between 0.1 and 0.5 mW) were used to resolve the bound excitons. The difference in the heavy-hole exciton luminescence intensity relative to the other features in these spectra is a consequence of the fact that they were recorded with different laser power. Their energies are similar in all three samples indicating that the exciton binding energy on Si donors is relatively insensitive to the impurity position inside the well, while the donor binding energy varies from  $\approx 10$  meV to  $\approx 5$  meV between center and edge. The relative intensity of feature (iv), i.e., the Si(c)  $\rightarrow$  VB transition, on the other hand, changes dramatically from sample to sample in Fig. 3. It is quite strong with respect to the bound excitons in the center-doped sample [Fig. 3(a)], significantly weaker in the bottom-edge-doped sample [Fig. 3(b)], and almost nonexistent in the top-edge-doped structure [Fig. 3(c)]. The variation in the intensity of the Si(c)  $\rightarrow$  VB transition can be understood simply in terms of impurity distribution in the wells. In sample 3, doped over the central one third of the wells, most of the Si donors are situated at, or near the well centers; thus the intensity of the Si(c)  $\rightarrow$  VB transition [feature (iv)] is strong with respect to the excitons. In sample 4, doped over the bottom one-third of the well some of the donors have been carried along the growth front in the growth direction towards the well center and contribute to the weak Si(c)  $\rightarrow$  VB transition observed. The energy of the transitions between electrons on donors at the edge of the wells and the highest valence-band confinement state [Si(e)  $\rightarrow$  VB] is larger than the energy of the heavy-hole exciton and thus is strongly absorbed. In sample 4, the Si(e)  $\rightarrow$  VB transition was observed as a weak feature at 1527.0 meV. The corresponding binding energy of these donors is 5.6 meV. (The theoretical value of Ref. 1 for edge donors is 5.2 meV.) Finally, in sample 5, doped over the top one-third of the wells redistribution of the Si donors during growth is away from the well center, into the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  barrier. No Si(c)  $\rightarrow$  VB transitions are thus expected, and as can be seen in Fig. 3(c) this transi-

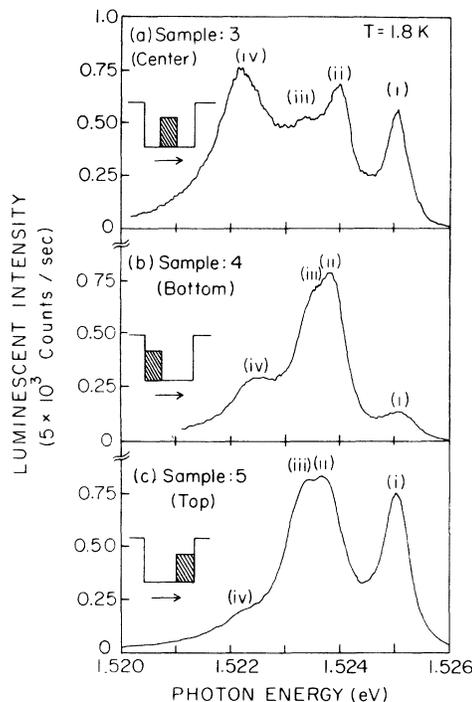


FIG. 3. Photoluminescence spectra recorded at  $T=1.8$  K with the 4880-Å line of an argon-ion laser. (a) Sample 3 (center doped); (b) sample 4 (bottom-edge doped); (c) sample 5 (top-edge doped). The insets represent the nominal doping profile. The arrows indicate the growth direction.

tion is practically absent. These results and their interpretation are in agreement with FIR magnetoabsorption line-profile measurements of the hydrogenic impurity transitions on the same samples.<sup>16</sup>

We have presented a systematic photoluminescence study of  $n$ -type, Si-doped  $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$  multiple quantum wells. The choice of experimental conditions allowed the observation of two new impurity-related features and led to a reinterpretation of the photoluminescence spectra which agrees with theoretical as well as with experimental values of the donor binding energies, and with theoretical values for the binding energies of the excitons on neutral donors, versus well width. This study has removed uncertainties of earlier work, permitted a consistent explanation of the observed features, and demonstrated the power of photoluminescence in the investigation of impurities in semiconductor heterostructures.

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<sup>1</sup>R. L. Greene and K. K. Bajaj, *Phys. Rev. B* **31**, 913 (1985).

<sup>2</sup>C. Mailhot, Y-C. Chang, and T. C. McGill, *Phys. Rev. B* **26**, 4449 (1982).

<sup>3</sup>W. T. Masselink, Y-C. Chang, and H. Morkoc, *Phys. Rev. B* **32**, 5190 (1985).

<sup>4</sup>R. C. Miller, A. C. Gossard, W. T. Tsang, and O. Munteanu, *Solid State Commun.* **43**, 519 (1982).

<sup>5</sup>B. V. Shanabrook and J. Comas, *Surf. Sci.* **142**, 504 (1984).

<sup>6</sup>B. V. Shanabrook, *Surf. Sci.* **170**, 449 (1986).

<sup>7</sup>Y. Nomura, K. Shinozaki, and M. Ishii, *J. Appl. Phys.* **58**, 1864 (1985).

<sup>8</sup>D. C. Reynolds, K. K. Bajaj, C. W. Litton, P. W. Yu, W. T. Masselink, R. Fischer, and H. Morkoc, *Phys. Rev. B* **29**, 7038 (1984).

<sup>9</sup>B. V. Shanabrook, J. Comas, T. A. Perry, and R. Merlin, *Phys.*

*Rev. B* **29**, 7096 (1984).

<sup>10</sup>D. Gammon, R. Merlin, W. T. Masselink, and H. Morkoc, *Phys. Rev. B* **33**, 2919 (1986).

<sup>11</sup>N. C. Jarosik, B. D. McCombe, B. V. Shanabrook, J. Comas, J. Ralston, and G. Wicks, *Phys. Rev. Lett.* **54**, 1283 (1985).

<sup>12</sup>A. A. Reeder, B. D. McCombe, F. A. Chambers, and G. P. Devane, *Superlatt. Microstruct.* **4**, 381 (1988).

<sup>13</sup>The Rydberg constant of Ref. 2 was 5.3 meV which is 9% lower than that used by the authors of Ref. 1. The latter agrees with the spectroscopic Rydberg constant from donors in bulk GaAs. When the appropriate correction is made in the Rydberg constant of Ref. 2, the two calculations agree.

<sup>14</sup>D. A. Kleinman, *Phys. Rev. B* **28**, 871 (1983).

<sup>15</sup>G. D. Sanders and Y-C. Chang, *Phys. Rev. B* **32**, 5517 (1985).

<sup>16</sup>J. M. Mercy, B. D. McCombe, W. Beard, J. Ralston, and G. Wicks, *Surf. Sci.* **196**, 334 (1988).