JOURNAL OF MATERIALS SCIENCE 32 (1997) 4377–4382

The near-infrared photoluminescence of GaAs epilayers grown on Si

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In heteroepitaxial GaAs grown on Si (GaAs/Si) there exist deep levels caused by various charged states of defects because of large lattice misfit and thermal expansion mismatch between GaAs and Si. The temperature- and excitation intensity-dependent near-infrared photoluminescence spectra related to the deep levels present in GaAs/Si grown by metal–organic chemical vapour deposition with different ratios of [As]/[Ga] were studied. In terms of configuration coordinate model, the Franck–Condon shifts of near-infrared emission in GaAs/Si were obtained by measuring the variation in full width at half-maximum with temperature. The band-gap shifts with temperature and with mismatch strain in GaAs/Si were considered. Taking Franck–Condon and band-gap shifts into account, the energy relations for the transitions from donor to acceptor, from conduction band to acceptor and from donor to valence band were revised. According to these transition-energy relations and the emission characteristics of GaAs/Si epilayers, three emissions were interpreted as the recombination luminescence of donor–acceptor pairs and two emissions were caused by As interstitial–Ga vacancy complex centres.

1. Introduction

Much attention has been paid to the heteroepitaxial growth of GaAs layers on Si (GaAs/Si), because the latter is an excellent semiconductor material for integrated circuits. Recently the electric and optical properties of GaAs/Si were studied [1, 2]. The major problems for GaAs/Si are large lattice misfit and thermal expansion mismatch between GaAs and Si. These result in the deformation of heteroepilayers, which leads to the creation of the various charged states of defects in GaAs/Si [3, 4]. Thus, there exist deep levels originating from these various charged states of defects. Mismatch between GaAs and Si causes a tensile strain in investigated GaAs/Si epilayers [5, 6], which leads to the band-gap constriction. Thus, the emission wavelength in heteroepitaxial GaAs grown on Si substrates is longer than that in bulk or in epitaxial GaAs grown on GaAs substrates.

In this work we studied the temperature- and excitation intensity-dependent near-infrared photoluminescence (NIPL) related to these deep levels present in GaAs/Si grown by metal–organic chemical vapour deposition (MOCVD) with different ratios of [As]/[Ga]. In terms of an Arrhenius plot and configuration coordinate model, the thermal activation energies and Franck–Condon shifts for $1.13-$, $1.04-$, and $0.94-$ eV emissions were obtained by measuring the variations in PL intensity and full width at half-maximum with temperature, respectively. The band-gap shifts with temperature and with mismatch strain in GaAs/Si epilayers were considered. Taking Franck–Condon and band-gap shifts into account, the energy relations for the transitions from donor to acceptor, from conduction band to acceptor and from donor to valence band were reformulated. According to these transition-energy relations and the emission characteristics of GaAs/Si epilayers, three emissions were interpreted as the recombination luminescence of donor–acceptor pairs (DAPs) and two emissions were caused by As interstitial–Ga vacancy complex centres.

2. Experimental details

The $1.2 \sim 1.5$ μm-thick heteroepitaxial GaAs used for the present experiments were grown by MOCVD on *n*-type (1 0 0) Si substrates misorientated 4° towards a $\langle 1\,1\,0 \rangle$ direction using the standard two-step method [7]. The Si substrates were chemically treated in NH_4OH, H_2O_2, H_2O then HCl, H_2O_2, H_2O and etched in HF for 1 min. In a H_2/AsH_3 ambience, they were heated initially at 950 °C for 10 min, and the temperature was lowered to 450 °C for GaAs buffer growth with thickness of 25 nm. Trimethylgallium and arsine in hydrogen were used as precursor chemicals. Then the temperature was raised to 700 °C, and the

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top GaAs epilayers were grown with a ratio of [As]/[Ga] = 20 to 50 and with growth rate of 100 nm min^{-1}. The samples were not intentionally doped. The carrier concentration at room temperature is 2×10^{17} cm^{-3}.

The temperature- and excitation intensity-dependent NIPL spectra of GaAs/Si samples with the ratio of [As]/[Ga] = 20 to 50 were obtained with an ordinary grating monochromator and were detected by a liquid helium-cooled Ge detector using conventional look-in techniques. Luminescence was excited with the 632.8 nm line of a He–Ne laser. The measured temperature was 14–300 K and excitation intensity 10^{-2}–10^{2} W cm^{-2}.

3. Results and discussion

Fig. 1a, b and c show the NIPL spectra of the GaAs/Si samples grown by MOCVD with [As]/[Ga] = 50, 30 and 20, respectively, at 77 K and excitation intensity of 1.0 W cm^{-2}. According to Fig. 1a, b, c and their temperature-dependent spectra (see Fig. 2), the NIPL spectra should contain five peaks (1.13, 1.04, 0.95, 0.84 and 0.79 eV). Indeed, Fig. 1a and b can be fitted adequately by a sum of five Gauss-type curves, where the peaks are labelled as A, B, C, D and E, and their peak energies are 1.13 (A), 1.04 (B), 0.94 (C), 0.84 (D) and 0.78 eV (E), respectively. Fig. 1c can be fitted by a sum of two Gauss-type curves, including a main peak 0.95 eV and a shoulder 0.84 eV, respectively. The discrepancy at the right tail, as shown in Fig. 1c, arises from the presence of an additional weak peak with energy 1.13 eV. Fig. 1a, b and c show that with increase of the ratio of [As]/[Ga] from 20 to 50, which decreases the concentrations of As vacancies (V_{As}) and creates As-interstitial (As_i) defects, the intensities of peaks A, B and C rapidly decrease and intensities of peaks D and E increase.

Fig. 2 shows the NIPL spectra of GaAs/Si sample grown with [As]/[Ga] = 30 in temperature range 14–300 K at excitation intensity 1.0 W cm^{-2}. As shown in Fig. 2, A emission is the dominant component at temperatures below 150 K. As temperature increases, the intensity of peak A rapidly decreases while that of peak B gradually increases. At temperatures higher than 200 K, peak A disappears, that is, A emission is quenched thermally, and B emission becomes dominant.

Fig. 3 shows the intensity variations with temperature for A, B and C emissions, respectively. In terms of these experimental data, the thermal activation energies $\Delta E = 170$, 48 and 100 meV for A, B and C emissions, respectively, were obtained by using an Arrhenius plot

$$I = C \exp(\Delta E/kT) \qquad (1)$$

where I is photoluminescence (PL) intensity and C is a constant.

Fig. 4 shows the variations of the full width at half maximum (FWHM) of A, B and C emissions with the square root of temperature. According to the configuration coordinate model [8], the theoretical temperature dependence of FWHM $W(T)$ is

$$W(T) = (8 \ln 2)^{\frac{1}{2}} S^{\frac{1}{2}} \hbar\omega[\coth(\hbar\omega/2kT)]^{\frac{1}{2}} \qquad (2)$$

where $\hbar\omega$ is a phonon energy and S the Huang–Rhys factor. The solid lines in Fig. 4 are the fit of Equation 2 to the experimental data with $(\hbar\omega)_A = 20$ meV, $(S)_A = 4.5$, $(\hbar\omega)_B = 36$ meV, $(S)_B = 2.4$, $(\hbar\omega)_C = 36$ meV and $(S)_C = 3.2$ for A, B and C emissions, respectively. The Huang–Rhys factor $S > 1$ indicates that there exists a stronger electron-lattice coupling, which leads to A, B and C emissions having broad Gaussian lineshapes without any fine structure [9]. Thus, the Franck–Condon (FC) shifts Δ_{FC} for A,

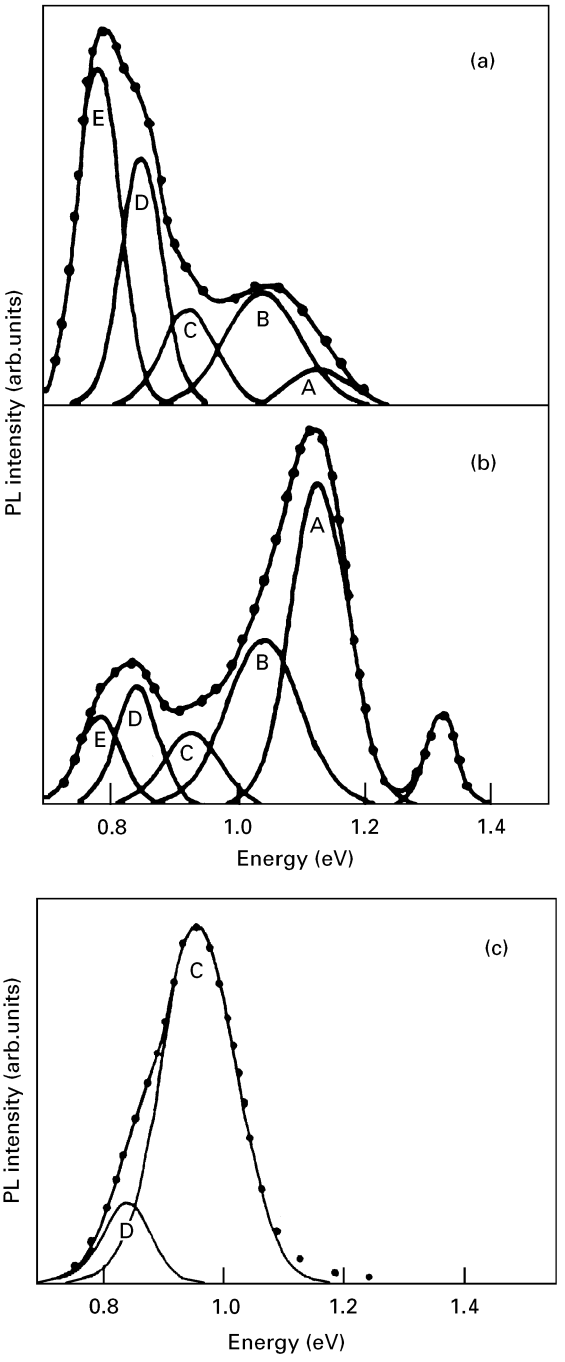

Figure 1 NIPL spectra of GaAs/Si epilayers grown with [As]/[Ga] = 50 (a), 30 (b) and 20 (c), respectively, at 77 K and excitation intensity of 1.0 W cm^{-2}. (● ● ●) : experimental points (—●—●—●—●—●—) : sum of Gauss-type curves.

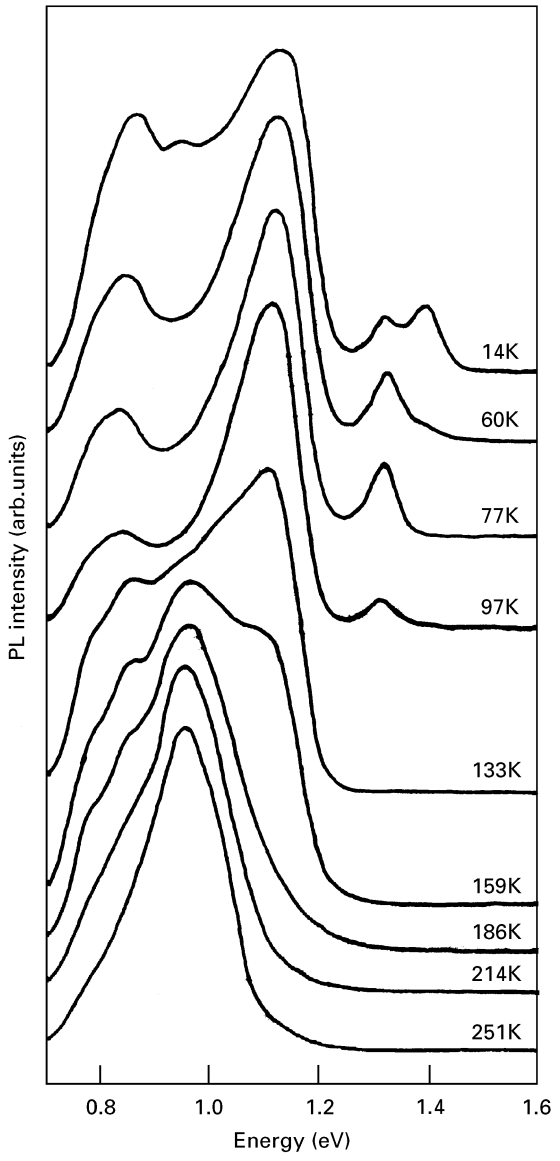

Figure 2 Temperature-dependent NIPL spectra of GaAs/Si sample grown with [As]/[Ga] = 30 in the temperature range 14–300 K at excitation intensity 1.0 W cm^{-2}.

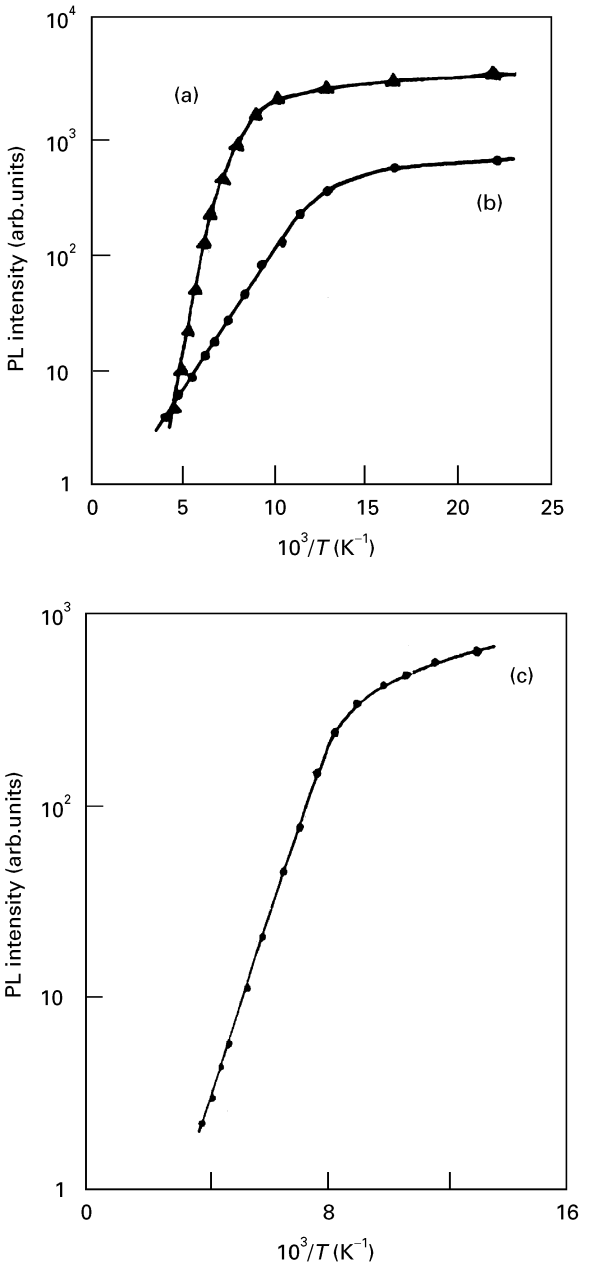

Figure 3 Temperature dependence of PL intensities for A (a), B (b) and C (c) emissions.

B and C emissions are given by

$$(\Delta_{FC})_A = (S)_A\,(\hbar\omega)_A = 90\ \text{meV}$$
$$(\Delta_{FC})_B = (S)_B\,(\hbar\omega)_B = 86\ \text{meV}$$
$$(\Delta_{FC})_C = (S)_C\,(\hbar\omega)_C = 110\ \text{meV} \quad (3)$$

Taking FC and band-gap shifts into account, the energy relations of DAP recombination luminescence should be revised as

$$h\nu = (E_g)_{max} - \Delta E_g - (E_d + E_a - e^2/\varepsilon r) - \Delta_{FC} \quad (4)$$

For the transition from donor to valence band or from conduction band to acceptor, Equation 4 can be simplified as

$$h\nu = (E_g)_{max} - \Delta E_g - E_d - \Delta_{FC} \quad (5)$$

or

$$h\nu = (E_g)_{max} - \Delta E_g - E_a - \Delta_{FC} + E_k \quad (6)$$

respectively, where $h\nu$ is an emission peak energy, E_d and E_a are the binding energies of isolated donor and acceptor, respectively, $-e^2/\varepsilon r$ is the Coulomb interaction energy of DAP, E_k the kinetic energy of the carrier at conduction band, $(E_g)_{max}$ the maximum of band-gap and ΔE_g the band-gap shifts with temperature (ΔE_{g1}) and with mismatch strain (ΔE_{g2}). Investigated GaAs/Si samples exhibit tensile stress ($\sim$100 MPa) and it shifts the band-gap of GaAs/Si to lower energies ($\Delta E_{g2} \sim 10$ meV). Kim *et al.* [10] established a relation of the band-gap shift with temperature in GaAs. O'Reilly [11] and Joshkin *et al.* [6] determined the strain-induced band-gap shift for GaAs/Si samples. Thus, for the GaAs/Si with mismatch strain

$$\Delta E_g = \Delta E_{g1} + \Delta E_{g2} = \alpha T^2/(\beta + T) + (a + 2b)\Delta V/V$$
$$(E_g)_{max} = 1.517\ \text{eV} \quad (7)$$

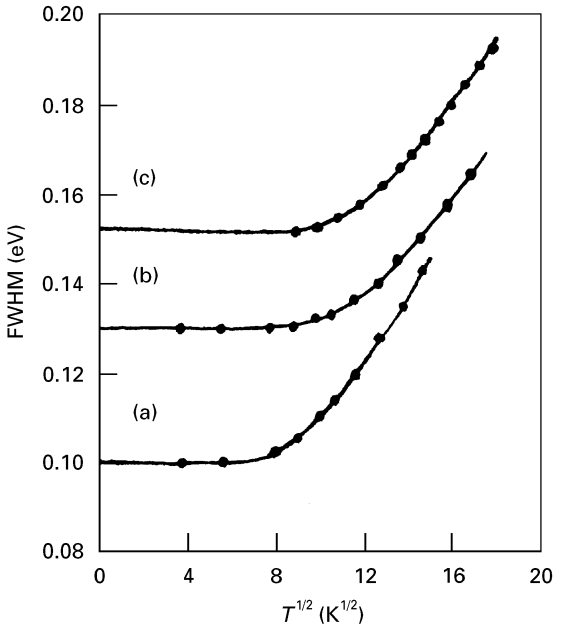

Figure 4 Variation of FWHM versus $T^{\frac{1}{2}}$ for A (a), B (b) and C (c) emissions.

where T is the temperature of GaAs/Si samples in K, $\alpha = 5.6 \times 10^{-4}$ eV K^{-1}, $\beta = 226$ K, a is the hydrostatic deformation ($a = 8$ eV for GaAs), b the axial tensile deformation potential ($b = 1.7$ eV for GaAs/Si) and $\Delta V/V$ hydrostatic strain (%) ($\Delta V/V \approx 0.1\%$ for investigated GaAs/Si samples). According to Colbow's model [12], we take $E_k = kT$.

The variation of peak energies for A and B emissions with excitation intensity at a temperature of 77 K were obtained, as shown in Fig. 5. The relationship between excitation intensity I_{ex} and peak energy $h\nu$ for the recombination luminescence of DAP can be described by [13]

$$I_{ex} = D[(h\nu - h\nu_\infty)^3/(h\nu_B + h\nu_\infty - 2h\nu)] \times \exp[-2(h\nu_B - h\nu_\infty)/(h\nu - h\nu_\infty)] \quad (8)$$

where $h\nu_\infty$ is the limiting photon energy of the recombination luminescence of infinitely distant DAP, $h\nu_B = E_B + h\nu_\infty$, $E_B = e^2/\varepsilon r_B$, r_B is the shallow impurity Bohr radius and D a proportional constant. Taking FC and band-gap shifts into account, the expression for $h\nu_\infty$ should be revised as

$$h\nu_\infty = (E_g)_{max} - \Delta E_g - (E_d + E_a) - \Delta_{FC} \quad (9)$$

Equation 8 has been fitted well to the experimental values for A and B emissions, as shown in Fig. 5 a and b, and we obtain

$$(h\nu_\infty)_A = 1.117 \text{ eV} \qquad (h\nu_\infty)_B = 1.019 \text{ eV}$$
$$(h\nu_B)_A = 1.169 \text{ eV} \qquad (h\nu_B)_B = 1.092 \text{ eV} \quad (10)$$

Using Equations 3, 7, 9 and 10, and taking $T = 77$ K, we have

$$(E_d + E_a)_A = 0.288 \text{ eV} \qquad (E_d + E_a)_B = 0.390 \text{ eV} \quad (11)$$

for A and B emissions, respectively.

Dong *et al.* [14] observed two electron-traps with energies 290 and 340 meV above the top of valence band, respectively, in heteroepitaxial GaAs/Si using a novel charge deep-level transient spectroscopy method. Xu *et al.* [15] performed the self-consistent tight-binding calculation of the energies and electronic structures on the neutral and charged states of As vacancy V_{As}^n ($n = 1+, 0, 1-, 2-, 3-, 4-$) and Ga vacancy V_{Ga}^n ($n = 1+, 0, 1-, 2-, 3-$) in GaAs with Lanczos–Haydock recursion method. The deep-level energies of V_{Ga}^{1-}, V_{Ga}^{2-}, V_{As}^{4-} and V_{As}^{3-} are equal to 0.283, 0.436, 1.505 and 1.468 eV, respectively, above the top of the valence band in GaAs with band-gap 1.51 eV. According to these experimental and theoretical data, we could take

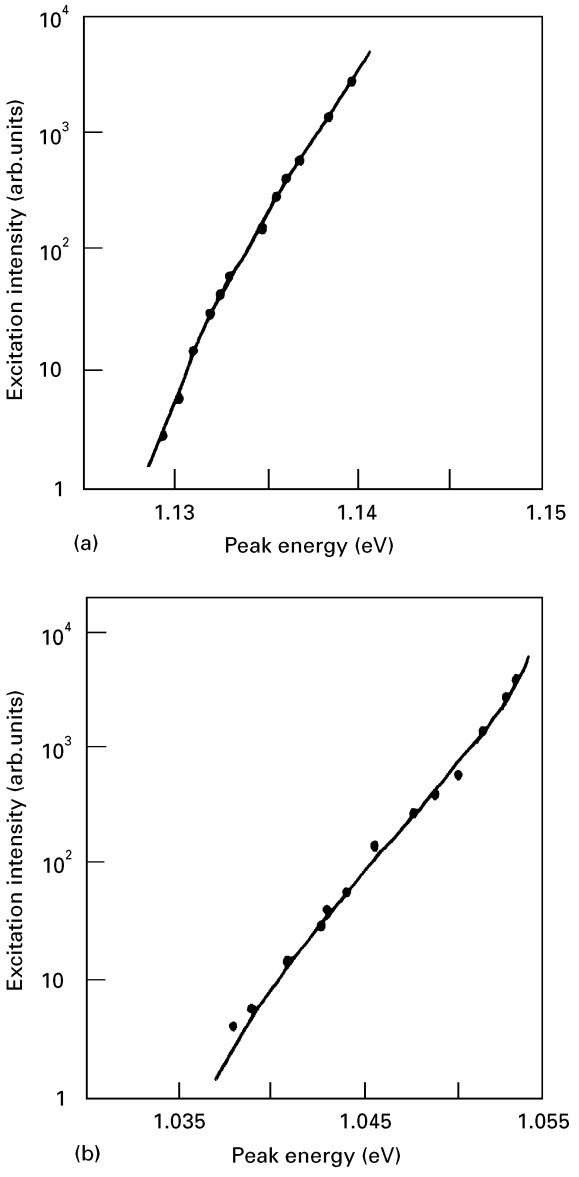

Figure 5 Variations of peak energies for A (a) and B (b) emissions with excitation intensity at temperature 77 K.

$$(E_a)_A = E_{VB} + 0.283 \text{ eV} \qquad (E_a)_B = E_{VB} + 0.340 \text{ eV}$$
$$(E_d)_A = E_{VB} + 1.505 \text{ eV} = E_{CB} - 0.005 \text{ eV}$$
$$(E_d)_B = E_{VB} + 1.468 \text{ eV} = E_{CB} - 0.042 \text{ eV} \quad (12)$$

where E_{VB} and E_{CB} are the top of valence band and the bottom of conduction band in GaAs, $(E_d)_A$ and $(E_a)_A$ the energies of donor V_{As}^{4-} and of acceptor V_{Ga}^{1-} for

A emission, $(E_d)_B$ and $(E_a)_B$ the energies of donor V_{As}^{3-} and of acceptor $V_{Ga}^{1-}V_{Ga}^{2-}$ complex for B emission, respectively, which are in good agreement with our experimental results shown in Equation 11. Therefore, A and B emissions are interpreted as the recombination luminescence of DAPs, composed of V_{As}^{4-} and V_{Ga}^{1-} for 1.13 −, and of V_{As}^{3-} and $V_{Ga}^{1-}V_{Ga}^{2-}$ complex for 1.04-eV emissions, respectively.

Thus it can be seen that A emission is caused by a shallow donor. The recombination luminescence of a shallow donor–acceptor pair can be approximately described by Equation 6 because of the thermal ionization of shallow donor. Fig. 6 shows the variation of the peak energy of A emission with temperature in GaAs/Si samples. Equation 6 has been fitted to the experimental values in Fig. 6 and the acceptor energy level $(E_a)_A = E_{VB} + 0.284$ eV for A emission is obtained. This value is in good agreement with the result shown in Equation 12.

Our experimental results demonstrate that with the increase of [As]/[Ga] ratio, which reduces the concentration of V_{As} in GaAs, the NIPL intensities of A, B and C emissions rapidly decrease, as shown in Fig. 1. It means that C emission also possibly depends on V_{As}. Gutkin *et al.* [16] proposed that the 0.95-eV emission in GaAs doped with Te or Sn was caused by $V_{As}V_{Ga}Te_{As}$ or $V_{As}V_{Ga}Sn_{Ga}$ complexes. Wong *et al.* [17] suggested that V_{Ga} complex in GaAs seems to be the defect responsible for a broad PL band at 0.95 eV. Using techniques based on positron annihilation, Ambigapathy *et al.* [18] have measured the ionization energies of the charged states of V_{As} in *n*-type Si-doped GaAs; one of those is located at 140 meV below the bottom of conduction band, which is in good agreement with the calculation value of the deep level for V_{As}^{1-} given by Xu [15]. So, we take

$$(E_d)_C = E_{VB} + 1.365\text{ eV} = E_{CB} - 0.145\text{ eV}$$
$$(E_a)_C = E_{VB} + 0.283\text{ eV} \quad (13)$$

where $(E_d)_C$ and $(E_a)_C$ are the energies of donor V_{As}^{1-} and of acceptor V_{Ga}^{1-} for C emission. According to Equations 3, 4, 7 and 13, the transition energy of DAP, composed of V_{As}^{1-} donor and V_{Ga}^{1-} acceptor, is equal to 0.95 eV, which is in good agreement with our experiments, as shown in Fig. 1.

Fig. 1 demonstrates that with the increase of [As]/[Ga] ratio, which leads to a decrease in As-vacancy concentration and to an increase in As-interstitial defects in GaAs/Si, the PL intensities of A, B and C emissions rapidly decrease and D, E emissions become stronger and stronger. Yu *et al.* [19, 20] indicated that with the increase of [As]/[Ga] ratio in the growth of GaAs epilayers on GaAs substrates by molecular beam epitaxy, the concentration of As-interstitial related centre increases. They attributed 0.8 − eV emission with $\Delta_{FC} = 0.34$ eV to the localized EL6 complex centre, composed of As interstitial and Ga vacancy, $As_i - V_{Ga}$, located at 0.36 eV below the bottom of conduction band. According to Equation 5, $h\nu = 0.78 \sim 0.79$ eV is obtained, by taking $(E_d)_E = E_{CB} - 0.36$ eV, $(\Delta_{FC})_E = 0.34$ eV, $(E_g)_{max} = 1.517$ eV and $\Delta E_g = 0.022$ eV. Thus, E emission in Fig. 1a and b corresponds to the transition from EL6 complex centre to the valence band in GaAs/Si epilayers. The wavelength of E emission in GaAs/Si is longer than that in epitaxial GaAs grown on GaAs substrates because of the tensile strain in heteroepitaxial GaAs/Si.

As to D emission in GaAs/Si, the variation of its PL intensity with temperature between 77 and 300 K was measured. The dependence of its PL intensity versus temperature cannot be fitted with an Arrhenius plot. It appears that the data could be fitted to a relation valid for amorphous semiconductors or localized states [21, 22]

$$I = I_0/[1 + A\exp(T/T_0)] \quad (14)$$

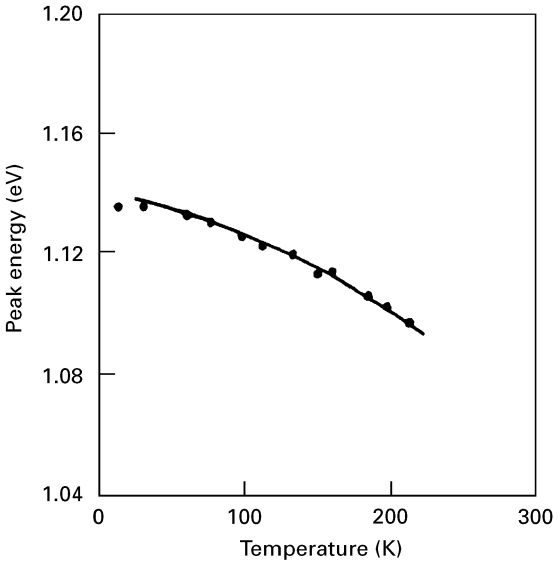

Figure 6 Peak-energy variation for A emission with temperature.

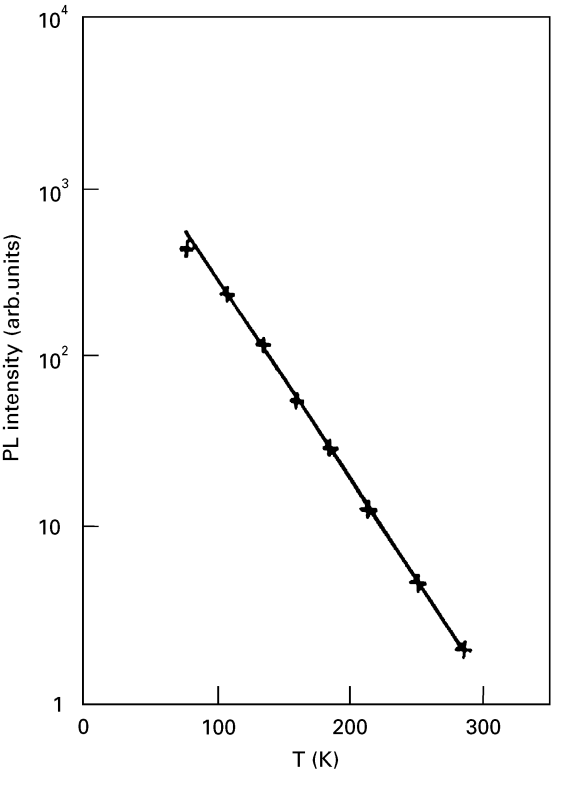

Figure 7 Dependence of PL intensity versus temperature for D emission. $T_0 = 37.4$ K.

which approaches

$$I = I'_0 \exp(-T/T_0) \quad (15)$$

when measured temperature $T > 77$ K, as shown in Fig. 7, where I'_0 scales PL intensity at low-temperature limit and T_0 is a characteristic temperature corresponding to the energy depth of localized states. This means that related defects cause the localized states with a characteristic temperature $T_0 = 37.4$ K, which reflects the degree of disorder in GaAs/Si epilayers. According to D-emission characteristics and Equation 4, where $(E_d)_D$ and $(E_a)_D$ are binding energies of As_i–V_{Ga} complex centre and V_{Ga}^{1-}, and which are equal to 0.36 eV below the bottom of conduction band [19, 20] and 0.283 eV above the top of valence band [15], respectively ($(E_g)_{max} = 1.517$ eV and $\Delta E_g = 0.022$ eV ($T = 77$ K)), D emission with no FC shift might originate from the transition between localized EL6 complex centre and V_{Ga}^{1-}.

In addition, there is a weak emission peak at 1.32 eV in Fig. 1b. Yu *et al.* [23] have attributed this emission to the recombination luminescence of DAP, composed of an effective mass donor and gallium antisite double acceptor.

4. Conclusions

We indicated that there exist deep levels originating from various charged states of defects in heteroepitaxial GaAs grown on Si. These deep-centre PL strongly depend on their growth conditions, and especially, on [As]/[Ga] ratio. Taking FC and band-gap shifts with temperature and with mismatch strain into account, we revised the energy relations of transitions from donor to acceptor, from conduction band to acceptor and from donor to valence band. In terms of these new transition-energy relations and emission characteristics, we explained 1.13 −, 1.04 − and 0.94 − eV emissions as the recombination luminescence of DAPs, composed of V_{As}^{4-} donor and V_{Ga}^{1-} acceptor, of V_{As}^{3-} donor and $V_{Ga}^{1-}V_{Ga}^{2-}$ complex acceptor and of V_{As}^{1-} donor and V_{Ga}^{1-} acceptor, respectively. Emissions of 0.84 − and 0.78 − eV were caused by As interstitial–Ga vacancy complex centres.

Acknowledgements

This work was supported by the Laboratory of Excited State Processes, Changchun Institute of Physics, Chinese Academy of Sciences.

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Received 5 March 1996
and accepted 18 February 1997