Studies on deep levels in GaAs epilayers grown on Si by metal–organic chemical vapour deposition, Part II: 1.13 eV photoluminescence emission

J. L. ZHAO, Y. GAO, X. Y. LIU, X. A. SU, S. H. HUANG, J. Q. YU
Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130 021, People's Republic of China

J. C. LIANG*
Department of Basic Sciences, Civil Aviation Institute of China, Tianjin 300 300, People's Republic of China

H. K. GAO
Xi'an Institute of Optics and Mechanics, Chinese Academy of Sciences, Xi'an 710 068, People's Republic of China

In recent years, the optical properties of hetero-epitaxial GaAs layers grown on Si substrates have been studied extensively because of their potential applications for integrated circuits and optoelectronics [1–4]. It has been reported that the larger misfit of lattice constants (4.1%) and discrepancies of thermal expansion coefficients of GaAs and Si cause stresses on the interface, leading to the creation of various defects. Deep levels originating from the stoichiometric defects, interfacial defects and surface states can strongly degrade the crystalline quality and deteriorate the optical and electrical properties of heterostructures. Recently, we reported studies on deep levels in epitaxial GaAs grown on Si by metal–organic chemical vapour deposition (MOCVD) and identified that the 1.04 eV emission could be explained well by the recombination luminescence of a negatively charged arsenic vacancy donor and a next-nearest neighbour gallium vacancy acceptor [5].

In this work, we did photoluminescence (PL) investigations of the 1.13 eV emission band at 77 K present in GaAs epilayers grown on Si with respect to changes of temperature and excitation intensity. We identified that the 1.13 eV emission originates from the recombination of a donor–acceptor pair (DAP), composed of an Si shallow donor on Ga site and a next-nearest neighbour Ga vacancy acceptor, and used a configuration coodinate model to locate the donor and acceptor level.

GaAs epitaxial layers used in the experiment were grown on 4° off toward [110] (100) n-type Si substrates using the two-step method [2] by MOCVD. The Si substrates were chemically treated in NH_4OH, H_2O_2, H_2O and HCl, H_2O_2, H_2O, and etched in HF for 1 min. In an H_2/AsH_3 ambient, 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. Trimethyl-gallium (TMG) and arsine in hydrogen were used as source chemicals. Then the temperature was raised

to 700 °C, and the top GaAs epilayers were grown with an As:Ga ratio of 30 and growth rate of 100 nm min^{-1}. The samples were not intentionally doped.

The PL spectra of GaAs epilayers were measured with an ordinary gating monochromotor and detected by a liquid nitrogen-cooled Ge detector using a conventional lock-in technique. Luminescence was excited with the 632.8 nm line of an He–Ne laser. The excitation intensity was varied between 10^{-2} and 10^2 Wb cm^{-2} using neutral density filters.

Fig. 1 shows the PL spectrum of the GaAs epilayer grown on Si with thickness of 1.5 μm at 77 K and excitation intensity of 1.0 Wb cm^{-2}. As can be seen from Fig. 1, the spectrum is very complex and can be fitted adequately by a sum of five Gauss-type curves, where the peaks are labelled A, B, C, D and E. Their peak energies are, respectively, 1.13 eV, 1.04 eV, 0.93 eV, 0.84 eV and 0.78 eV. In addition, a weak emission peak observed at 1.32 eV was attributed to a gallium antisite double acceptor–effective mass donor pair complex [6].

The temperature-dependent PL spectra of the samples were carried out in the temperature range
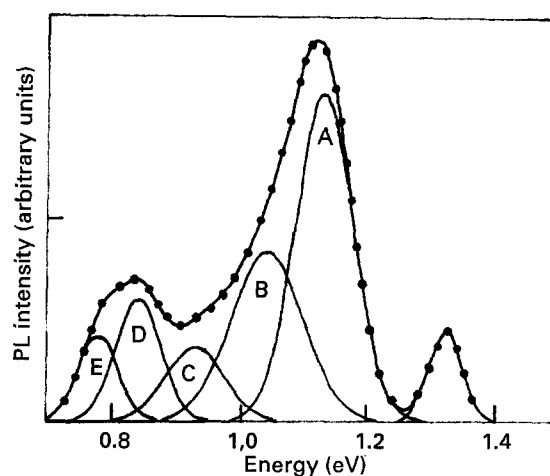

Figure 1 Photoluminescence spectrum of GaAs epilayer grown on Si at 77 K and excitation intensity 1.0 Wb cm^{-2}. (●) Experimental points.

---

*To whom all correspondence should be addressed.

14-300 K [5]. The 1.13 eV PL emission is the dominant recombination process at temperatures below 150 K. As the temperature is increased, the intensity of this peak decreases rapidly while that of peak B increases gradually. At temperatures higher than ~200 K, peak A disappears very rapidly, that is, the 1.13 eV PL emission is quenched thermally, and peak B becomes dominant.

The intensity variations with temperatures are shown in Fig. 2. In the range 14-70 K, the intensity changes very little, according to the following equation:

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

where I is the PL intensity and C a constant. An activation energy of 0.17 eV was obtained from the exponential decrease of intensity with $1/T$ in the temperature range 130-200 K, and agreed well with that of the 1.22 eV PL band in GaAs bulk materials [7].

Fig. 3 shows the variation of the full width at half maximum (FWHM) of 1.13 eV emission in the GaAs epilayer with temperature. Using the configurational coordinate model in the Gaussian approximation [7], the temperature dependence of $W(T)$ can be expressed by

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

where S is the Huang and Rhys constant, and $\hbar\omega$ is the vibrational phonon energy. The Frank–Condon shift Δ_{FC} is $S\hbar\omega$ with assumption of a linear electron–lattice interaction. The values of $S = 4.5$, $\hbar\omega = 20$ meV and $\Delta_{FC} = 90$ meV were obtained for the 1.13 eV emission. The Huang–Rhys factor $S > 1$ indicates that there exists a strong electron–lattice coupling in the epilayer, resulting in the 1.13 eV emission having a Gaussian line shape without any fine structure.

The temperature dependence of the peak energy of the 1.13 eV emission is shown in Fig. 4. The peak moves to lower energy with the increase of temperature. The solid curve is due to the $(e-A°)$ recombin-
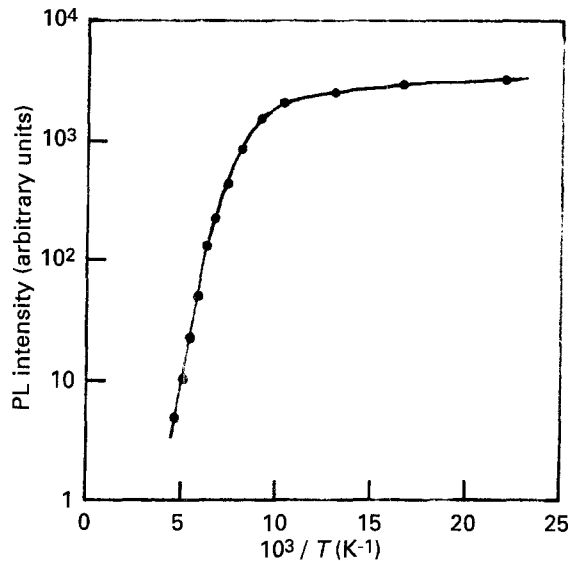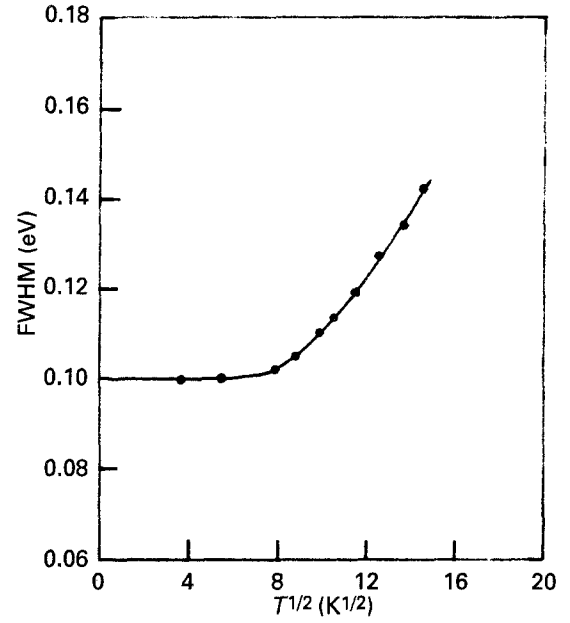
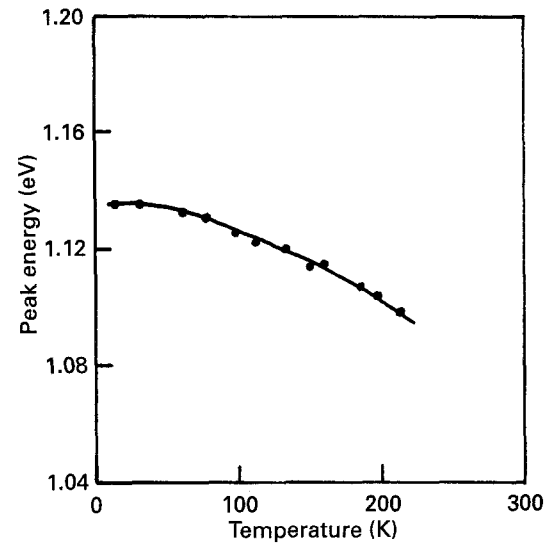Figure 3 Variations in FWHM of the 1.13 eV emission with $T^{1/2}$.

Figure 4 Temperature dependence of peak energy for the 1.13 eV emission.

ation model [8]. The peak position of the (eA) transition was described by:

$$hv = E_g(T) - E_a + E_k \qquad (3)$$

where E_k is the kinetic energy of carriers and E_a is the acceptor binding energy. However, Liang et al. [9] have indicated that for DAP recombination luminescence bands, the Frank–Condon shift energy should be taken into account and the peak position of the (eA) transition can be revised as:

$$hv = E_g(T) - E_a - \Delta_{FC} + E_k \qquad (4)$$

The temperaure dependence of $E_g(T)$ was given [10] as:

$$E_g(T) = E_g(0) - \alpha T^2/(\beta + T) \qquad (5)$$

where $E_g(0) = 1.517$ eV, $\alpha = 5.6 \times 10^{-4}$ eV K^{-1} and $\beta = 226$ K. It was found that the experimental peak energy agrees well with Equation 4 with $E_k = kT$. The acceptor binding energy was determined to be ~295 meV and possibly originated from

Figure 2 Temperature dependence of photoluminescence intensity for the 1.13 eV emission.

V_{Ga} at about 0.3 eV above the valence band [7, 11–13].

In the nominal DAP transition energies hv in the ordered structure phase has been revised [9] as:

$$hv = E_g(T) - (E_d + E_a) - \Delta_{FC} + e^2/\varepsilon r \quad (6)$$

where E_d and E_a are donor and acceptor binding energies, respectively, ε is the static dielectric constant and r is the DAP separation. Increasing excitation intensity (I_{ex}) favours close pairs, and the transition energy moves to higher energy, according to Equation 6. The relationship between I_{ex} and hv for the DAP transition can be described [14] by:

$$I_{ex} = D\frac{(hv - hv_\infty)^3}{(hv_B + hv_\infty - 2hv)}\exp\left(-\frac{2(hv_B - hv_\infty)}{hv - hv_\infty}\right) \quad (7)$$

where

$$hv_\infty = E_g - (E_d + E_a) - \Delta_{FC} \quad (8)$$

which corresponds to the limiting photon energy of infinitely distant DAP, $hv_B = E_B - hv_\infty$, $E_B = e^2/\varepsilon r_B$, r_B is the shallow impurity Bohr radius and D is a proportionality constant.

Excitation intensity dependence of the 1.13 eV PL emission was made in the range of $I_{ex} = 10^{-2}$–10^2 Wb cm^{-2} at 77 K. The PL intensity was found to increase linearly with the excitation intensity in this range. The excitation intensity dependence of the peak energy of the 1.13 eV PL emission is shown in Fig. 5. It indicates that the emission is mainly due to the DAP transitions, since the peak position moves to higher energy with increasing excitation intensity. The experimental data were well fitted by Equation 7 and the values of hv_∞, hv_B and E_B were determined to be 1.117, 1.169 and 0.52 eV, respectively. According to Equation 8, we obtain $E_d + E_a = 300$ meV. Furthermore, the donor binding energy E_d was also obtained to be about 5 meV. It is well known that an Si on Ga site is a shallow donor, locating at $\sim$5 meV below the bottom of the conduction band [11, 15]. Thus the donor is an Si on Ga site, resulting from the
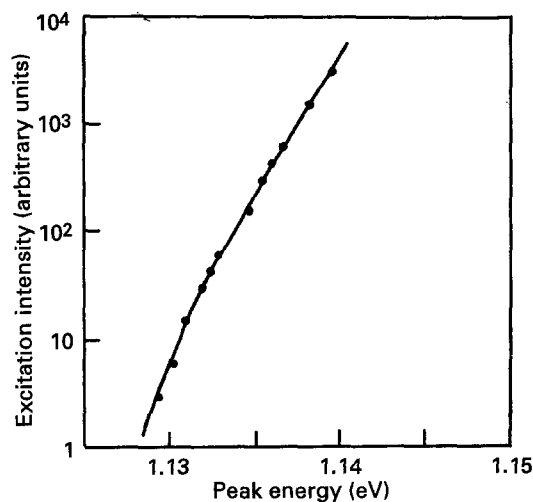

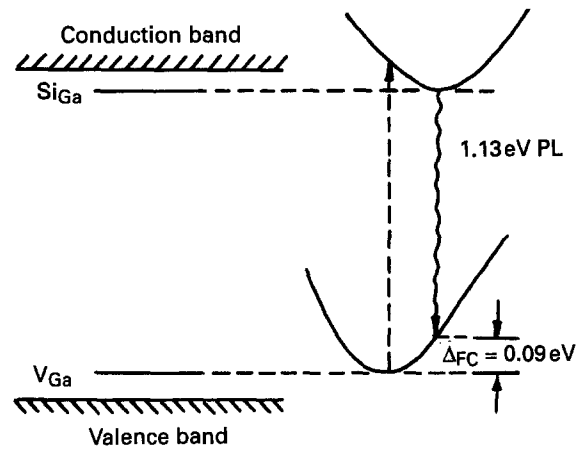*Figure 5* Relationship between excitation intensity and peak energy for the 1.13 eV emission.

Figure 6 Schematic diagram of energy levels of DAP luminescence with electron–phonon coupling.

self-diffusion of Si. On the other hand, it was found that the PL characteristics of the 1.13 eV emission are quite similar to those of 1.22 eV emission in GaAs crystals [7]. Therefore, based on donor and acceptor binding energies obtained in the experiment, the 1.13 eV PL emission can be explained well by the recombination of the DAP, composed of a Si shallow donor on Ga site and the next-nearest neighbour Ga vacancy acceptor (Si_{Ga}–V_{Ga}) and shown in Fig. 6. The origins and characteristics of the other deep-level photoluminescence are under investigation.

Acknowledgement

References
1. S. ZEMON, S. K. SHASTRY, P. NORRIS, C. JAGANNATH and G. LAMBERT, *Solid St. Communs* **58** (1986) 457.
2. R. M. LUM, J. K. KLINGERT, B. A. DAVIDSON and M. G. LAMONT, *Appl. Phys. Lett.* **51** (1987) 36.
3. Y. HUANG, P. Y. YU, M. N. CHARASSE, Y. LO and S. WANG, *ibid.* **51** (1987) 192.
4. J. E. FOUQUET, R. R. SAXENA and G. A. PATTERSON, *IEEE J. Quantum Electron.* **25** (1989) 1025.
5. J. C. LIANG, Y. GAO, J. L. ZHAO, X. Y. LIU, X. A. SU and H. K. GAO, *Semicond. Sci. Technol.* submitted.
6. P. W. YU, D. W. FISCHER and J. R. SIZELOVE, *Semicond. Sci. Technol.* **7** (1992) 556.
7. E. W. WILLIAMS, *Phys. Rev.* **168** (1968) 922.
8. K. COLBOW, *ibid.* **141** (1966) 742.
9. J. C. LIANG, Y. GAO and J. L. ZHAO, *J. Mater. Sci. Lett.* **12** (1993) 355.
10. C. K. KIM, P. LAUTENSCHLAGER and M. CARDONA, *Solid St. Communs* **59** (1986) 797.
11. F. BRIDGES, G. DAVIES, J. ROBERTSON and A. M. STONEHAM, *J. Phys. C* **2** (1990) 2875.
12. I. OHBU, M. TAKAHAMA and K. HIRUMA, *Appl. Phys. Lett.* **61** (1992) 1679.
13. H. XU and U. LINDEFELT, *Phys. Rev. B* **41** (1990) 5979.
14. E. ZACHS and A. HALPERIN, *ibid.* **6** (1972) 3072.
15. S. A. McQUAID, R. C. NEWMAN, M. MISSOUS and S. O'HAGAN, *Appl. Phys. Lett.* **61** (1992) 3008.