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Studies on deep levels in GaAs epilayers grown on Si by metal–organic chemical vapour deposition, Part III: 0.78 and 0.84 eV photoluminescence emissions

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Midgap deep levels have enjoyed a special status in semiconductor technology ever since Shockley and Read [1] and Hall [2] first pointed out their role as most efficient recombination centres on the basis of kinetic considerations. Several midgap luminescence bands trapped at deep levels have been found in GaAs and some of them are not yet well understood. The 0.635 eV photoluminescence (PL) emission in oxygen-doped semi-insulating GaAs was attributed to a complex centre involving the deep oxygen donor on an arsenic site and a gallium vacancy as a nearest neighbour [3, 4]. The 0.64, 0.68, 0.77, and 0.8 eV PL bands in undoped semi-insulating GaAs were related to the electron traps EL2 and EL6, respectively [5–10]. The origin of the 0.8 eV emission in Si-doped GaAs layers was suggested to arise from an As_{Ga}–V_{As} centre [11]. The emission at about 0.85 eV in low-temperature GaAs was associated with emission from the surface states [12, 13]. However, Yu *et al.* [14] recently studied the 0.8 eV emission from low-temperature GaAs layers and attributed the 0.8 eV emission to an As_i–V_{Ga} centre (EL6).

In this work, the 0.78 and 0.84 eV photoluminescence bands present in GaAs epitaxial layers grown on Si by metal-organic chemical vapour deposition were studied at various excitation intensities and temperatures and it was shown that they originate from the recombination of arsenic defects such as As interstitials (As_i), and gallium vacancies (V_{Ga}). The temperature dependence of the PL intensities obeys the relation $I_{PL} \propto [1 + A\exp(T/T_0)]^{-1}$, previously reported for amorphous semiconductors. A model for the recombination mechanism is given and the results are explained well by thermally activated tunnelling.

GaAs epitaxial layers used in the experiment were grown on 4° off toward [1 1 0] (1 0 0) n-type Si substrates using the two-step method 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 a H_2/AsH_3 ambient, they were heated initially at 950 °C for 10 min, and then the temperature was lowered to 450 °C for GaAs buffer growth with a thickness of 25 nm. Trimethylgallium and arsine in hydrogen were used as source chemicals. The temperature was then raised to 700 °C, and the top GaAs epilayers were grown with an As:Ga ratio of 20–50 and growth rate of 100 nm/min. The samples were not intentionally doped.

The PL spectra of GaAs epilayers were measured with an ordinary gating monochrometer 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 a He–Ne laser. The

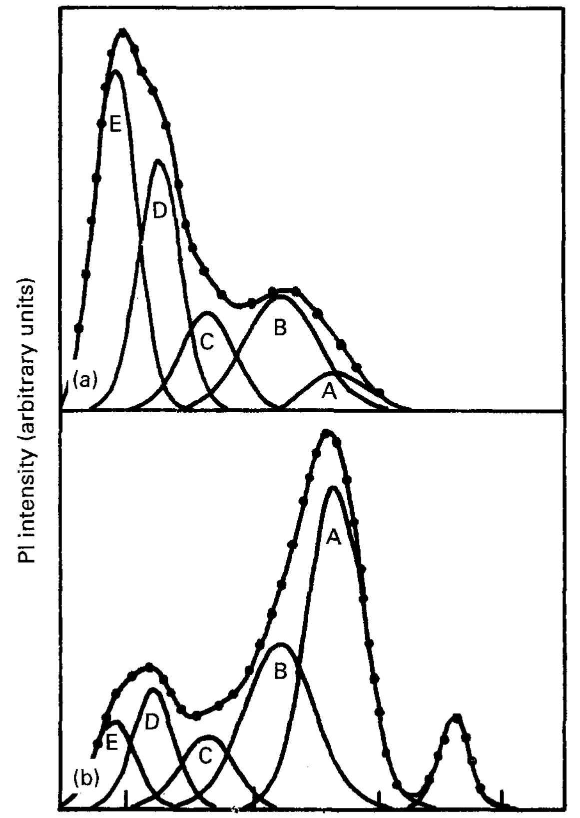

Figure 1 Photoluminescence spectra of samples 1(a) and 2(b) for the GaAs epilayers grown on Si at 77 K and excitation intensity 1.0 W/cm^2. (• Experimental points.)

excitation intensity was varied between 10^{-2} and 10^{2} W/cm^2 using neutral density filters.

Fig. 1 shows the PL spectra of samples 1 and 2 for the GaAs epilayers grown on Si with a thickness of 1.5 μm at 77 K and excitation intensity 1.0 W/cm^2. The As:Ga ratios of samples 1 and 2 are 50 and 30, respectively. As can be seen from Fig. 1, the PL spectra are very complex and indicate that in the GaAs epilayers there are a number of trapped centres that can degrade dramatically the crystalline quality, and deteriorate the optical and electrical properties of heterostructures. The spectra of the two samples can be fitted adequately by a sum of five Gauss-type curves, where the peaks are labelled as A, B, C, D and E, respectively. Their peak energies are given as follows: A(1.13 eV), B(1.04 eV), C(0.93 eV), D(0.84 eV), and E(0.78 eV). More recently, we reported studies on deep levels in the epitaxial GaAs layers grown on Si, and indentified that the 1.13 and 1.04 eV emissions could be explained well by the recombination luminescence of a Si shallow donor on the Ga site or a negatively charged arsenic vacancy as a donor and a next-nearest neighbour gallium vacancy as an acceptor [15]. It is found that the relative PL intensities of the 0.78 and 0.84 eV emissions for sample 1, compared with those of sample 2, increase obviously because sample 1 incorporates more excess arsenic during the growth process than sample 2. Recently Yu *et al.* [14] attributed the 0.8 eV emission from low-temperature GaAs layers to an As_i–V_{Ga} centre (EL6). It is reasonable that the 0.78 and 0.84 eV PL emissions in whis work are also related to arsenic defects such as As interstitials (AS_i), and gallium vacancies (V_{Ga}).

To further characterize the nature of the 0.78 and 0.84 eV emissions, excitation intensity dependence of the emissions was made in the range $I_{ex} = 10^{-2}$–10^{2} W/cm^2 at 77 K. It is found that the shapes of the spectra are independent of the excitation intensity and the PL intensities increase linearly with excitation intensity in this range. Temperature-dependent PL spectra of sample 1 were carried out in the temperature range 77–300 K and are shown in Fig. 2. The 0.78 and 0.84 eV PL emissions for sample 1 are two dominant recombination processes within the temperature range of measurement. The positions of the 0.78 and 0.84 eV PL bands do not follow the band-gap dependence, while they change with temperature (between 77 and 300 K) by no more than 0.005 eV.

Fig. 3 shows the PL intensities of the 0.78 and 0.84 eV PL emissions as a function of temperature of sample 1. The temperature dependence of the PL emissions cannot be fitted by an Arrhenius plot. Instead, it can be fitted well with the following formula used for amorphous semiconductors because of the existence of localized states therein [16, 17]

$$I_{PL} = \frac{I_0}{1 + A\exp(T/T_0)} \qquad (1)$$

where I_{PL} is the PL intensity, T is the measured temperature, T_0 is a characteristic temperature corresponding to the energy depth of localized states, A is the tunnelling factor, and I_0 scales the PL intensity at the low temperature limit.

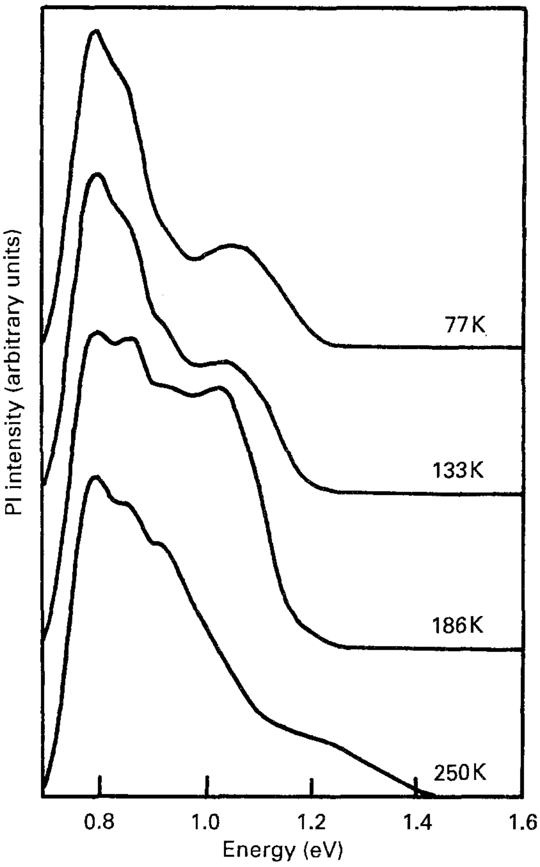

Figure 2 Photoluminescence spectra of sample 1 at different temperatures, and excitation intensity 1.0 W/cm^{-2}.

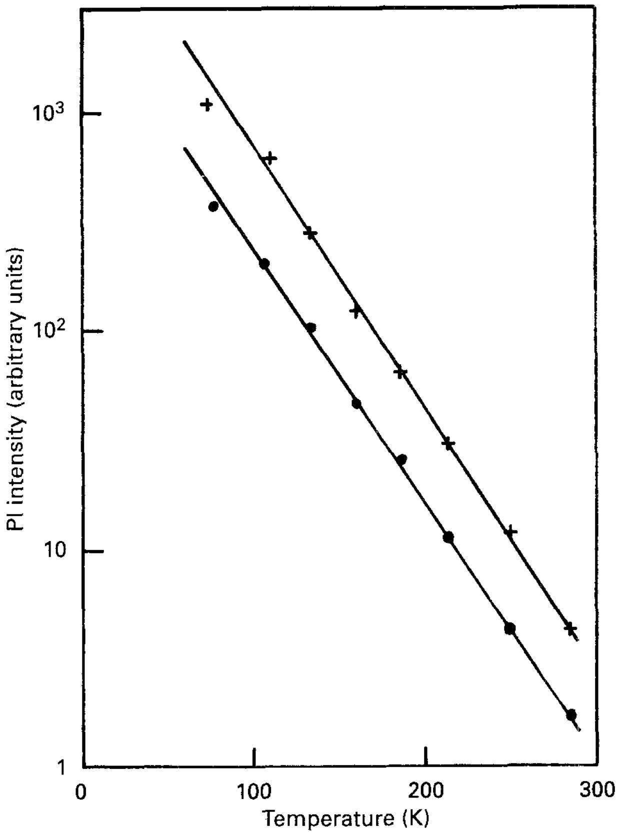

Figure 3 Temperature dependence of the photoluminescence intensities: + 0.78 eV; ● 0.84 eV.

We posit that there are three kinds of trapping sites in the recombination process of the 0.78 eV emission as shown in Fig. 4. One is radiative and two are non-radiative. The transition rates are k_1, k_2, and k_3. In a thermally activated tunnelling process between traps, the transition rate is given by [16]

$$k = k_0 \exp(T/T_0) \tag{2}$$

where k_0 is related to the tunnelling frequency and

$$T_0 = \frac{1}{4a^2r^2\kappa} \tag{3}$$

if parabolic potential wells are assumed for the trapping sites. Both a and r depend on the shape of the parabolic potentials, and κ is the Boltzmann constant.

The electrons trapped at the localized states can either undergo direct recombination or be trapped at rates k_1, k_2 and k_3 to three different trapping sites. The rate equation describing the electron is given by [17]

$$\frac{dn}{dt} = \frac{\alpha I}{h\nu} - (k_1 + k_2 + k_3)n - Bn^2 - Cn^3 \tag{4}$$

where B and C are constants representing bimolecular and Auger recombination, respectively. The latter can be ignored at low intensity. The direct recombination intensity is therefore proportional to

$$I_d = \frac{k_d}{(k_d + k_1 + k_2 + k_3)} \tag{5}$$

The single exponential decay for I_d can be obtained only if one of the non-radiative centres dominates, e.g. $k_2 \gg k_d$, k_1 and k_3. The assumption if $k_2 \gg k_d$ is in general reasonable since it is well known that photoluminescence is quite inefficient in semiconductors since the traps a non-radiative centres dominate the recombination dynamics. Then Equation 1 can be simplified to

$$I_d \approx k_2^{-1} \approx \exp(-T/T_0) \tag{6}$$

where T_0 is the tunnelling temperature for the k_2 process. The experimental data were fitted well by Equation 6 as shown in Fig. 3. The coefficient $T_0 = 36.1$ K for the k_2 process is obtained, and a dominant trapping site in the recombination dynamics is identified in the GaAs epilayers by fitting the temperature dependence of the PL signals. Similarly, the recombination process of the 0.84 eV emission is illustrated in Fig. 4. The coefficient $T_0' = 37.4$ K for the k_2' process, which corresponds to the k_2 process in Fig. 4, is also determined and another trapping site is verified in the process. The results obtained above show that the recombination processes for the 0.78 and 0.84 eV emissions are quite similar, and this suggests that the two emissions possibly originate from the recombination luminescence of two kinds of localized states with the similar structure. More work is needed to understand the correlation between the two emissions and the two dominant trapping sites identified in the GaAs epilayers.

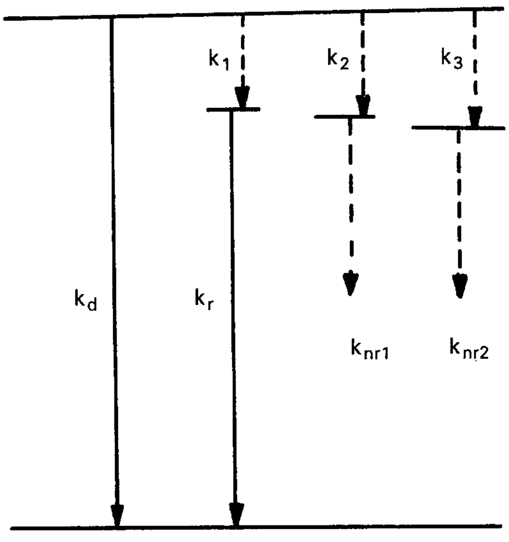

Figure 4 Schematic diagram of the recombination process.

Acknowledgements

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