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Identification of the 0.95 eV luminescence band in n-type GaAs:Si

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Abstract

The luminescence band at 0.95 eV has been identified as originating from the transition within $(\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}\text{Si}_{\text{Ga}})$ complexes by comparing cathodoluminescence and positron annihilation spectra. The upper and lower energy levels of the molecule-like defect complexes are suggested to lie at 22 meV below the conduction band and at about 0.5 eV above the valence band, respectively.

1. Introduction

Defects and defect complexes in semiconductors are still attractive topics. They can significantly influence the electrical and optical properties of the materials. Most theoretical calculations [1, 2] and experiments [3, 4] predict that negatively charged gallium vacancies (V_{Ga}) are dominant vacancies in n-type GaAs. Isolated gallium vacancies usually combine with donors by Coulomb interactions to form donor– V_{Ga} complexes. The donor– V_{Ga} complexes are frequently believed to be responsible for the band around 1.20 eV [6–8]. The defect-related luminescence band at 0.95 eV in n-type GaAs doped, e.g., with silicon, sulfur, or tellurium, has been known of for a long time, but its origin is still controversial [9–12]. This band was suggested to be correlated with acceptors [9, 10], with the $\text{V}_{\text{As}}\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}$ complexes [11], or with the $\text{Si}_{\text{Ga}}\text{—Si}_{\text{As}}$ pairs [12]. Further investigations are hence necessary to elucidate from what kinds of defect the 0.95 eV band really originates. With this purpose, cathodoluminescence (CL) and positron annihilation (PA) studies were carried out on two kinds of n-type GaAs:Si sample with different doping levels. By comparing the CL and PA information, the defects responsible for the 0.95 eV band will be determined in this paper.

2. Experiments

Two kinds of n-type GaAs:Si wafer (Nos n3# and w2#) were grown by the vertical gradient freezing (VGF) technique. The wafers were supplied by Freiburger compound materials. The average free-electron concentration was determined by Hall effect measurements as 1.0×10^{17} and $7.8 \times 10^{17} \text{ cm}^{-3}$ in the samples n3# and w2#, respectively. The total silicon and boron concentrations in w2# were determined by secondary ion mass spectroscopy (SIMS) to be 1.5×10^{18} and $5.5 \times 10^{18} \text{ cm}^{-3}$. The samples were investigated in the CL mode in a JSM 6400 scanning electron microscope (SEM) equipped with an Oxford monochromatic system at temperatures from 20 to 100 K. A 20 keV electron beam was selected to excite the sample. A germanium (Ge) detector was used to collect the corresponding CL images and spectra. Positron lifetime spectroscopy was performed by using a conventional fast-fast spectrometer at temperatures from 30 to 500 K. A $^{22}\text{NaCl}$ source was deposited on a thin aluminium foil and placed in a sandwich of identically treated samples. More than 1.0×10^7 events were collected for a complete positron lifetime spectrum. The annihilation momentum distribution of positrons was measured by Doppler broadening coincidence spectroscopy using a set-up of two Ge detectors.

3. Results and discussion

The luminescence bands of the samples n3# and w2# are shown in figure 1(a). The band A around 1.50 eV is due to the near band-gap-related emission (NBE); the band B at 1.33 eV originates from the transition from states near the conduction band to the energy level of B_{As}^- , i.e. (eB_{As}^-) [13, 14]; the band C at 1.14 eV is connected to $(\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}})$ complexes [6–8]. The origin of the band D at 0.95 eV cannot be determined at this stage. It might be related to $(\text{V}_{\text{Ga}}\text{Si}_{\text{Ga}}\text{V}_{\text{As}})$ complexes [11], to $\text{Si}_{\text{Ga}}\text{--Si}_{\text{As}}$ pairs [12], or to others. For convenience, we call the defect responsible for band D defect X. The band C correlated with the $(\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}})$ complexes is much stronger in sample w2# than in n3#. As a matter of fact, band A has shifted from 1.51 eV in n3# to 1.47 eV in w2# because of a higher concentration of free electrons [15] and boron atoms in w2#. The large number of boron atoms in w2# result in a high intensity of band B. It is worth noting that a boron atom can form a neutral acceptor (B_{As}^0) or a singly charged one (B_{As}^-). This is why the sample w2# is still n-type despite the silicon concentration ($1.5 \times 10^{18} \text{ cm}^{-3}$) being lower than the boron one ($5.5 \times 10^{18} \text{ cm}^{-3}$). As will be revealed by positron lifetime spectra, the concentration of shallow positron traps, mainly attributed to B_{As} acceptors, is about $4.4 \times 10^{18} \text{ cm}^{-3}$ in w2#, much higher than the concentration of shallow positron traps, $1.2 \times 10^{17} \text{ cm}^{-3}$, in n3#.

Positron lifetime spectra were obtained to study further the characters of the bands C and D. In the case of the sample n3#, figure 1(b) displays a typical temperature dependence of the average lifetime of positrons trapped in negatively charged vacancies in competition with trapping in shallow positron traps [16]. The trapping coefficient of negatively charged vacancies decreases with increasing temperature due to the temperature dependence of the diffusion-limited trapping, so the average positron lifetime decreases above 200 K. The two-component lifetime fitting indicates that the positron lifetime of the vacancy-related defects is 260 ± 6 ps, the same as the value at V_{Ga} or $(\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}})$ complexes [17]. It can thus be deduced that X includes a negatively charged vacancy. It is certainly a gallium vacancy because an arsenic vacancy is always positively charged and a gallium vacancy negatively charged in n-type bulk GaAs [5]. Theoretical calculations showed that the positron lifetime for $(\text{V}_{\text{As}}\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}})$ complexes is about 320 ps [17], far larger than the 260 ps measured here. Therefore, it is concluded that there is no arsenic vacancy included in X. From the different

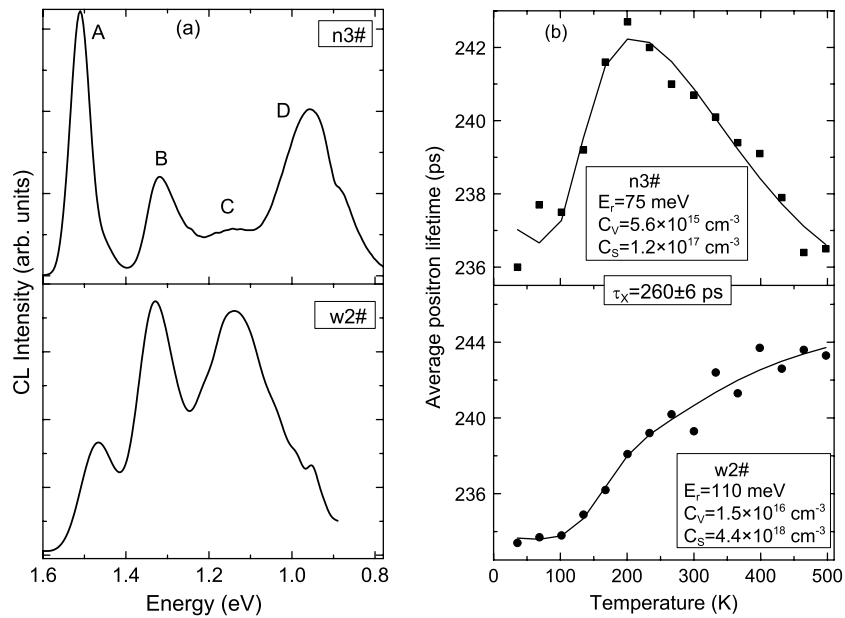


Figure 1. (a) CL spectra measured by the Ge detector at 75 K. The CL spectra are not corrected for the spectral sensitivity of the Ge detector. (b) Average positron lifetime as a function of temperature for the samples n3# and w2#. The symbols represent experimental data and the curves the fitting. In (b), E_r denotes the average binding energy of positrons to Rydberg states of vacancies, C_v the concentration of vacancies, C_s the concentration of shallow traps, and τ_X the positron lifetime of the vacancy-related defects.

pressure dependences of the polarizations for the band D in n-type GaAs doped with different donors, Reshchikov *et al* [11] concluded that the main dopant (Si_{Ga}^+ here) is one component constituting X.

The course of the average positron lifetime in the sample w2# is similar to that in the sample n3# below 200 K. A fit of the temperature dependence of the average positron lifetime has been made for both samples. This fit is based on the model of competitive trapping and detrapping in a shallow positron trap and a negatively charged vacancy [16, 18]. The characteristic quantities of the fit are the positron binding energy E_r for binding to the Rydberg state of the vacancy, the concentration of shallow traps, and the concentration of the vacancy-related defects X. The Coulomb interaction between a vacancy and a positron gives rise to Rydberg states acting as precursor positron traps for the deep bound state of the vacancy (see figure 2). It thus appears reasonable to assume that the Coulomb potential between a positron and a negative vacancy, and thus the positron binding energy E_r for binding to the Rydberg state of the vacancy, is stronger in w2# than in n3#. Indeed, by considering positron trapping and detrapping at the shallow traps and the Rydberg states according to the model of [18], the fit of the positron lifetime gives $E_r = 110 \text{ meV}$ for w2# and $E_r = 75 \text{ meV}$ for n3#. Therefore, the charge state of X in n3# must be smaller than $2-$, which corresponds to the charge state of a $(\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}})$ complex in w2# since a gallium vacancy is endowed with a triply charged state, i.e., $\text{V}_{\text{Ga}}^{3-}$ [1–4]. Taking into account the concrete condition in n-type GaAs:Si suggests that Si_{Ga}^+ is still one component of X. As a result, X must consist of a gallium vacancy (V_{Ga}) and two Si_{Ga}^+ donors forming a $(\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}\text{Si}_{\text{Ga}})^-$ complex. Although a gallium sublattice has 12 nearest-neighbour gallium sublattices, the Coulomb repulsion between the two Si_{Ga}^+

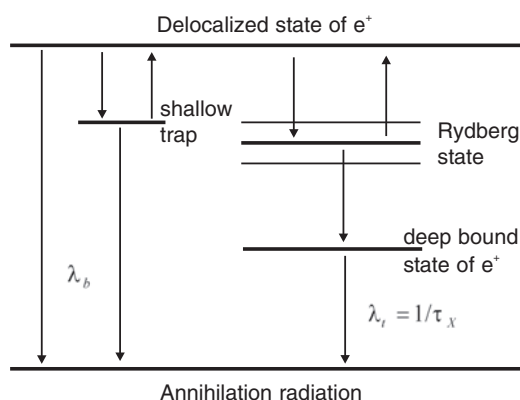


Figure 2. The scheme for the two-stage trapping into a negatively charged vacancy. The positrons may also annihilate through shallow positron traps at nearly the same annihilation rate λ_b as in defect-free bulk. A negatively charged vacancy results in both Rydberg states and a deep bound state for capturing positrons.

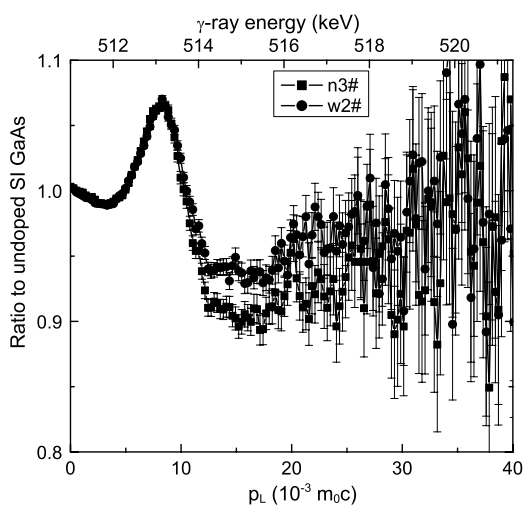


Figure 3. The PA momentum distribution measured at 200 K for sample n3# and at 400 K for sample w2#. The intensity is normalized by taking the ratio to undoped SI GaAs as a reference.

donors separates them to a distance as large as possible, resulting in a linear atomic structure of the $(\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}\text{Si}_{\text{Ga}})^-$ complex; that is, the distance between the two Si_{Ga}^+ donors is $\sqrt{2}a$ (a is the lattice constant of GaAs) and V_{Ga} lies at the mid-point between them. The fitting of the positron lifetime additionally indicates that the concentrations of gallium vacancies (C_V) and shallow traps dominated by B_{As} (C_S) are higher in w2# than in n3# (see figure 1(b)).

In order to acquire more information on PA at the gallium vacancies, the PA momentum distributions were measured at 200 K for n3# and at 400 K for w2# by Doppler broadening coincidence spectroscopy. The temperatures chosen correspond to maximum trapping in vacancies, as shown in figure 1(b). Figure 3 shows the PA momentum distribution in the samples w2# and n3#. The data are normalized by taking the ratio to undoped semi-insulating (SI) GaAs references, in which there is no positron trapping, thus representing the PA character in bulk GaAs. In a vacancy, the fraction of valence electrons taking part in the annihilation

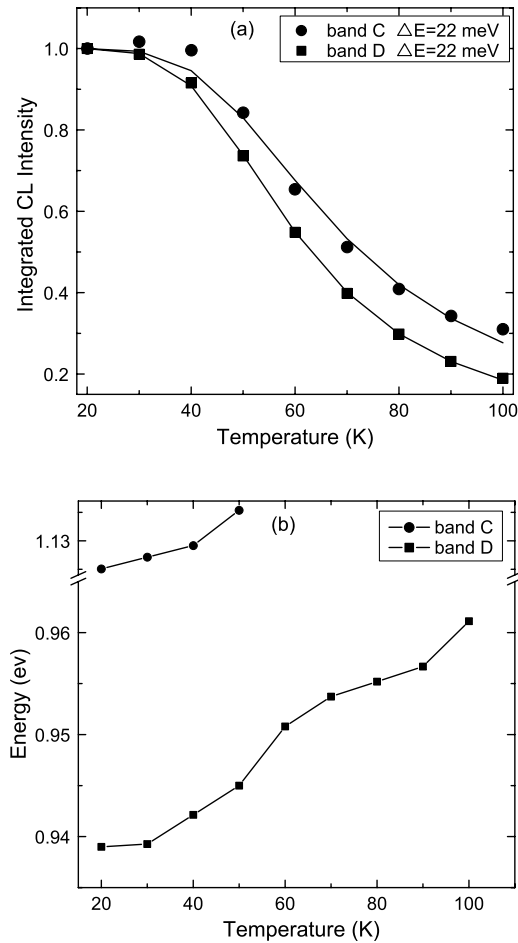


Figure 4. (a) The integral CL intensity and (b) the energy position of the luminescence bands C and D as a function of temperature in the sample n3# detected by the Ge detector. The integral CL intensity has been normalized to the one at 20 K; the symbols represent experimental data and the curve the fitting based on equation (1). ΔE obtained by fitting the experimental data is presented in the inset in (a) and shows the same value for the bands C and D.

process increases, resulting in a narrower momentum distribution with a higher annihilation intensity at the low annihilation momentum (i.e. $p_L < 10 \times 10^{-3} m_0 c$), compared to that in the bulk GaAs. At high annihilation momentum ($p_L > 10 \times 10^{-3} m_0 c$), the PA with the core electrons is much more intense than with valence electrons, dominating the high-momentum distribution. The core electrons are tightly bound to the nuclei and thus the high-momentum part of the PA momentum reflects the chemical environment where the annihilation event takes place. In bulk GaAs, the dominant contribution to the core annihilation comes from 3d electrons of Ga and As atoms; the intensity of the core annihilation at Ga 3d is stronger than at As 3d [19]. The PA at a gallium vacancy occurs mainly with 3d electrons of As atoms which are closest to this gallium vacancy. Therefore, the intensity of the high momentum for the two kinds of complex is smaller than the one for bulk GaAs, as shown in figure 3. The chemical environments at $(\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}})$ and $(\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}\text{Si}_{\text{Ga}})$ are almost the same, so their momentum distributions are very similar.

The luminescence bands C and D of sample n3# were measured at temperatures from 20 to 100 K. Their CL intensities are shown in figure 4(a) as a function of temperature, indicating that the CL intensities of the two bands always follow an approximately exponential decay with increasing temperature, as expected from the relationship

$$I = I_0[1 + f \exp(-\Delta E/k_B T)]^{-1} \quad (1)$$

where f is a temperature-independent constant; ΔE represents an activation energy for thermal quenching processes; k_B is the Boltzmann constant and T the temperature in kelvins. Equation (1) states that the CL intensity of the luminescence band decays with temperature in the form of a Fermi–Dirac-like statistics [20], which is consistent with the statistical character of the electrons and holes. However, our fit is inconsistent with those obtained by Williams [6] and by Sauncy *et al* [8], who achieved a Boltzmann-type decay of the intensity of band C with temperature. From a least squares fit of the experimental data, the ΔE for the different luminescence bands were obtained and they are almost the same (see figure 4(a)). In addition to the possible increase in competition from nonradiative transitions with temperature [21], the decrease in the number of electron–hole pairs available for radiative recombinations in unit volume due to an enhanced thermal activation may reduce the CL intensity of the bands. As a matter of fact, if we assume that the radiative recombination passing through a path involves at least one trap in the band gap which captures an electron or a hole, ΔE can be understood as the energy level of the trap lying below the conduction band or above the valence band or the activation energy for nonradiative relaxation processes on the basis of the configurational coordinate model [6, 8].

In general, band C originates from the transition from the upper (excited state) to the lower (ground state) energy level of a molecule-like ($\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}$) complex [6, 8]. The lower energy level of the molecule-like ($\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}$) complex is a deep one, like that of a gallium vacancy—at least about 0.3 eV above the valence band [8]. Thus it is difficult for the hole trapped in the complexes to escape from this level to the valence band. So it should be the electrons lying at the level of ΔE below the conduction band which are thermally activated into the conduction band with a probability given in equation (1). In this way, the number of electrons available for transitions is reduced, suppressing the intensity of band C with increasing temperature. In other words, figure 4(a) implies that the upper level of a ($\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}$) complex lies at $\Delta E = 22$ meV below the conduction band. Similarly, the upper level of a ($\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}\text{Si}_{\text{Ga}}$) complex is estimated to be at 22 meV below the conduction band and the lower level at least at about 0.5 eV above the valence band. The analysis indicates additionally that the lower level of a molecule-like ($\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}$) or a ($\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}\text{Si}_{\text{Ga}}$) complex is different from that of an isolated V_{Ga} .

The detailed examination of the peak energy position for bands C and D (see figure 4(b)) indicates that the peak positions for both bands C and D, unlike the band gap, shift to higher energies with increasing temperature, implying that the effect of the temperature on the energy levels responsible for the two bands is different from that for the band gap. Since the CL intensity of band C is too weak to be distinguished at temperatures above 50 K, no peak position is determined there. Since the shallow donor (acceptor) levels are known to shift rigidly with the conduction (valence) bands [22] and since the upper level of the complexes is a shallow level below the conduction band, it should be the lower deep level that shifts down to the valence band with increasing temperature, resulting in blue-shifts of the bands C and D.

4. Conclusions

In conclusion, the combination of CL with PA suggests that there are two possible kinds of gallium vacancy-related complex, ($\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}$) and ($\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}}\text{Si}_{\text{Ga}}$), resulting in the luminescence

bands at 1.14 and at 0.95 eV in n-type GaAs:Si, respectively. The ground states of the two kinds of complex lie respectively at least at 0.3 and 0.5 eV above the valence band while their excited states are shallow levels (22 meV) below the conduction band. It is well known that light with wavelengths ranging from 1300 nm (0.96 eV) to 1550 nm (0.80 eV) travelling through quartz fibres suffers minimum energy loss, so the existence of the band at 0.95 eV allows GaAs to be applied in the field of optical-fibre communications. Further efforts are required to systematically explore which conditions are essential for growing GaAs wafers with a strong luminescence band at 0.95 eV, such as the sample n3# used here.

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