The Carbon implication in p-n junction's gallium arsenide electroluminescence

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Abstract: In this paper, electroluminescence (EL) characteristic study of $p-n$ GaAs gallium arsenide junction is reported. The spectral range for which EL spectra were recorded is 650nm to 950nm. Three main structures noted (a), (b) and (c), located respectively at 911.839 ± 1.443 nm, 885.98 ± 1.03 nm and 812.199 ± 0.845 nm are shown on the spectra. The phonon replica of $2\hbar\omega_{LO}$ is shown and other sequence of transitions separated approximately by 11 meV ($\hbar\omega_{TA}$) is also observed. The electron-phonon coupling strength as well as the Franck-Condon shift of (a) and (b) are extracted from the configuration coordinate model and temperature–dependence of linewidths and EL intensity. The (b) and (a) structures are due respectively to shallow donor-acceptor pair ($D-C_{As}$) and its phonon replica related to C_{As}.
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I-Introduction

The gallium arsenide (GaAs) is a direct band gap semiconductor with an optical efficiency greater than that of silicon but its integration with silicon technology is difficult. GaAs remains interesting candidate for the light emission diode (LED) sources. The GaAs properties have been studied extensively using various characterization techniques (electroluminescence (EL) photoluminescence (PL), capacitance-voltage (C-V)…) and theoretical calculations to determine the atomic structures of the defects. Several studies concerning GaAs were reported [1-11]. These studies show that the GaAs emission is in infra red and visible spectral range. The multitude mechanisms and attributions of EL and PL spectra show a great divergence in their interpretation and prove that the origin of some peaks is not yet well defined and remains in debate. This dispersion is due to different spectra presented for many years. The growth technology has changed over this period; in particular the purity of the microelectronic materials has increased dramatically. In this study, we present temperature effect and offer a speculation for the atomic structure involved in the light emission. Our EL measurements were taken at the optic laboratory of physic's department of Sherbrooke University in Canada.

II-Experiments

Infrared and hermetic GaAs LED type OP133 commercialized and manufactured by OPTEK was used. The light is focused using a convergent lens and dispersed by a Jarrel-Ash 1 meter grating spectrometer (180 lines per millimetre) and detected by R636. This detector is equivalent to RCAC31034 used for silicon junction and $In_xGa_{1-x}N/Al_yGa_{1-y}N/GaN$ heterostructure studies [12,13]. The detected EL signal is amplified by ORTEC9301 amplifier and recorded by GaAs Hamamatsu photomultiplier whose domain wavelength sensitivity is 185 nm to 930 nm. The temperature is measured by a controller Lake Shore $DT-470-SD-13$ using either silicon diode or $Au-Cr$ thermocouple fixed near the sample. The Air Product Heli-Trans cryostat is used and it is in helium continuous circulation which enables us to achieve lower temperatures.

III-Experimental Results

Figure 1 shows the EL spectrum at room temperature and modeled by the Gaussian profile. We notice that the spectrum contains two main structures. The first noted (c) is located at 812.199 ± 0.845 nm (1.5265 ± 0.0016eV). The second band seems to contain a more complex structure than (c). Its behavior is not Gaussian and its deconvolution shows two structures noted (a) and (b). These later are located respectively at 911.839 ± 1.443nm (1.3597 ± 0.0022eV) and 885.98 ± 1.03 nm (1.3994 ± 0.0016eV). This deconvolution is confirmed by Gershezon measurements [14]. The peak (a) is always present in our spectra but absent in those of Michel et al [3]. The (a) and (b) structures energies are lower than GaAs band gap energy at room temperature which is equal

to 1.4304eV [15]. Then, these structures can be due to the recombination implying the defects situated in the forbidden band. The (c) energy is greater than GaAs band gap energy at 300K. It can be due to interband recombination through the gap in which the hot carriers are implied or to intra sub conduction band or to phonon replica (PR). In the spectral range included between 800nm and 860nm, a multitude peaks noted $1, 2, 3$ and 4 for which the intensity is weak are obsered. This sequence is separated approximately by 11meV. This energy corresponds to transverse-acoustic phonon at the X point of the Brillouin zone (TA_x) [16]. We can see also a peak located at 830.253 ± 1.326nm (1.495 ± 0.002eV) which is attributed to $2\hbar\omega_{LO}$ phonon replica related to the carbon in arsenic site (C_{As}) [17]. This result is in good agreement with that of Kuriyama et al [18] which have observed this replica at 872nm.

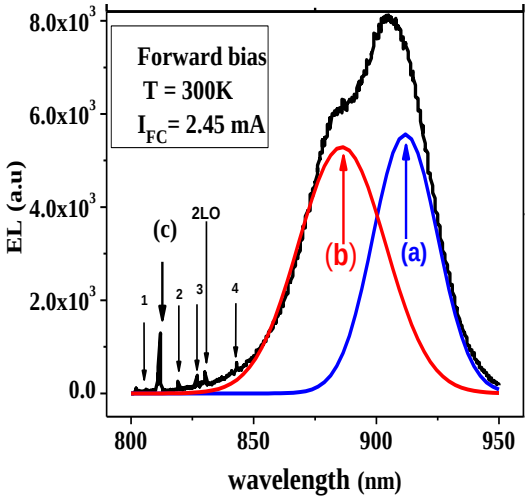

Figure1: EL spectrum at room temperature as function of photon wavelength of unirradiated GaAs LEDs for forward bias.

Figure 2 illustrates the temperature effect on EL spectra for forward polarization. It shows that when the temperature decreases, (a) and (b) structures intensities increase. This effect can be explained by the phonons reduction and consequently nonradiative transitions are reduced to depend of the radiative transitions. It also appears that EL maximum of the resultant structure moves to higher energies when the temperature decreases. This behavior is in good agreement with the temperature dependence of the band gap energy. When the temperature passes from 300K to 29K, the bleu shift of (a) is more marked than that of (b) i.e. (a) and (b) interpenetrate while shifting to lower wavelengths. In this trend, at low temperature (a) disappears because it is probably related to an indirect transition implying phonons. The (c) structure and (PR) sequence are more marked at room temperature but disappear completely at lower temperatures as indicated in figure 2 (bottom). Thus (c) is probably due also to a phonon replica (PR).

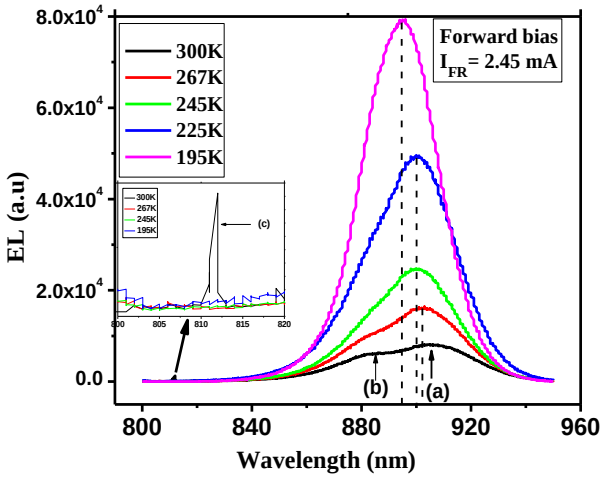

Figure 2: EL spectra as function of photon wavelength of unirradiated GaAs samples. The temperature effect is included.

To explain the electron-phonon coupling associated to (a) and (b), we have used the configuration coordinate (cc) model. Let us assume that the (cc) curves for ground and exited states of localized defect are parabolas having the same frequency. The full width at half-maximum (FWHM), depends of the temperature and it is defined as follow [19].

$$w(T) = \sqrt{8\ln 2}\sqrt{S}\hbar\omega\sqrt{\coth\left[\frac{\hbar\omega}{2k_BT}\right]} \qquad (1)$$

Where S is the Huang-Rhys factor which is a measure of strong ($S >> 1$) or weak ($S << 1$) electron-phonon coupling, $\hbar\omega$ is the phonon energy, k_B is Boltzmann's constant and T is the absolute temperature.

The FWHM of (a) and (b) was obtained as function of temperature and the results are shown in figure 3. The experimental results are fitted by equation (1) for which S and $\hbar\omega$ are the fitting parameters. This procedure gives $\hbar\omega = 31.92 \pm 1.63$ meV and $S = 0.35 \pm 0.02$ for (a) and $\hbar\omega = 27.82 \pm 1.32$ meV and $S = 0.52 \pm 0.03$ for (b). The phonon energy associated with (a) is approximately equal to 3TA (transverse acoustic) ($\hbar\omega_{TA} \approx$ 11 meV) mode at the X point of the Brillouin zone [16]. On the other hand, the phonon energy associated with (b) is approximately equal to the longitudinal optic (LO) mode ($\hbar\omega_{LO} \approx 29.5$ meV) at the X or L point of the Brillouin zone [20]. The phonons energies obtained using the configuration coordinate model may not present the natural phonon modes because deeps centres are coupled more strongly to local phonon modes.

The coupling of (b) to LO vibrations suggests that it may be a simple pair defect while the coupling of (a) to TA vibrations may indicate an inward relaxation. Such a phenomenon exists when the vacancy(ies) are implied in the defect atomic structure. The Franck-Condon (d_{FC})

shift, related to the atomic displacement from its regular site in the crystal, is defined as follow:

$$d_{FC} = S.\hbar\omega = \frac{1}{2}kQ^2 \qquad (2)$$

Where k is the first order elastic constant and Q is the cc which measures the atomic displacement from its regular site. We obtain 11.17±1.21 meV for (a) and 14.47±1.52 meV for (b). The d_{FC} and S obtained for (b) are greater than those of (a). Then, the EL structure of (b) contains more defects than (a). Indeed, an earlier study [21] of doping in melt growth GaAs by column IV and VI impurities shows that the peaks due to elements belonging to column IV always appeared on the low energy side of the peaks due to elements of column VI. Following this trend, the atomic structure of (a) can be postulated as a complex in which the vacancy(ies) (V) is involved. If (a) is an acceptor defect, then (V) can be a gallium vacancy(ies) (V_{Ga}) or a complex formed by gallium and arsenic vacancy(ies). If (a) is a donor, then (V) can be an arsenic vacancy(ies) (V_{As}). At this point, the number of vacancies remains unknown. From the earlier discussion, one can argue that (b) structure may presumably be due to the isolated impurities such as Si, Zn, Ge, Te…

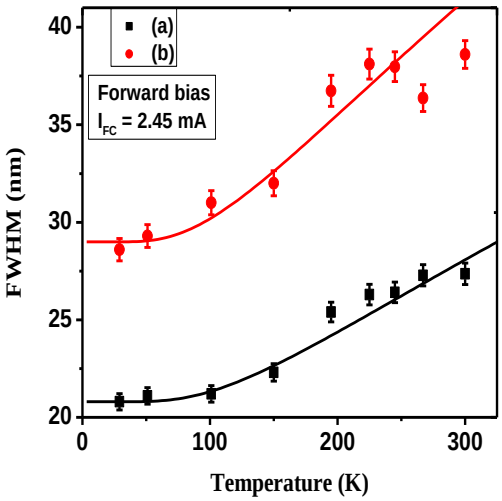

Figure 3: The FWHM of structures (a) and (b) as function of temperature for a constant forward current. The full curves are the plot of equation (1) for which S and ħω are the fitting parameters.

The electroluminescence intensities of (a) and (b) were studied as function of temperature. The results are illustrated in figure 4. The experimental data are fitted by the followed expression:

$$I = B.\exp\left[\frac{E_a}{k_B T}\right] \qquad (3)$$

Where I is the EL intensity, B is a constant, k_B is the Boltzmann constant, E_a is the activation energy which is the fitting parameter and T is the absolute temperature.

The fitting procedure gives $E_a = 76.51 \pm 3.87$ meV for (a) and $E_a = 114.23 \pm 8.16$ meV for (b). The activations energies obtained are different and show that probably the defects involved in (a) and (b) are not the same. The present values are greater than those obtained for $Al_{0.28}Ga_{0.72}As$ system (32meV) [22]. They are also smaller than those obtained for GaAs: Se and GaAs: Te systems (180meV) [21].

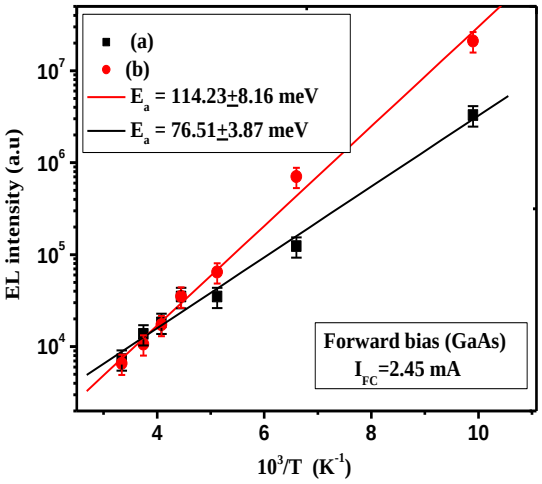

Figure 4: Semilog plot of EL intensities of (a) and (b) as function of reciprocal temperature for a constant forward current. Solid lines result from the fitting procedure.

IV-Discussion

From figure 2, we have shown that the resultant structure shifts to the bleu and its intensity increases when the temperature decreases. These effects are more consistent with the inter band transitions through the gap. The energies of structures (a) and (b) are smaller than GaAs band gap. This effect confirms that (a) and (b) result from transitions implying the defects in the forbidden band. From the FWHM study, we have shown that (a) is a transition in which the vacancies are involved. In this trend, on the basis of ionization energies presented in table 1, we can attributed (a) to donor-acceptor $(D-A)$ recombination in which V_{As} and C_{As} on the one hand and V_{Ga} and Te on the other hand are involved. The first assumption is in good agreement with that of [27] which has identified the emission around 910nm with $V_{As} - C_{As}$ complex. It was also reported that the emission band at 1.36eV can be related with a V_{As}^{+} – acceptor complex [1,2]. These results show that probably (a) is assisted by V_{As} than by V_{Ga}. These attributions are completely different from that of [14] which identified (a) as a phantom peak due to self-absorption attributed to the light absorption mechanism into the diode. On the other hand, the energetic separation between (a) and (b) at room temperature is equal to 39.69 ± 0.02meV. This later is equal approximately to LO PR ($\hbar\omega_{LO} = 37$meV) related with C_{As} [17]. Then (a) can be also assigned to the transition assisted by LO phonon. In the previous works

described in this paper, V_{Ga} and V_{As} vacancies appear under irradiation by different type of particles (electrons, neutrons, protons, oxygen, lithium,α particle and ^{60}Co rays). Our samples are not irradiated; then, the later assumption is the most probable that we retain.

In the same context, the temperature effect shows that (b) is coupling to LO vibrations. This effect indicates that (b) is related with isolated defects. The energetic separation between (b) and GaAs band gap is $30.98 \pm 0.04meV$, and then we can suggest that (b) is due to:

- $CB - Zn$ recombination $(e - Zn)$,
- $Te - VB$ recombination $(Te - h)$
- $D - A$ recombination $(Si - C)$, $(Se - C)$ or $(Ge - C)$.

When the temperature passes from 195K to 300K (as shown in fig. 2), the (b) red shift (RS) is equal to $4.57 \pm 0.03meV$. This displacement is typical of that between the CB and the shallow donors in GaAs. So, we can deduce from these arguments (LO, RS) that (b) result from the transition implying the carbon. The activation energy obtained for (b) is equal to $114.23 \pm 8.16meV$ and it is smaller than those of Williams obtained for $GaAs:Se$ and $GaAs:Te$ systems [21]. This result enables us to reject the assumption in which Se and Te are implied. At this point, we can speculate that the most transitions which describe (b) and (a) are $D - A$ $(Si - C)$ or $(Ge - C)$ and its PR related with C_{As} respectively.

Table 1: Ionizations energies measured of impurities in GaAs as reported in ref [22,24]. 1 and 2 are obtained from [10] and [25,26] respectively. Donors and acceptors energies are obtained from CB minimum and VB maximum respectively.

Native	impurities	C	Zn	Si	Ge	Te	Se	V_{Ga} [1]	V_{As} [2]
Donor	Energy	-	-	5.8	6	30	5.9	-	45
acceptor	(meV)	26	31	35	40	-	-	42.3	-

Conclusion

The optical characterization of $p - n$ GaAs LEDs has been discussed in this article. Light is emitted in infra-red range. The temperature effect suggests that the transitions appeared at $1.3994 \pm 0.0016eV$ and $1.3597 \pm 0.0022eV$ are associated with $D - C_{As}$ ($D \equiv$ Si or Ge) and its PR related with C_{As}respectively.

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