Excitonic recombination processes in GaAs grown by close-space vapour transport

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Abstract

Epitaxial GaAs layers were grown using the close-space vapour transport. From deep level transient spectroscopy measurements, the native EL2 donor has been observed in all of the layers with deposition temperature-dependent concentration. On the GaAs samples, also performed are photoluminescence experiments in the temperature range 10–300 K. Two peculiar features were revealed: (i) the radiative recombination in GaAs layers is increasingly dominated by bound–exciton transitions, (ii) the excitonic luminescence is found to be very sensitive to the growth conditions. A study of the near-band-edge photoluminescence as a function of power excitation and temperature has been done in an attempt to elucidate the origin of the enhanced bound–exciton luminescence.

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1. Introduction

The growth of epitaxial layers in III-V semiconductors by close-space vapour transport (CSVT) has been paid recently a great deal of interest for both fundamental and applied physics. The CSVT technique is characterised by a close spacing between source and substrate. This arrangement in space provides a large mass transfer during the decomposition and the recomposition reactions. Additionally, the rate of transport can be easily controlled by monitoring both the source and substrate temperatures and the water vapour pressure. Epitaxial GaAs layers of high crystalline quality and having a reasonable electron mobility have been realised using CSVT [1]. Electrical and optical properties of CSVT deposited GaAs have been investigated [2–4]. To judge the interest of this material, it is required to know in more detail the effects of the growth conditions on the characteristics of deposited layers. On the other hand, it was evidenced from thermodynamical considerations that the CSVT GaAs is As-rich [5]. This property can favour the formation of the EL2 centre in these layers [6,7]. Indeed, standard deep level transient spectroscopy (DLTS) measurements have shown unambiguously the existence of the EL2 level in all of the CSVT samples studied [4]. The assignment of this deep donor is also supported by optical quenching [8]. It is worth to notice that the occurrence of deep acceptor states related to possible gallium vacancies (V Ga ) has been invoked as well in materials grown by CSVT, based on experimental and theoretical investigations [9–13].

This paper reports on a DLTS and photoluminescence (PL) study of CSVT deposited GaAs layers. The deep EL2 donor has been observed with substrate temperature-dependent concentration. From PL measurements, the bound–exciton (B–E) recombination was revealed to be dominant at low temperature. It was also found that the B–E PL intensity increases with the substrate temperature. An attempt to assign the latter behaviour to increased concentration of impurities and/or stoichiometric defects that bind the excitons will be presented.

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2. Results and discussion

The epitaxial set-up used for this investigation consists of CSVT deposited GaAs layers. The samples are undoped. The source and substrate are both a high-purity (001) oriented GaAs. The substrate temperature ($\theta$) was varied in the range 750–800 °C. A nominal temperature difference of 50 °C has been established between source and substrate. The water vapour pressure is fixed at 1.25 mm Hg during the growth. The DLTS measurements were performed in the temperature range 77–450 K using a double lock-in amplifier and a PAR 410 capacitance meter. The luminescence was excited by a 514.5 nm line from an argon ion laser. The emission spectra were analysed using a 0.6 m double monochromator. The samples were mounted in a helium cryostat for the temperature dependence studies.

For our analysis, we have selected results of two representative samples prepared at $\theta = 750$ and 800 °C and which are labelled A and B respectively. Capacitance–voltage $C(V)$ measurements at room temperature showed that these epilayers are n-type with a net donor concentration in the range $2–8 \times 10^{16}$ cm$^{-3}$. A typical DLTS spectrum of the CSVT GaAs layers is shown in Fig. 1. It is obtained for an emission rate $e_n = 426$ s$^{-1}$, a reversed bias $V_0 = -3$ V, a pulse amplitude $\Delta V = 3V$ and a filling time $t_p = 0.5$ ms. As clearly seen, this spectrum exhibits a single peak at 377 K, which corresponds to an electron trap. The ionization energy of this trap, evaluated from the signature, is in the order of 0.76 eV (see the inset of Fig. 1). These observations are consistent with EL2 centre formation in the CSVT GaAs layers investigated. From the plot of the logarithm of $T^{-1/2} \times ln(1 - \Delta C_m/\Delta C_0)$ versus $1/T$, we have deduced a capture barrier energy of 60 meV for this donor level. It was also found that the concentration of this electron trap increases from $10^{12}$ to $10^{14}$ cm$^{-3}$ as the substrate temperature varies between 750 and 800 °C; result in an agreement with that reported in Ref. [4]. As well demonstrated from the DLTS study, the dominant defect in the samples is the native EL2 donor. Which means that the usual growth conditions in CSVT epilaxy favours the formation of As antisites. This does not, however, exclude the presence of deep acceptors related to possible Ga-vacancies.

It is obvious that stoichiometry-induced defects have also an influence on the optical behaviour of materials grown by CSVT. In the following, we analyse PL properties of the GaAs layers studied. Fig. 2 shows the near-bound-edge (NBE) luminescence at low temperature of samples A (spectrum a) and B (spectrum b). As can be noticed, the dominant emission is at 1.512 eV. It corresponds most probably to donor bound excitons, since the GaAs layers are found to be n-type. The PL spectrum also shows a series of relatively weak luminescence lines of extrinsic nature. A brief analysis of the extrinsic luminescence reveals the presence of free-to-bound (F-B) transition of C$_{Ga}$[14] with its 1 LO phonon replica. The PL peak at 1.477 eV, has been ascribed to a donor–acceptor (D–A) transition associated with Ge as an acceptor [15]. But Ge seems to be a rare non-intentional impurity in GaAs compared to C, Si or Zn for instance. As to the peak at 1.418 eV, its photon energy is close to the energy associated to the complex Si$_{Ga}$–As vacancy [16]. The luminescence band at 1.405 eV could be a (D$^0$ – Mn$_{Ga}^0$) pair transition [17]. This PL line is not, however, broad enough. The reason is that Mn acceptors do not show an increased coupling to the lattice. According to

![Fig. 1. Typical DLTS spectrum of CSVT deposited GaAs. In the inset, is shown the signature of the observed electron trap.](image1)

![Fig. 2. Photoluminescence intensity as a function of the photon energy in CSVT GaAs samples grown at a substrate temperature $\theta = 750^\circ$C (a) and $\theta = 800^\circ$C (b).](image2)
In this analysis, stoichiometry defect-related donor and acceptor levels are expected to be present in epitaxial GaAs layers prepared by CSVT. In Fig. 2, also reported is the evolution of the NBE luminescence as a function of the growth conditions. As shown, an increase in the substrate temperature \( \theta \) does not affect appreciably the photon energy as well as the intensity of the extrinsic PL lines. In contrast, the B–E luminescence shows a rapid growth as \( \theta \) increases from 750 to 800 °C. Moreover, in the high temperature \( \theta \) sample, a new luminescence line labelled L–E is resolved at 1.499 eV. A study of this band versus excitation power shows a linear increase with a change in the slope, similar to that of the 1.512 eV B–E luminescence (see Fig. 3). This implies that the new PL peak at 1.499 eV arises from a radiative recombination involving localised excitons. Stoichiometric defects could be at the origin of the localised exciton formation. While, the increasing of the B–E PL intensity with the substrate temperature is due to increased concentration of residual impurities that bind excitons. This proposal is supported by the \( C(V) \) obtained data which show that the net donor concentration increases with \( \theta \). Another recombination mechanism able to affect the B–E luminescence of the GaAs layers is the non-radiative transitions. For this purpose, we have investigated the luminescence at 1.512 eV in sample B as a function of temperature between 10 and 300 K. As a result, the B–E PL intensity shows a thermal quenching at high temperature (see Fig. 4a). From the plot of the PL intensity versus 1000/T, we have deduced an activation energy in the order of 56 meV. It is to be noticed that this energy is close to the electron capture barrier of the EL2 centre as measured by DLTS. This can lead to assign the B–E PL quenching to capture on EL2. If this is true, as the EL2 concentration increases with the substrate temperature, an increase in this growth parameter would lead to increased non-radiative recombination. Such a process can limit the performance of the CSVT GaAs epilayers. What is observed in the set-up of samples investigated is that the NBE PL usually shows an enhancement, due probably to increased concentration of bound–excitons. The latter mechanism competes the non-radiative recombination. In the GaAs layers studied, the increasing of \( \theta \) between 750 and 800 °C for a partial water pressure fixed at 1.25 mm Hg operates in favour of the B–E binding. A study of the B–E PL peak energy versus temperature has been also done. The results are depicted in Fig. 4b. As shown, the maximum of the B–E line does not exhibit a significant shift in energy with respect to the band gap edge in the temperature range 10–60 K. It, however, shifts towards the band gap beyond this temperature. The latter behaviour of the B–E PL peak shows, at relatively high temperature, that the radiative recombination is increasingly dominated by electron-hole pair transitions.

### 3. Conclusion

Epitaxial GaAs layers were grown by CSVT under different growth conditions. They have been investigated using DLTS and PL. The native EL2 donor is consistently observed in all of the layers. It was found that...
the concentration of this centre increases with the substrate
temperature. The PL study led to two main observations:
(i) the NBE luminescence is increasingly dominated by B–E transitions at low temperature, (ii) the efficiency of the B–E luminescence increases with the substrate temperature. The latter feature has been explained as due to an increase in the concentration of residual impurities and/or stoichiometric defects that bind the excitons. It was also found that non-radiative centres are present in the samples and could cause a PL quenching. In technological device applications, an increase in the B–E PL intensity is of great interest in CSVT epitaxy, since it allows to realise active layers of high performance using GaAs.

References