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Growth temperature effects on boron incorporation and optical properties of BGaAs/GaAs grown by MOCVD

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ABSTRACT

Structural and optical studies of $B_xGa_{1-x}As$ epilayers, grown by metal organic chemical vapor deposition (MOCVD), at different growth temperatures (580 °C and 500 °C), have been achieved by high-resolution X-ray diffraction (HRXRD) and photoluminescence spectroscopy (PL). They have shown that the boron content increases up to 8% with decreasing growth temperature. Low temperature (10 K) PL study has shown an asymmetric broad PL band around 1.34 eV, and a decrease of the intensity with increasing boron composition. The evolution of the emission energy versus temperature can be described by the Varshni law for the high temperature range, while a relative discrepancy has been found to occur at low temperature. Moreover, depending on the temperature range, the PL intensity quenching is found to be thermally ensured by three activation energies for the smallest boron composition ($x_b \approx 3\%$) and by two for the highest ($x_b \approx 8\%$) one. These results are attributed to the localized states induced by the non-uniform insertion and the clustering of the boron atom in BGaAs bulk.

1. Introduction

Great efforts have recently been dedicated to obtain high-quality BGaAs epilayers with high B incorporation. The properties of BGaAs epilayers have played a great part in the development of devices using BGaAs-based materials. The BGaAs epilayers with B contents up to 5% have been grown on a GaAs (0 0 1) substrate by metalorganic chemical vapor deposition [1,2]. Thus, the incorporation of boron in binary and ternary alloy -GaAs and InGaAs respectively, compounds is of special interest for growing lattice-matched material on GaAs substrates. These are a promising way to develop solar cell devices or active materials for 1.3 μm laser diodes [3–5]. Incorporating boron in InGaAs/GaAs quantum wells may extend the emission wavelength towards 1.33 μm by reducing the compressive strain. Moreover, higher flexibility in strain compensation and band gap engineering could be reached with the combined incorporation of boron and nitrogen supported by the fact that in MOVPE, the N- or B-incorporation are unaffected by each other [6]. However, the optical quality of BGaAs has been found to degrade with high B incorporation [7]. This may be due to higher growth temperature compared to that for GaAs. Nevertheless, growth mechanism and features of boron-contained III–V semiconductors are still not well understood because little attention has been paid to the growth of boron contained III–V semiconductors. A few reports on the epitaxial growth and characterization of single-crystal zinc-blende BGaAs alloys have been available since Geisz carried out the pioneer work [3].

In this work, we have investigated the influence of the growth temperature on boron composition, on structural and optical properties of the high B-content $B_{0.08}Ga_{0.91}As$ epilayers. High resolution X-ray diffraction (HRXRD) has been used to evaluate the boron concentration. The PL emission of BGaAs epilayers on GaAs substrate with different boron compositions has also been investigated and the optical properties versus temperature exploited. The experimental results indicate that the carrier recombination mechanisms are governed by that via the clustering of the boron atom formed in BGaAs bulk at low growth temperature.

2. Experimental details

The growth of BGaAs layers has been performed at atmospheric-pressure (MOVPE) in a T-shape horizontal reactor. The layers were deposited on (0 0 1) GaAs substrates misoriented 1° off (±0.05°) towards [1 1 0] direction. Triethylgallium (TEG) and diborane (B_2H_6) were used as group III precursors. Arsine (AsH_3) was used for the arsenic source as group V precursor. Hydrogen was used as carrier gas. Diborane flow-rate was kept constant. The boron gas-phase concentration was quantified by the initial molar flow-rate ration: $X_\nu = 2[B_2H_6]/(2[B_2H_6]+[TEG])$. The same value of the initial molar flow-rate $X_\nu = 62\%$ and flux B_2H_6 equal 7.5 sccm were used for both samples. Prior to BGaAs growth, a GaAs buffer layer of approximately 0.1 μm thick was grown at the same temperature as the epilayers.

X-ray $\omega/2\theta$ measurements of (0 0 4) plane reflection was performed systematically with copper target ($\lambda_{CuK\alpha 1} = 1.54056$ å) radiation from a discover D8 (40 kV 55 mA) high power X ray generator. The lattice mismatch ($\Delta a/a$) of the epilayer was

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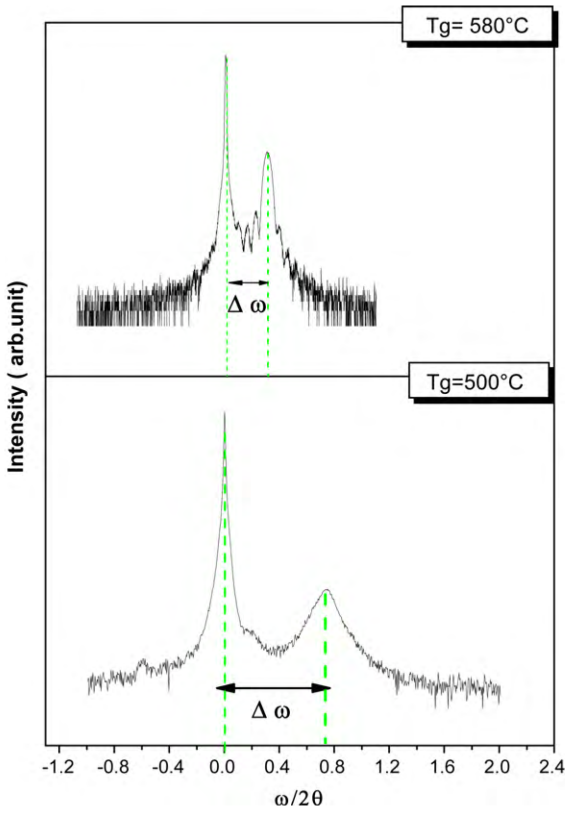

Fig. 1. High resolution X-ray diffraction $\omega/2\Theta$ spectra of two $B_xGa_{1-x}As$/GaAs layers grown at (a) $T_g = 580\,^{\circ}C$ and (b) $T_g = 500\,^{\circ}C$.

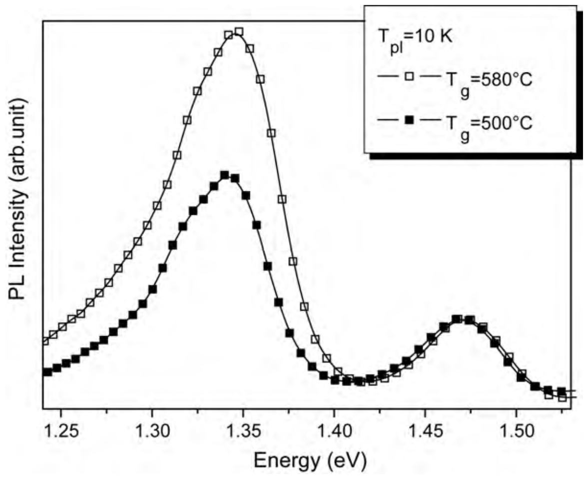

Fig. 2. Low temperature photoluminescence (10 K) spectra of $B_xGa_{1-x}As$/GaAs epilayers with 580 °C and 500 °C of growth temperature.

evaluated and the boron composition was determined using Vegard's law from separation angle between the epilayers and substrate (4 0 0) diffraction peaks, assuming coherent tensile strain and a Poisson ratio of 0.313 [3].

Photoluminescence measurements were carried out between 10 and 300 K while keeping the samples in a closed-cycle helium circulation cryostat. The excitation wavelength used is the 514.5 nm line of the cw Ar^+ laser. The emission was dispersed by a high-resolution spectrometer and detected by a thermoelectrically cooled InGaAs photodetector with a built-in amplifier.

3. Results and discussion

The lattice constant of ternary $B_xGa_{1-x}As$ can be expressed as $a(x) = 5.6533 - 0.8763x$ using Vegard's law. Assuming the complete relaxation of $B_xGa_{1-x}As$ epilayer and BAs Poisson ratio of 0.313, the boron composition (x) could be calculated from X-ray diffraction. High resolution X-ray diffraction (HRXRD) pattern of epilayers grown at 500 °C and 580 °C are shown in Fig. 1. A splitting of 972 and 2690 arcsec is clearly visible between the (4 0 0) diffraction peak of GaAs substrate and BGaAs layer indicating a boron content of ≈3% for $T_g = 580\,^{\circ}C$ and 8% for $T_g = 500\,^{\circ}C$, respectively. The FWHM value of two (4 0 0) BGaAs diffraction peaks is $x = 3\%$ and 8% equal 180 and 595 arcsecond, respectively. In fact, when increasing the boron composition the FWHM increased. This is due to a degradation of the crystalline quality [8]. However, we have clearly observed the peak splitting for $B_xGa_{1-x}As$ epilayer.

Since 2003, Dumont et al. have optimized the best growth condition for BGaAs epilayer [8]. They used two TMG and TEG precursors. They found that TEG to be the best precursor. They varied the temperature from 550 °C to 600 °C and they did not decrease below 550 °C. Moreover, Geisz and al deduced that the boron incorporation efficiency is maintained at lower temperatures when using TEG rather than TMG [3]. In the basic of this optimization, Rodriguez et al. have used TEG III group precursor [9]. They have decreased the growth temperature and have increased the initial mole flow-rate X_v to 62%. In fact, they have shown that low growth temperatures promote the incorporation of high boron composition.

Indeed, when the growth temperature increases, the diffusion length of boron atoms increase. This allows the migration of these atoms at the surface, which causes less incorporation in the bulk. This may explain the reduction of the boron composition when increasing the growth temperature.

The low temperature (10 K) photoluminescence spectra of the BGaAs/GaAs epilayers for varied growth temperature are shown in Fig. 2. We have observed the PL emission from the GaAs substrates to be dominated by the transition (e-C_{As}) carbon impurity and its optical LO phonon replica at 1460 meV [10]. These observed carbon impurities originated from the precursors (organic material such use triethylgallium (TEG) and arsine (AsH_3)), which is associated to the growth condition [8]. In addition, an asymmetric and broad PL band is observed at 1341 meV for both structures. This emission band is associated to the exciton recombination in the BGaAs epilayers. We have not observed any shift with varied boron composition. This is due to narrow bowing parameter of BGaAs [5].

The broadening of the $B_xGa_{1-x}As$ PL emission band and the decrease of the PL intensity with increasing boron composition could be attributed to the crystal imperfections (surface roughness ...) and composition fluctuations in BGaAs epilayer. A previous study has shown these crystal imperfections by the atomic force microscopy [9,11]. Rodriguez has shown by AFM for layers grown at 580 °C a transition from a surface with indistinct terraces (2D nucleation) to a bunching step/terrace structure B_2H_6 flow rate [9]. To explain this abnormal behaviour, we could suggest the carrier localization effects.

In order to confirm this attribution, temperature dependent PL measurements have been carried out.

Fig. 3 shows the temperature dependence of the PL emission energy of the BGaAs/GaAs epilayers. These spectra could be fitted by the empirical law proposed by Varshni [12] by using Eq. (1).

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{(\beta + T)} \tag{1}$$

where α is an empirical parameter related to the joint density of states and β is an effective temperature. By fitting the experimental results with Eq. (1), we have deduced the different values of α and β shown in Table 1. In comparison to pure GaAs, the higher or the lower effective temperature β is sensitive to the band gap variation E_g.

At low temperatures the Varshni law fails to fit the experimental data for epilayer grown at high temperature (580 °C). At 10 K, stokes

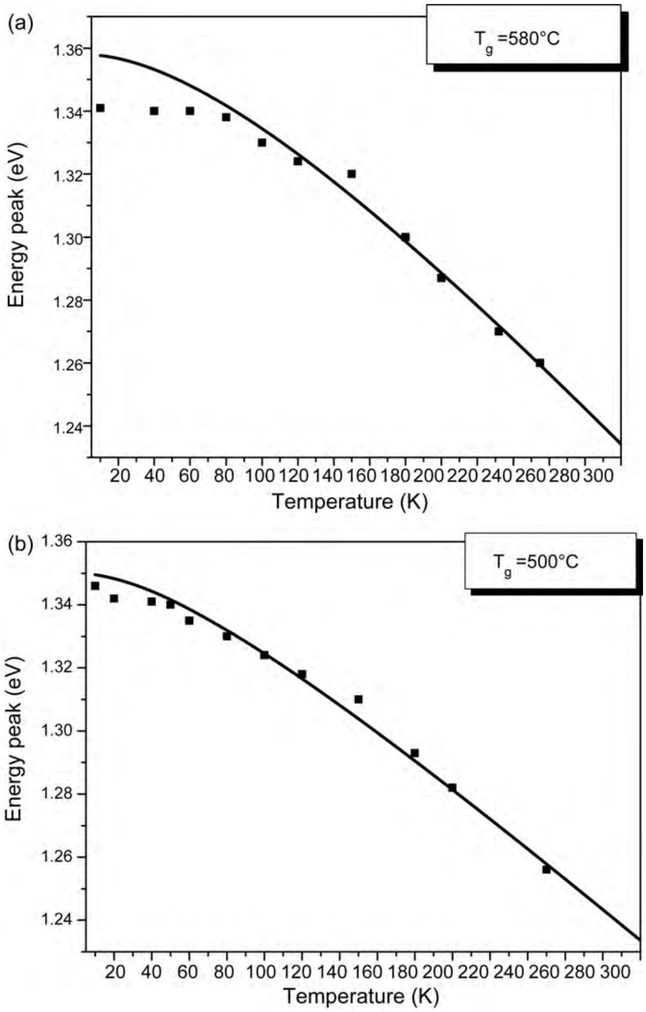

Fig. 3. Temperature dependence of the peak energy, with high excitation density (80 W/cm^2), of $B_xGa_{1-x}As$ epilayers with growth temperature, respectively: (a) $T_g = 580\,^\circ C$ and (b) $T_g = 500\,^\circ C$.

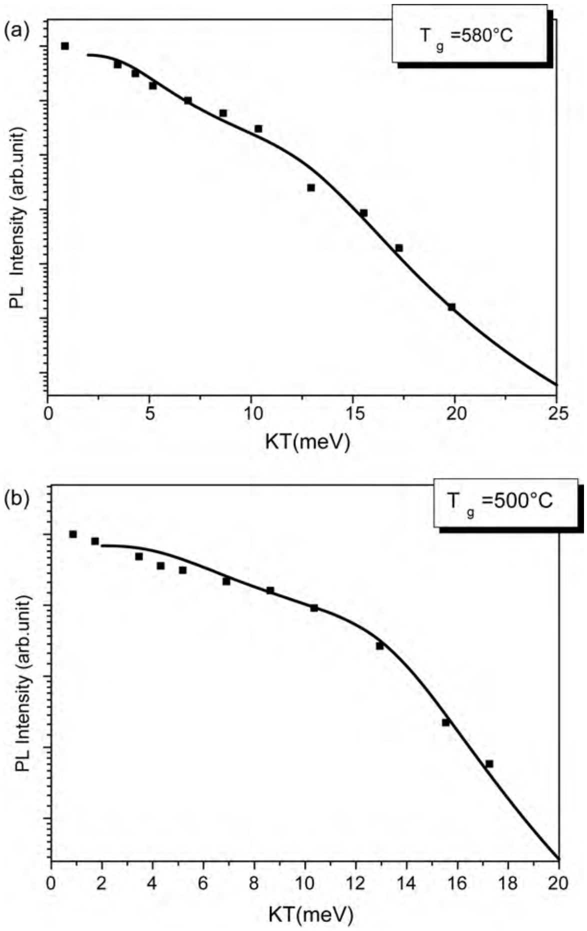

Fig. 4. PL Intensity dependence temperatures are presented in a semi-log plot for $B_xGa_{1-x}As$ epilayers with growth temperature, respectively: (a) $T_g = 580\,^\circ C$ and (b) $T_g = 500\,^\circ C$.

shift between theoretical and experimental values lies between 17 meV. However, the epilayer grown at 500 °C ($x_b = 8\%$) is adjusted by this model and the localization energy is around 4 meV at 10 K.

This may be due to the recombination of photogenerated carriers trapped by localized states within BGaAs. This phenomenon is observed in GaAsN [7], which exhibits an anomalous behaviour. This is often explained in terms of exciton localization at potential fluctuations induced by the presence of nitrogen. Specifically, at low temperature this phenomenon is more pronounced in GaAsN than BGaAs structure [7,13].

In fact, at low temperatures, the PL spectrum of dilute boron semiconductors is governed by the recombination of the excitons trapped by the lowest energy state. These states originate from the boron clustering which can introduce a discrete energy level into GaAs band gap. Moreover, a disorder in local structure and a surface roughness are traditionally associated with compositional inhomogeneities and boron complexes [14] that form shallow localized states and produce extended band tails.

Therefore, photoexcited electrons become readily localized, while the photoexcited holes remain mobile and can form spatially correlated pairs (excitons) due to the Coulombian interaction. This exciton trapped in localized states performs phonon assisted hopping transitions between localized states in the band gap. At high temperature, no distinction can be seen between the Varshni expected energy band-gap and the PL energy peak as carriers are thermally delocalized.

Recently, a theoretical study has shown that a random BGaAs alloy contains not only isolated B atoms, but also B–B pairs, where an As atom has two B neighbours, and larger clusters increasing rapidly with increasing composition x_b [7,14] similar to that observed in GaAsN. Thus, the anomalously large electron mass, low mobility and anomalous electron gyromagnetic ratio are due to the distribution of energy states associated with N–N pair and cluster states. That is also shown, due to the large size and electronegativity difference between B and Ga, isolated B atoms, and B–B pair and cluster states, all introduce resonant defect levels above the conduction band edge of BGaAs [14,15]. Moreover, this phenomenon decreases with increasing boron composition. Consequently, this shows that low growth temperature 500 °C promote the incorporation of boron and reduce localization phenomenon for boron composition up to 8%.

The optical characteristics exhibit a strong quenching of the PL intensity with increasing temperature (Fig. 4). The prominent features of the temperature-induced quenching of the PL

Table 1
Varshni parameter of GaAs and of $B_xGa_{1-x}As$ grown at 500 °C and 580 °C for Boron compositions 3% and 8%, respectively.

	α (eV/K)	β (K)
$x_b = 0\%$	5.405E−4	204
$x_b = 3\%$	6.6E−4	180
$x_b = 8\%$	5.25E−4	106

Table 2
Activation energies E_i in meV and parameter values A_i of $B_xGa_{1-x}As$ grown at 500 °C and 580 °C for B compositions 3% and 8%, respectively.

	$T_g = 580\,^\circ C$	$T_g = 500\,^\circ C$
E_1	18.75	19
E_2	80	
E_3	148.2	165
A_1	18	8
A_2	90	
A_3	1.48×10^5	3×10^5

are the relatively weak temperature dependence at low temperature, succeeded by a steep drop by several orders of magnitudes and subsequent saturation of the PL. That suggests an activated character of non-radiative processes. In order to explain this phenomenon, a model has been used to describe the strong quenching of the PL intensity with increasing temperature, According to this model; the temperature dependence of the PL intensity is described by

$$I(T) = I_0 \left[1 + \sum_i A_i \exp\left(\frac{-E_i}{\kappa_B T}\right) \right]^{-1} \qquad (2)$$

where E_i are the heights of the energy barriers, A_i are constants which are proportional to the transition probabilities between radiative and metastable states, and I_0 is the PL intensity at $T = 0$ K. The interpretation of the parameters in Eq. (2) depends on the particular experimental situation. For instance, in case of excitons bound to shallow defects, the activation energies E_i are associated with the exciton binding energy and with dissociation energy of the bound exciton. In case of bulk epilayers, the activation energies E_i are attributed to the energy differences between extended states in the band gap and in the barrier (GaAs).

Eq. (2) provides an excellent fit to the experimental data for temperature quenching of the PL in dilute boron semiconductors, the assumption regarding the discrete energy states requires a better justification. The results are summarized in Table 2; E_1 and E_2 are close in magnitude to the energy spacing between two bound states localized state. E_3 might be associated with the barrier height between the second bound states and the GaAs barrier. In contrast, we show in Fig. 3(b) for structure grown at 500 °C ($x = 8\%$), the PL intensity can be fitted by two activation energies E_1 and E_3. The emission energy of the investigated sample is slightly shifted with increasing boron composition keeping the energy difference between the family of localized state emission energy and the GaAs gap energy close to the extracted value for the activation energy E_3.

In the present work, and for all the investigated samples, the carrier's thermal activation in the high temperature range could be associated with the barrier height between the localized state on BGaAs band gap and the GaAs barrier.

Thus at low temperatures, excitons trapped into localized states perform energy-loss hopping transitions between the traps. Concomitantly, the energy distribution of excitons shifts towards deeper states in BGaAs band gap with respect to the mobility edge.

In fact, the thermal quenching of the PL is shown to be a result of the interplay between two competing processes: radiative recombination of charge carriers from the localized states and their thermal release to the delocalized states and subsequent non-radiative recombination. To explain qualitatively this phenomenon, this is deducted by the motion of excitons via localized states, induced in bulk's clusters. With rising temperature, excitons become more mobile and they can be trapped by centers with lower energies and, hence, the lower-energy states become increasingly more populated with rising temperature. This phenomena decrease with decreasing growth temperature.

The reasonable explanation for the temperature dependence of boron incorporation is that reaction kinetics plays the leading role in such behaviours. At a much higher temperature, the boron-contained intermediate species originally formed in gas phase may further recombine or polymerize to the high molecular-weight species which could be hardly incorporated into GaAs [1,2]. At a much lower temperature, pyrolysis of diborane that mainly contributes to the incorporation of boron into GaAs has been significantly suppressed due to the relatively stronger thermal stability.

4. Conclusion

In this work, we have investigated the effect of growth temperature on structural and optical properties of $B_xGa_{1-x}As/GaAs$ layers grown by MOVPE. It has been clearly shown that boron incorporation will increase significantly up to 8% at low temperature (<500 °C). We have shown a difference in the temperature behaviour of the PL peak energy between the BGaAs epilayers grown at 580 °C and at 500 °C. Thus, the peak energy and the PL intensity versus temperature have shown that for the BGaAs epilayer we have a localization effect due to the non-uniform insertion of boron and the clustering of the boron atom in BGaAs bulk. Moreover, a localization state increases while decreasing growth temperature. For that, low growth temperatures should also have the advantage of promoting the incorporation of boron which is identified by the optical properties. It can be concluded that the growth at low temperature (500 °C) promotes the incorporation of boron in GaAs.

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