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Investigation of recombination processes involving defect-related states in (Ga,In)(As,Sb,N) compounds

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Abstract. Recombination processes in GaAsN, GaInAsN, and GaAsSbN compounds have been analysed and compared. The following properties like: broad photoluminescence band at energy of ~ 0.85 eV, an emission band aproximately 80 meV below band gap energy, and annealing-induced blue shift of the energy gap have been found for all three compounds. In order to explain these features a simple band gap diagram with N defect-related levels close to conduction band edge and fluctuations in the energy of the conduction band minimum has been proposed.

PACS. 78.55.Cr III-V semiconductors – 71.35.Cc Intrinsic properties of excitons; optical absorption spectra

Nitrogen containing III-V alloys have recently become a subject of considerable interest due to their unusual physical properties [1–10] and a promise for long-wavelength optoelectronic devices [11,12]. Unlike conventional III-V compounds where the band gap energies of host binary or ternary compounds (with a small quadratic correction or bowing parameter), III-V-N alloys exhibit very strongly non-linear variation. For example, an addition of 1% of nitrogen to GaAs leads to a decrease in band gap energy from 1.42 to 1.25 eV at room temperature, although the GaN band gap energy is much higher (~ 3.2 eV in the qubic structure). A theoretical model based on a band anticrossing (BAC) interaction between the highly localised nitrogen-derived states and the zone-center (Γ point) conduction band Bloch states has been constructed and used to explain the band-gap behaviour [1]. The model was then improved by including the X and L coupling [5]. However, more sophisticated calculations have shown that the band structure is more complicated [6–10]. It includes two types of electronic states in the nitride compound. First, the perturbed host states represent mixing of the Γ-X-L and other conduction states by the nitrogen-induced perturbation. Second, cluster states are formed by single nitrogen atoms, nitrogen pairs or trimers, that are randomly created in the bulk during growth. The localised energy levels, due to a presence of nitrogen pairs or other atomic clusters, are formed around the conduction band edge either in the gap or in the continuum. Some of the unusual optical properties of the compounds could be due to a hybridisation of the conduction band minimum with these localised states [8]. In this paper we have proposed a simple band gap diagram which takes into consideration these theoretical results and explains experimental facts observed in optical spectra.

The samples were grown by molecular beam epitaxy on semi insulating GaAs substrates. They consist of a 120 nm thick GaAs buffer layer followed by 100 nm thick $GaAs_{0.98}N_{0.02}$, $Ga_{0.95}In_{0.05}As_{0.98}N_{0.02}$ and $GaAs_{0.90}Sb_{0.08}N_{0.02}$ layers and capped by 20 nm of GaAs. Further details of the growth process are described elsewhere [13]. The annealing process was conducted at 750 °C for 10 minutes. We carefully analysed the structural properties of the samples, comparing their characteristics before and after annealing. High resolution X-ray diffraction did not reveal any change of the average composition of these three samples. In addition, transmission electron microscopy did not show significant alloy fluctuation, suggesting that composition uniformity was not affected by annealing. We therefore consider that the compound content is the same before and after annealing. Moreover, it is to be noted that the transition energies are not sensitive to eventual interdiffusion at the interfaces, since the layers are thick enough to have negligible quantum confinement. Standard reflectance (R), photoreflectance (PR) and photoluminescence (PL) setups have been used to measure the optical spectra. In the case of PR, a 150 W tungsten-halogen lamp was used as a probe beam source whereas the 632.8 nm line of a He-Ne laser served as the pump beam. The probe and pump beams were focused onto the sample to the diameter of 1 mm and the power of pump beam was reduced to 0.1 mW using a gray filter. A single

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grating monochromator (with focal length of 0.55 m) and a thermoelectrically cooled GaInAs *pin* photodiode were used to analyse the reflected light. Other details of the PR setup can be found elsewhere [14]. Photoluminescence was excited by a 514.5 nm line of an Ar^{+} laser, using various excitation powers with a beam diameter of 0.1 mm, and analysed by the same monochromator and detector in the so called 'lock-in' technique. The samples were mounted on a cold finger in a helium closed cycle refrigerator coupled with a programmable temperature controller allowing measurements in the 10–300 K temperature range.

Figure 1(a), (b) and (c) show a comparison of the absorption-like (reflectance and photoreflectance) and emission-like (photoluminescence) spectra for GaAsN, GaInAsN and GaAsSbN layers, respectively. Each figure shows spectra for as-grown and annealed samples. In the case of absorption-like spectra, which are not sensitive to defect related states, we observe features related to absorption between extended states (band-to-band transition) or band gap related free exciton. It has to be noted that all the three layers have different values of strains. The GaAsN ternary layer is tensile strained ($\varepsilon = -7.9 \times 10^{-3}$), and its R and PR spectra shown in Figure 1(b), exhibit clearly a double structure which is related to heavy and light hole valence band splitting. The GaInNAs layer close to the lattice-matched conditions to GaAs substrate ($\varepsilon = -0.7 \times 10^{-3}$), and thereby almost unstrained. In consequence, we do not observe any splitting of the valence band in this sample, and only a single structure is seen in the PR spectra within the line broadening. For both GaAsN and GaInAsN layers the nature of the R and PR lines is excitonic at 10 K. In the case of GaAsSbN layers the line shape of R spectrum suggests a band-to-band transition. From X-ray analysis we have obtained that the layer is compressively strained ($\varepsilon = 4.5 \times 10^{-3}$). Such strain leads to quite significant splitting of the valence band. The line shape of PR spectrum confirms the splitting, however a detailed analysis of the PR spectrum is rather complex in this case. A detailed discussion of these PR spectra is presented elsewhere [15,16]. Results obtained from absorption-like experiments determine energy band gap in the compound and they enable an identification of the nature of PL bands which are the issue of this paper.

The photoluminescence of the three compounds possesses similar features:

(i) *Very broad emission band at* ~ 0.85 *eV (B1 in Figures 1 and 2).* It exhibits a strong dependence on temperature (see Figure 2(a), (b), and (c)) and rather weak dependence on the excitation power. This band is the least intensive for GaAsSbN layer and it almost disappears for this layer after annealing.

(ii) *A band* ~ 80 *meV below the energy band gap (B2 in Figures 1 and 2).* This band shifts to blue with an increase of the excitation power and it depends strongly on temperature. We have observed that this band disappears above 80 K and the post-growth annealing evidently reduces its intensity.

(iii) *Not well resolved band gap-related emission (B3 in Figures 1 and 2).* This band is not observed for as-grown layers and it appears after annealing. The intensity of this B3 band depends strongly on the excitation power and at low excitation conditions is almost not observable. With an increase of the excitation power the B3 band becomes dominant in the PL spectrum. In the case of the GaAsSbN layer, this band is already dominant for low excitation powers.

(iv) *A blue shift of the optical transitions after annealing.* The shift is observed in absorption-like experiments and is directly associated with an increase of band gap energy. In case of photoluminescence, the blue shift is seen mainly for the band gap-related emission (B3 band) whereas it is rather not observed for B1 and B2 bands.

The similar emission and absorption features of the three compounds suggest that the optical properties could be explained on the same band gap diagram in a first approximation. In order to explain the optical properties, we have proposed a model as this one shown in Figure 3. It assumes that some defect states exist within the band gap, and the conduction band possesses some fluctuations in the minimum energy.

The existence of defect states within the energy band gap has been suggested many times and it has been also confirmed by DLTS spectroscopy [17–19]. However, the nature of the defect states is unclear and is still being investigated. In our model, we assume, after Kent et al. [10] calculations, that N pairs and triplets lead to defect states which are close to the conduction band edge. We believe that these defect states are crucial in the III-V-N compounds. In addition, we introduce some defect levels which are rather close to the valence band and they are probably not associated with N-atoms. The existence of such defect levels have been confirmed by DLTS investigations [17], but their origin has not been identified yet.

The fluctuations of conduction band minimum result from both alloy content fluctuations and a non-homogenous distribution of the N-related defects. Usually, alloy content fluctuations lead to band gap fluctuations where both conduction and valence bands have their extrema. Nitrogen content fluctuations in III-V-N compounds, like GaAsN, GaInAsN, and GaAsSbN, lead to a specific variation of the band gap energy. In this case, the variation of band gap is mainly due to the changes of conduction band energy while the change of valence band can be neglected [18]. Such behaviour is simple to explain within the BAC model which assumes that the resonant nitrogen level interact only with the conduction band of host matrix (i.e. compound without nitrogen atoms). The magnitude of the interaction strongly depends on the nitrogen content and a small fluctuation in N content, which is not detectable by TEM measurements, leads to significant fluctuation in energy of the conduction band.

The non-homogenous distribution of the N-related defects is another phenomena, which takes place in these compounds and leads to a local conduction band edge minima in the real space. In this case, energy levels related to

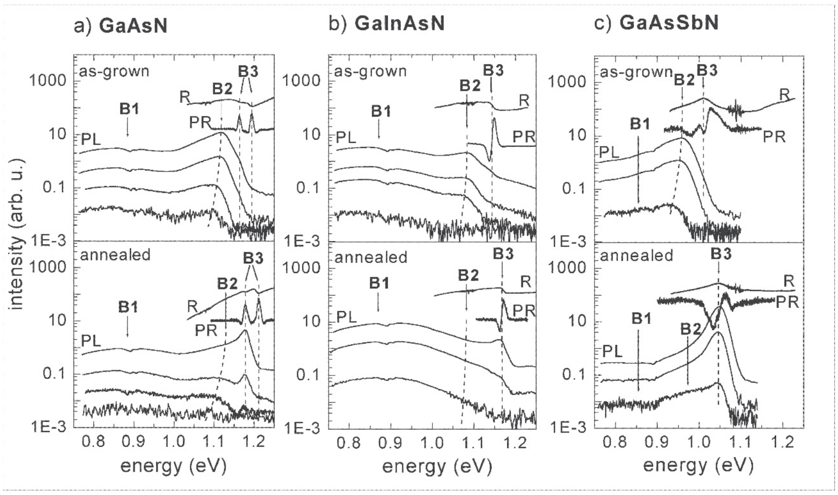

Fig. 1. PL, R, and PR spectra of GaAsN (a), GaInAsN (b), and GaAsSbN (c) layers recorded at 10 K. In the case of PL spectra the density of excitation power is 0.08, 0.24, 0.54, and 7.5 W/cm^2 for solid, dashed, dotted, and dash dot lines, respectively.

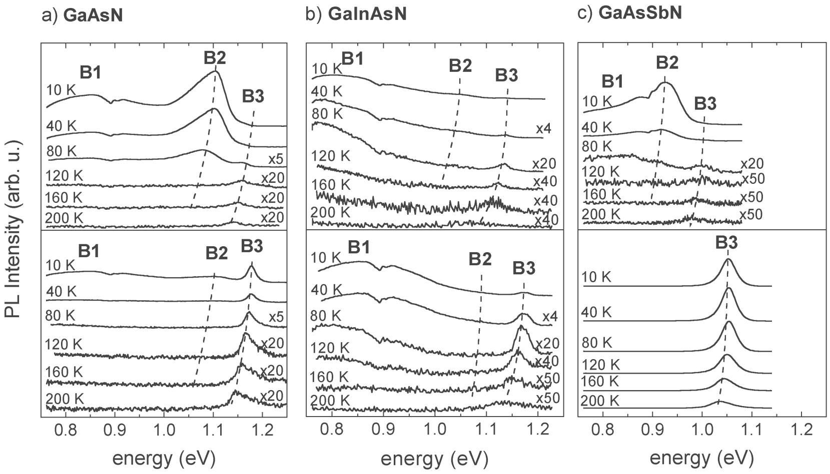

Fig. 2. Temperature dependence of PL from GaAsN (a), GaInAsN (b), and GaAsSbN (c) layers. The density of excitation power is 10 W/cm^2.

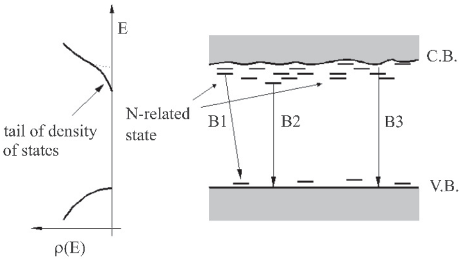

Fig. 3. Band gap diagram of the III-V-N compound.

N-defects are close to conduction band, and lead to a tail of density of states in conduction band and a shrinkage of the band gap.

The structural investigations have shown that the post growth annealing causes a homogenisation of the compound content and a reduction of point defects density. Within our model, it is expected that after annealing the magnitude of conduction band fluctuations decreases, tail band reduces, and energy levels within the energy band gap disappear. All these facts should have essential influence on optical properties of a compound described by this model.

The band at 0.85 eV is attributed to radiative recombination between the N-related levels and states at valence band. A spatial distribution of the states causes this band to be very broad. The second band (B2) ∼ 80 meV below band gap energy has been attributed to the recombination between N-related defect levels and valence band. This band strongly depends on temperature, excitation power and post growth treatment. The blue shift of this band observed with the increase of excitation power is attributed to saturation of the N-related energy levels. We have observed that this band disappears for temperatures above 80 K. The low temperature quenching suggests that the recombination is excitonic in nature, and the excitons have a localised character. The post growth annealing evidently reduces the intensity of this band. It can mean that the number of N-related defects and/or the localisation energy decreases after annealing. In this case, the localisation potential is attributed to some non-homogeneities in N-defect distribution and N-content fluctuations.

The third band (B3) related to energy band gap strongly depends on post-growth treatment. This band is almost not observed for non-annealed layers at 10 K and it appears after annealing. In contrast to the B1 and B2 bands, the intensity of this band exhibits much weaker temperature dependence. With the temperature increase the B3 band becomes dominant in PL and the character of the recombination changes from excitonic to band-to-band. In the case of the GaAsSbN layer, the recombination is rather band-to-band at 10 K already. We have found that the B3 band shifts to blue after annealing. It means that the post-growth treatment causes an increase of the band gap energy. In order to make detailed analysis of this phenomenon we have considered PR spectra because a shift observed in the absorption-like experiment is directly related to the change of band gap energy. We have found that the blue shift of band gap features equals 20, 27, and 54 meV for GaAsN, GaInAsN, and GaAsSbN layers, respectively. Within our model, a reduction of potential fluctuations and tail band states is responsible for an increase of the effective band-gap. Experimental data show that the blue shift is correlated with the intensity of the B2 band (N-defect related band). The highest reduction of this band intensity is observed for GaAsSbN layer and also for this layer the blue shift has the highest value. Therefore, we have attributed the blue shift to the reduction of the tail of density of states.

In case of the GaInAsN compound, a change of nitrogen nearest-neighbour environment can lead to a blue shift [3,21], besides the reduction of tail band states. It has been shown that annealing process changes the nitrogen atomic environment from Ga-rich to In-rich [22–24]. The change in the atom configuration influences strongly the energy of the band gap [3,7]. Therefore, in GaInAsN compounds, the blue shift is a sum of two effects: a reduction of band tail states and the change in the nitrogen nearest-neighbour configuration.

In summary, a simple band gap diagram has been proposed in order to explain the origin of the three usually observed PL bands in nitrogen diluted GaAs-based materials and their behaviour after annealing. It has been assumed in this model that the conduction band edge has local energy minima (fluctuations in the real space). The fluctuations are caused by N-related defect, which cause an appearance of energy levels close to conduction band and N content fluctuations. We are convinced that the number of defect states in the III-V-N compounds is rather huge and many detailed investigations are necessary in order to understand their nature. However, we believe that many of them will lead to the energy band gap diagram which is proposed in this paper.

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