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Optical Properties of GaNAs Grown by MBE

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Optical properties of the GaN_xAs_{1-x} layers grown on (001) GaAs substrates by molecular beam epitaxy have been studied. The samples can be classified into three categories with respect to the concentration of N, as determined by x-ray diffraction and secondary-ion mass spectrometry: (i) with doping nitrogen concentration, (ii) with average content of N less than 30 %, and (iii) with x close to 100 %. From optical measurements of photoluminescence and Raman scattering, combined with analysis of x-ray diffraction spectra, different phases are observed in the GaN_xAs_{1-x} layers: GaAs, GaN and the solid ternary solution GaN_xAs_{1-x}. We have estimated the fundamental band-gap energy in the GaN_xAs_{1-x} alloy with low nitrogen concentration (up to $x = 0.04$) from absorption measurements, and in GaN_xAs_{1-x} with low arsenic concentration (up to $1-x = 0.04$) - from photoluminescence spectra. An analysis of the dependence of the experimental values of the GaN_xAs_{1-x} band-gap energy on the nitrogen composition indicates a constant bowing parameter b as large as $b = -18$ eV.

1 Introduction

Studies of mixed group-V alloys like GaNAs are currently of great fundamental interest, and they may also offer application possibilities for optoelectronic devices. The large difference in lattice constant (20%) between GaAs and GaN leads to a nonlinear behavior of the energy gap versus nitrogen concentration. Recent optical measurements show a considerable red shift of the band edge in GaN_xAs_{1-x} alloys with increasing x for low x values [1] [2] [3]. This property may be used for applications of GaN_xAs_{1-x} as a novel III-V compound material integrated with Si [4]. Growth of GaN_xAs_{1-x} with a nitrogen concentration varying in the broad range $0 < x < 1$ can give a promising semiconductor alloy for fabrication of light-emitting devices covering the whole visible and ir spectrum.

Theoretical predictions of the GaN_xAs_{1-x} electronic structure depend strongly on the model used and show contradictory results. Sakai *et al.* [5], using Van Vechten's model [6], and Neugebauer and Van de Walle [7], using first-principles total energy calculations, predicted a negative band gap for N concentrations in the range 0.09 - 0.87 and 0.16 - 0.71, respectively. In contrast, calculations of Bellaiche *et al.* [8], based on a supercell representation of the alloy, confirmed the previous suggestion of Wei and Zunger [9] that GaN_xAs_{1-x} is a semiconductor rather than a semimetal for the whole range of x, and that the optical bowing parameter is strongly composition dependent, unlike the case of conventional III-V alloys.

The band gap energy estimated from photoluminescence and absorption measurements follows a linear dependence on nitrogen concentration x up to 4% [1] [2] [3] [4] [10], which implies a constant bowing parameter. However, Bi and Tu [11] have shown from optical absorption measurements that the bowing parameter of GaN_xAs_{1-x} is composition dependent for $x = 0 - 0.15$. Transmission electron microscopy studies of the microstructure of GaNAs reveal a tendency to phase separate [12] [13] [14] if the nitrogen content is above the nitrogen solubility level in the ternary alloy [15].

In this work we report the results of low temperature optical characterization of GaN_xAs_{1-x} grown by MBE with different nitrogen concentrations. We discuss the optical transitions close to the GaAs- and the GaN- band gap, respectively. X-ray diffraction (XRD), photoluminescence (PL) and Raman spectroscopy confirm a phase separation in the GaN_xAs_{1-x} layers. We estimate the

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band-gap energy dependence on nitrogen concentration and the value of the bowing parameter.

2 Experimental

GaN_xAs_{1-x} layers of different thickness (1 – 6 μm) were grown by MBE on semi-insulating GaAs substrates. The samples can be divided into three categories depending on the average nitrogen content in the layers: (i) GaAs:N-layers containing low concentrations of isovalent doping nitrogen, (ii) As-rich GaN_xAs_{1-x} layers with average x values from 0.01 up to 0.3, and (iii) As-poor GaN_xAs_{1-x} layers with average nitrogen concentration of x_{avg}>0.95. Further details about the growth procedure can be found in Ref. [16].

The average composition was determined by secondary ion mass spectrometry (SIMS), using Cs^+ as primary ions. The single crystalline structure was characterized by double crystal XRD. Figure 1(a) illustrates a typical x-ray diffraction spectrum of a GaNAs sample with an average nitrogen composition of ~ 8.6% obtained from the SIMS measurements. Analysis of XRD spectra for the epitaxial layers distinctly indicates the presence of three different crystalline phases: there are two features at ~ 33°, corresponding to the GaAs and GaN_xAs_{1-x}, and a rather broad peak at ~ 43°, identified as GaN(As), i.e. GaN with dissolved arsenic. The position of the GaN_xAs_{1-x} peak depends on the average nitrogen concentration. Applying the linear Bragg and Vegard's law, the N-composition is about 1.85% for this sample, which is much smaller than indicated by the SIMS measurements. The discrepancy between the nitrogen content as determined by SIMS and by XRD becomes more significant with increasing average N-composition and indicates the presence of phase separation. The maximum concentration we could achieve was $x = 3.6\%$ in As-rich GaN_xAs_{1-x} layers as determined by XRD. For this sample, the SIMS data [16] gives much higher average nitrogen content in the epilayer, ~ 36%. For As-poor GaN_xAs_{1-x} layers we observed only features close to GaN, shown in Figure 1(b) for two samples. The peak maximum is shifted from the GaN-position and the linewidth becomes broader with increasing arsenic concentration, i.e. formation of GaN(As) occurs. Finally, for the samples with low average nitrogen concentration ($x < 1\%$) there is no GaN-diffraction peak. In the following we denote nitrogen composition determined by SIMS as x_{avg}, and by XRD as x.

The layers of GaN_xAs_{1-x} with thickness of a few μm are relaxed, as shown by XRD-measurements (we could not see any satellite fringes around the GaAsN-peak). However, one cannot exclude the possibility that there might be some random strain contribution, since different phases exist in the layer.

3 Results and Discussion

We have studied the low temperature photoluminescence in GaNAs samples over a wide range of compositions, and found that PL spectra are rather different for the three types of samples.

Figure 2 illustrates a typical photoluminescence spectrum of the GaAs:N sample with low (doping range) average nitrogen concentration. The luminescence exhibits a pronounced GaAs spectrum with an excitonic transition at 1.514 eV close to the GaAs band gap, together with a dominating line at E=1.492 eV corresponding to the free-to-bound transition involving the C-acceptor. We observed also additional GaAs-related features connected with emission of the Cu_{Ga}-acceptor (1.356 eV) and its two LO-phonon replicas at 1.320 eV and 1.284 eV, respectively. In summary, no clear N-related features are observed.

As-rich GaN_xAs_{1-x} samples reveal either a relatively weak luminescence corresponding to the GaAs-phase, or they show a very broad emission band with maximum at ~ 0.8 eV, as Figure 3 demonstrates for a layer with x_{avg}=0.066. The appearance of such an emission is usual for highly defective material, and is an additional proof that with increasing of N-content in the layers the concentration of defect states dramatically increases. It is well known that in such material the near-band-gap excitonic luminescence is suppressed, thus it is difficult to expect any pronounced luminescence corresponding to the GaN_xAs_{1-x} solid solution phase. The structure observed in the spectral range 0.86 – 0.94 eV in Figure 3 is due to absorption by water vapor.

In the ultraviolet region we have observed similar spectra for GaAs:N layers and for As-rich GaN_xAs_{1-x} layers. These spectra consist of two relatively narrow (7 meV wide) lines with peak positions at 3.31 eV and 3.364 eV, respectively. Figure 4 illustrates a spectrum from a layer with 8.6% average nitrogen concentration. The nature of these lines has been frequently discussed in the recent literature on GaN [17] [18], however, there is no satisfactory explanation of their origin. Attempts have been made to attribute these lines to localized excitons in wurtzite GaN [18], to the shallow bound exciton in the cubic GaN [17], and recently to quantum confined states in cubic inclusions in GaN [19]. Similar features have also been observed in materials apparently containing no GaN at all. These lines may therefore be connected with an unknown localized defect level [20]. As stated above we have observed the same spectra for a GaAs layer with doping concentra-

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tion of nitrogen, where there is unlikely to be a GaN-phase.

Arsenic-poor GaNAs layers, on the contrary, provide different spectra in the ultraviolet region, but have the common characteristic of a broad emission band. Figure 5(a) presents spectra for two As-poor GaN(As) samples with average arsenic concentration 0.3 % and 4 %, respectively. A red shift of the peak position and a drastic widening of the bandwidth with decreasing nitrogen concentration indicate a near-band-gap transition in the cubic GaNAs phase. This result is consistent with XRD data shown in Figure 1(b) for As-poor GaN(As) samples. The broadening is associated with inhomogeneity of the layers with increasing arsenic content in the alloy. The shape and peak position of the emission band from the layer with low arsenic concentration 0.3% is similar to that for cubic GaN [21], as Figure 5(b) illustrates. It confirms the XRD data about the cubic symmetry of the structures.

For the As-rich GaN_xAs_{1-x} layers, the photoluminescence data do not give much information about near-band-gap transitions to confirm the presence of different phases in the samples. Therefore we use Raman spectroscopy as a rapid and sensitive method to determine the phase composition of these GaN_xAs_{1-x} layers. A depolarized Raman spectrum excited at 3.53 eV is shown in Figure 6 for the sample with 19% average nitrogen concentration. It clearly reveals two narrow features at 292 cm^{-1} and 740 cm^{-1} with a full width at half maximum (FWHM) of 10 and 20 cm^{-1}, respectively. The position of the first peak fits with the well-known LO phonon mode in GaAs. The line observed at 740 cm^{-1} corresponds to the LO phonon frequency in cubic GaN [22]. Recent experiments on Raman scattering in amorphous $GaN_{0.3}As_{0.7}$ show a very broad weak feature around 750 cm^{-1} with FWHM of 280 cm^{-1} [23]. Thus, we can conclude that in our As-rich GaN_xAs_{1-x} layers, crystalline phases of cubic GaAs and cubic GaN coexist, in agreement with the XRD results. However, we have not observed any specific manifestation of the GaN_xAs_{1-x} ternary alloy in the Raman spectra, probably because the vibrational LO mode in GaAs is close to the one in the solid solution with very low nitrogen concentration $x = 0.017$ (as determined by XRD). A recent Raman scattering study of GaN_xAs_{1-x} layers with $x = 0 – 0.05$ [24] demonstrated the presence of diagonal components for both the GaAs- and GaN-type optical phonons.

In addition, we present in Figure 7 the estimation of the band gap energy as a function of the nitrogen concentration in the GaN_xAs_{1-x}alloy. Our experimental data of E_g for low x (up to 0.04) extracted from absorption measurements [3] are shown as solid circles. Also shown in the figure are results of PL measurements for x close to 1 (open circles). The line presents the fitting of the experimental values of E_g assuming that the GaN_xAs_{1-x} band gap composition dependence obeys the simple parabolic law:

$$E_g(x)=xE_g(GaN)+(1-x)E_g(GaAs)-bx(1-x),$$

where b is the bowing coefficient, $E_g = 1.519$ eV for GaAs and $E_g = 3.3$ eV for cubic GaN [25]. We conclude from these data that the bowing parameter is constant and equals -18 eV. A good correspondence between calculations and experiments both for low x and x close to 1 suggests that at least in the investigated range of x the bowing coefficient in GaN_xAs_{1-x} is composition independent. Assuming that the bowing parameter is a constant for all x it is reasonable to expect semimetallic properties of the GaN_xAs_{1-x}alloy for a broad range of x between approximately 12% and 75%.

Our values of the GaN_xAs_{1-x} band-gap energy and the value of the bowing coefficient are in a good agreement with calculations by Sakai *et al.* [5] and Neugebauer and Van de Walle [7] for the relaxed superlattice and very close to the recent experimental result of Francoeur *et al.* [26]. They determine b=-19 eV for the strained GaNAs layers [27] [28] with nitrogen concentration up to ~3%.

4 Conclusion

In conclusion, GaN_xAs_{1-x} layers prepared by MBE have been characterized by XRD, SIMS, PL, and Raman scattering., We divided the samples into three groups according to the nitrogen content: (i) GaAs:N with doping concentration of nitrogen, (ii) As-rich GaN_xAs_{1-x} with average x<0.3, and finally As-poor GaN_xAs_{1-x} with x close to 1. We have found that different phases, which have been identified as GaAs, GaN and the ternary alloy GaN_xAs_{1-x}, are present in samples with nitrogen concentration exceeding the N solubility limit. We have discovered a strong red shift of the PL peak energy from the GaN band gap for As-poor GaN_xAs_{1-x} layers with increasing As content. We interpret this emission as a near-band-gap transition in GaN_xAs_{1-x} layers with x close to 1. Analysis of the dependence of E_g on x for low x and for x close to 1 allows us to assume a constant bowing parameter -18 eV for the GaN_xAs_{1-x} ternary compound alloy.

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FIGURES

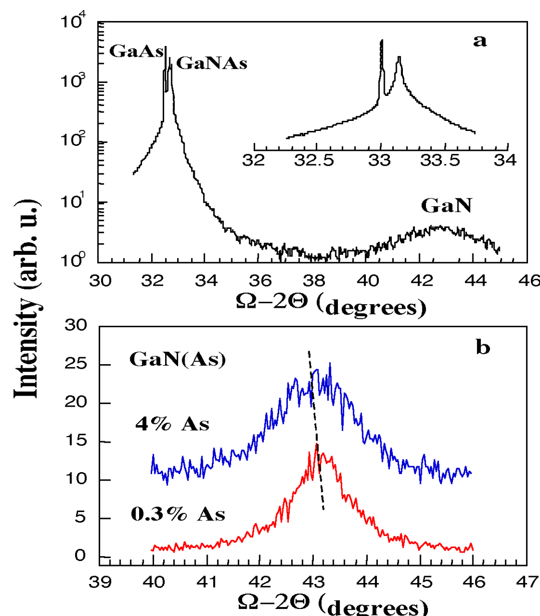

Figure 1. The XRD spectrum of the GaN_xAs_{1-x} sample with 1.85% nitrogen (a), and XRD spectra for two GaN(As) layers with low arsenic content of 0.3% and 4%, respectively (b).

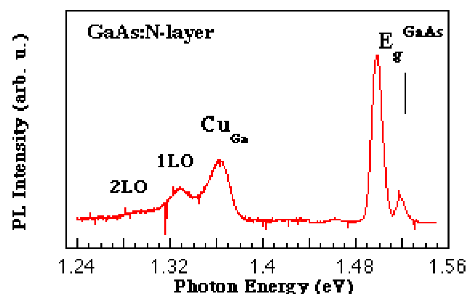

Figure 2. The low temperature (T=2 K) photoluminescence spectrum in the infrared region for the GaAs:N sample with an isoelectronic nitrogen doping concentration of 10^{18} cm^{-3}.

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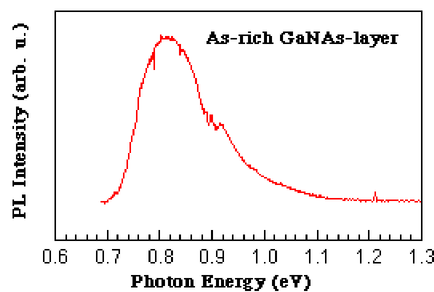

Figure 3. Typical defect emission band in the As-rich GaN_xAs_{1-x}-layers with an average nitrogen concentration of 6.6%.

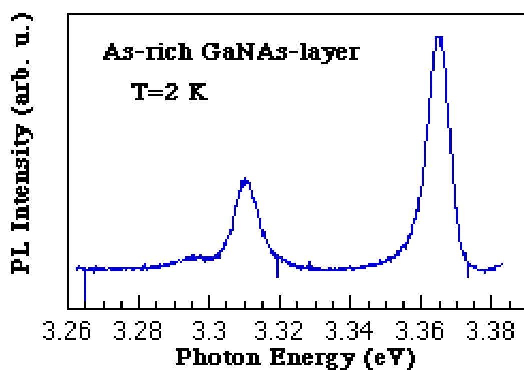

Figure 4. The low temperature (T=2 K) photoluminescence in the ultraviolet region for an As-rich GaN_xAs_{1-x} layer with 8.6% average nitrogen concentration.

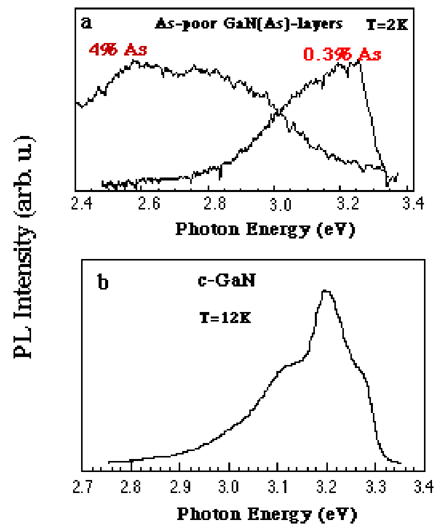

Figure 5. Photoluminescence measured at T = 2 K for two As-poor GaN_xAs_{1-x} layers with arsenic concentration of 0. 3% and 4%, respectively, (a), and a photoluminescence spectrum of the cubic GaN taken from Ref. 21 is shown for comparison (b).

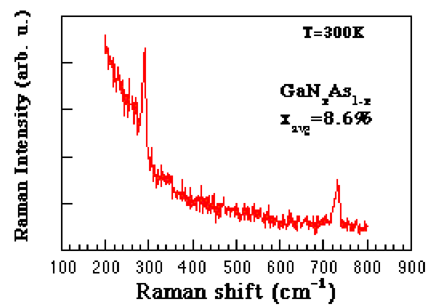

Figure 6. Depolarized Raman spectrum measured at room temperature for an As-rich GaN_xAs_{1-x} layer with 8.6% average nitrogen concentration.

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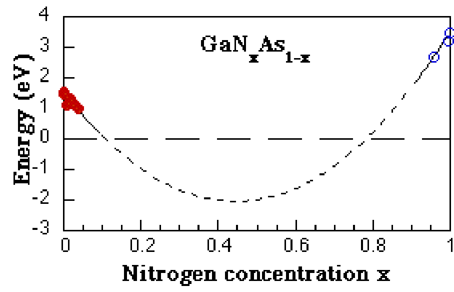

Figure 7. The band-gap energy of GaN_xAs_{1-x} as a function of nitrogen concentration. Experimental results are shown by the solid circles for absorption data and by the open circles for the PL measurements. The solid line is fitting of E_g using parabolic law with b = -18 eV (the part of the calculated curve in the inexperienced region of nitrogen concentrations is shown by the dashed line).

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