

The Effect of Al in Plasma-assisted MBE-grown GaN

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ABSTRACT

We have grown GaN, with addition of a 0.10 to 0.33 % Al, on sapphire(0001) substrates by solid-source RF-plasma assisted MBE. The Al-concentration was determined by secondary ion-mass spectrometry and Auger-electron spectroscopy, while the layer quality was assessed by photoluminescence and high-resolution scanning electron microscopy. Microscopy revealed a meandering pattern and a surface roughness varying with Al-content. The smallest surface roughness was obtained at 0.10 % Al. Photoluminescence revealed two main peaks attributed to the neutral donor-bound exciton. Its energy increased slightly with Al-concentration, which established a correlation between the Al-concentration and the band gap.

INTRODUCTION

Optoelectronic devices, based upon heterostructures of GaN and its ternary AlGa_xN, have attracted great interest during the recent years. By varying the Al-content the whole ultraviolet range around 3.4 - 6.2 eV can be covered [1,2]. It has earlier been shown that GaN surface morphology can be improved during GaN molecular beam epitaxy (MBE) growth by adding In as a surfactant, enhancing the migration of the impinging Ga-atoms on the surface [3,4]. Addition of alloy material in form of isoelectronic doping is easily made in the epitaxy process. Such small concentrations have definite effects by improving the crystalline quality in compound semiconductors in terms of deep levels, unintentional doping concentrations and dislocation density [4]. Earlier photoluminescence investigations on Al_xGa_{1-x}N at low temperatures have shown that the neutral donor bound exciton emission (D⁰,X) dominates in the PL spectrum [5,6].

To the best of our knowledge, no systematic investigation of (Al)GaN with Al at doping concentrations has been undertaken before. In this work we have grown a series of GaN samples containing small amounts of Al. The incorporated concentration ranged from 0.10 up to 0.33%. The aluminium concentration was controlled by the Al furnace temperature and measured by secondary ion-mass spectrometry (SIMS) and Auger-electron spectroscopy (AES). We assessed the layer quality by photoluminescence (PL), Hall effect measurements and high-resolution scanning electron microscopy (SEM). The PL-peaks were deconvoluted to determine the main transitions contributing to the PL signal. Our investigations revealed that adding a small amount of Al, improved the electrical, optical and even morphological properties of the GaN.

EXPERIMENTAL DETAILS

The structures were grown in a Varian GEN II MBE-system with a solid Ga-source and plasma-assisted activation of N₂, using a liquid nitrogen cooled Oxford CARS25 RF-source. The process gas was of 5N5-quality and additionally purified in an Aeronex catalytic gas purifier. The Ga-flux was calibrated by RHEED-oscillations during GaAs growth and converted to the growth rate of hexagonal GaN. The substrates were sapphire

(Al₂O₃), cut along the (0001)-plane, with a 0.5 μm thick Ti-layer on the backside and the growth temperature was measured by a pyrometer. Before insertion into the MBE-system the substrates were ultrasonically degreased in trichloroethylene, acetone and methanol and etched for 15 min at 48 °C in a mixture of HCl:H₃PO₄ (3:1). In the growth chamber the samples were first outgassed at 700 °C for 30 minutes, and thereafter nitridised by exposure to active nitrogen for another 30 minutes. At the same temperature a 110 nm thick GaN buffer-layer was subsequently grown at low growth rate 0.15 μm/h and with minimum nitrogen flow (0.6 sccm) and power (200 W) in order to maintain the RF-plasma of the nitrogen source. A (2x2) reconstruction pattern was obtained after a few minutes growth of the buffer layer, and this surface periodicity remained throughout the whole deposition. We denote the dilute Al_xGa_{1-x}N alloy layers by (Al)GaN which are intermediate between normal alloys with $x > 1\%$ and isoelectronically doped layers, GaN:Al with $x < 10^{-4}$. The (Al)GaN bulk layer was grown (with the Al shutter open) using a nominal Ga-flux corresponding to a growth rate of 1 μm/h. The growth temperature was 750 °C, and RF-power and N₂-flux were 600 W and 3.0 sccm, respectively. The (2x2) reconstruction has been taken as a proof of a Ga-rich growth [7]. For a growth time of 1 h, cross-sectional SEM investigations indicated a thickness of only 600 - 700 nm which is a result of Ga desorption.

A measure of the Al-concentration in the samples was made by SIMS, using the peak intensity ratio between the Al and Ga-signals. The relation between the SIMS-signal and the Al-composition provided by the MBE-growth was fairly linear. The absolute calibration of about 3% Al in GaN was made by AES through the intensity ratio of the Al_{KLL} and Ga_{LMM} peaks. This value was used as the calibration value for the SIMS results. The AES was made with a Perkin-Elmer Physical Electronics PHI 590 equipment. An electron accelerating voltage of 3 keV at 1.5 μA beam current provided an analysis spot size of 3 μm.

For the PL investigation the samples were mounted on the cold finger of a closed cycle Cryogenic Lab System, CSW-204SLB cryostat, allowing the temperature to be varied between 6.5 and 350 K. The excitation was made by a Liconix He-Cd UV laser, giving a typical power of 25 mW at a wavelength of 325 nm. The monochromator was a Spex 270M single grating monochromator with a Photometrix AT200 CCD camera as detector. Hall effect measurements were obtained using 3x3 mm samples in the van der Pauw geometry. The contacting material was In and the contacts were annealed at 425 °C for 2 minutes. To characterise the sample surfaces a JEOL JSM-6301F scanning electron microscope was used.

RESULTS

Low-temperature PL-spectra (at 6.5 K) from two representative samples are shown in Figure 1. The upper spectrum is from pure GaN while the other is from (Al)GaN. The peak is non-symmetric with a low-energy tail, which is reduced with Al-concentration. The spectra have a typical peak width of ~20 meV. In order to resolve the intensity contributions, the peaks were fitted with Gaussian functions. Four Gaussian curves were extracted, except for the GaN-spectrum where 5 individual peaks were used. In this case a very good fit, better than 99%, was obtained to the measured results. This gives an estimated maximum error of ±2 meV in the extracted peak positions. In GaN, the two extracted peaks with the highest energies at 3.476 and 3.470 eV were clearly more intense and had a smaller line width than the others, 10 and 17 meV, respectively. These peaks are neutral donor-bound excitons (D₁⁰,X) and (D₂⁰,X), respectively [8]. The third deconvoluted peak is at 3.45 - 3.46, representing recombination from excitons bound to neutral acceptors (A⁰,X) [6,9]. The two further

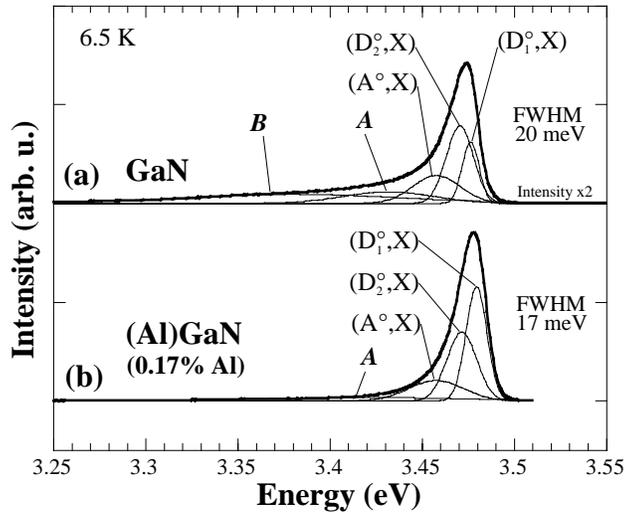


Figure 1. Low-temperature photoluminescence spectra for a) pure GaN and b) (Al)GaN with 0.17% Al. Since the spectra clearly contain a low energy tail, especially for GaN, the peaks have been deconvoluted into 4 (Al)GaN or 5 (GaN) Gaussian peaks. The high-energy peaks were assigned to the (D_1°, X) , (D_2°, X) and (A°, X) , respectively. Peak A is from the recombination of a free hole with an electron bound on an impurity centre, identified with oxygen, while peak B is related to excitons deeply bound to defect centres at dislocations.

peaks, A, at 3.41-3.43 eV and B around 3.36 eV, have clearly lower intensity and much larger line width compared to the previous ones. Peak A in the shoulder region is typical for free-to-bound emission involving shallow oxygen donors [10], while the very broad peaks around 3.36 eV can be attributed to localised excitons, deeply bound to defects, such as dislocations close to the interface [10,11]. At 0.17% Al-content the FWHM of the PL intensity was slightly reduced to 17 meV, due to the decreasing shoulder region and vanishing low-energy tail. This can be assigned to the decreased (A°, X) intensity and partly to the strongly reduced concentration of shallow oxygen donors related to the free-to-bound emission. The peak B vanished by adding small amounts of Al to the GaN, which may be due to improved surface morphology as a result of the reduction of defects.

In Figure 2 the energy position of the resolved peaks (solid lines) are shown as a function of the Al-concentration. The dashed line represents the position of the PL-peak. Its energy increases linearly with Al-concentration given by

$$E_{\text{peak}}^{\text{alloy}} = E_{\text{peak}}^{\text{GaN}} + bx. \quad (1)$$

In our case we get $b = 2.7 \pm 0.3$ eV. This represents the linear change of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ band gap energy. The GaN-matrix is distorted by the Al-atoms and therefore the band gap is modified already at the low compositions of $\sim 0.10\%$ Al. The rate of change for the (D_2°, X) and (A°, X) is similar, but somewhat smaller, to the one for the (D_1°, X) , which strengthens the suggestion that the peak positions are due to the band gap change. The variation of the peak position for A has a well defined minimum at

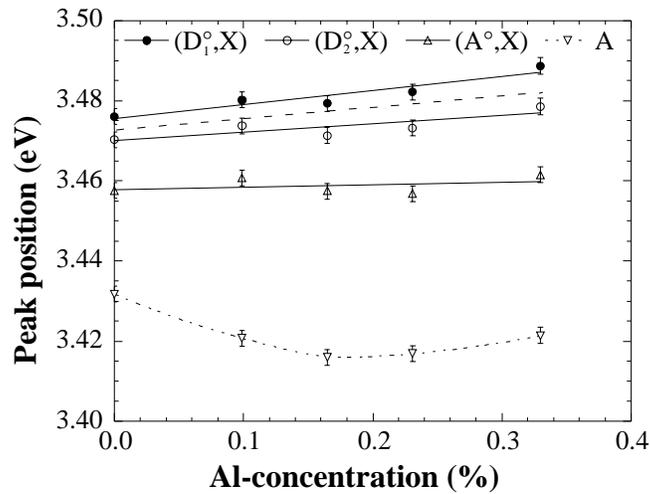


Figure 2. The extracted peak positions as a function of Al-concentration. The lines represent the change of the (D_1°, X) , (D_2°, X) and (A°, X) peaks which is parallel with the increase of the AlGaIn-alloy band gap. The dashed line is the PL-peak position, while the dotted line represents the position of peak A.

~0.17%. However, this may be a result of peak mixing, which can not be resolved at the fitting procedure we used. The relative area of the extracted peaks increased linearly with the Al-concentration, except the (D_1°, X) -peak, which had a definite maximum at ~0.1 %Al. The FWHM of the donor-bound excitons increased more pronounced above 0.1% Al.

In Figure 3, high-resolution SEM images demonstrate the familiar meandering pattern of the GaN surface when grown on sapphire. On the pure GaN-sample, Figure 3a, the presence of crystallites is significant. Adding small Al-concentrations smoothens the surface. One effect in PL was to reduce the peak B, which was attributed to excitons deeply bound to defect centres correlated to dislocations. Our sample surfaces are different from the results in an earlier investigation by SEM on surfaces of AlGaIn, where hexagonally shaped depressions with some micrometre diameter were observed on otherwise smooth surfaces [12].

The Al-concentration in AlGaIn films grown by MBE at high growth temperatures depends on Ga-desorption and the supply of nitrogen [13]. In our films the accuracy of the Al-concentration is determined within 10% based on SIMS measurements and the AES calibration. It is clear that adding a small, well controlled concentration of Al to the GaN has a definite effect on the PL-spectrum. We emphasise the difference in energy between the optical band gap and the excitonic peaks (D°, X) and (A°, X) . These extracted peak positions are close to the measured peak maximum in Figure 1, which therefore follows the plotted lines in Figure 2 within ~ 5 meV. The (D°, X) transitions are believed to be only ~30 meV from the band edge. Therefore, this small difference between the band gap and the experimental peak with its excitonic transitions, support that the shift of the peak positions is due to the increase of the band gap despite the dilute alloy concentration.

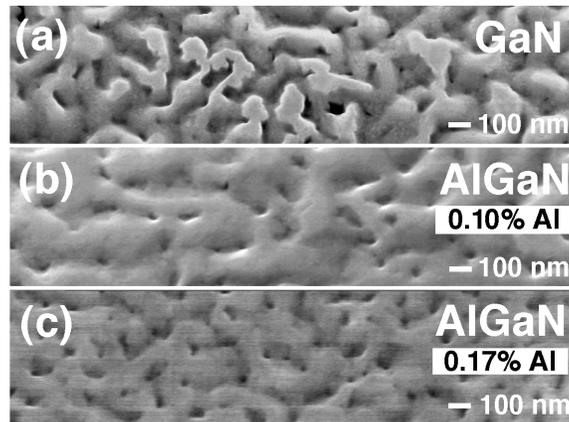


Figure 3. High-resolution scanning electron microscopy images of the sample surfaces with increasing Al-content from GaN to (Al)GaN with 0.17% Al. In general there is an improvement of the surface morphology with Al-content in the layers.

The variation of the band gap, or the PL peak position, with alloy concentration is usually described by

$$E(x) = E_{\text{GaN}} + b \cdot x + c \cdot x^2, \quad (2)$$

where $E(x)$ is the measured peak (band gap), E_{GaN} is the reference peak (the GaN band gap), and b and c are constants (c is the bowing parameter). When the position of the PL-emission follows the change in band gap, almost identical parameters, b and c , are used for band gap and exciton emissions in PL spectra. In some cases the band gap variation has been considered linear, i.e. $c=0$. For small concentrations, $x < 0.05$, the third term in the quadratic approximation is negligible. The values of b range from 0.64 [14] to 2.8 [15]. Most measurements have been made for x -values above 5% and typically much larger values. The slope in Figure 2 depends very much on the accuracy in determination of the Al-concentration and contributions to the band gap from strain due to differences in lattice constant and thermal expansion coefficients. The strain effect is believed to be limited at thin film thicknesses, below 1 μm , since the columnar GaN-structure is formed to relax strain energies, but peak shifts of 11 meV due to strain have been reported [6]. From these considerations we estimate $b=2.7 \pm 0.3$. The ~ 4 meV increase in band gap at only 0.10% Al is due to the relatively short distances between the isoelectronic atoms, $\sim 18 \text{ \AA}$ which is enough to modify the band gap due to the shorter bonding length around the Al-atoms.

During growth of GaN by MBE, impurities from oxygen contamination of the nitrogen gas will be introduced together with the activated nitrogen and incorporates in the layer besides the column III material. The unintentional doping of the GaN by oxygen results in free electrons in the conduction band. Since both aluminium and oxygen are reactive, it is expected that the Al/O-ratio affects the incorporation in the alloy as well as the free electron concentration. The electrical characteristics change with Al-concentration, and details of this will be reported elsewhere.

As shown in the high-resolution SEM images in Figure 3, the concentration of the small dark areas, which are local hollows, have only a low or no dependence on the aluminium concentration. These are a result of the lattice mismatch which is almost constant. It is also clearly notable that the average surface smoothness improves with Al-

concentration. This smoothness, and the presence of good RHEED patterns during growth, indicate very flat upper surfaces on the extended 10 - 100 nm wide terraces. A detailed analysis of the morphology shows a somewhat smoother surface for alloy concentrations giving improved electrical characteristics.

CONCLUSIONS

We have grown GaN and (Al)GaN by MBE, and characterised GaN with small Al-concentrations, in the range of 0.10 - 0.33%. The Al-concentration was determined by SIMS and AES. Low-temperature PL-emission indicated a linear increase of the band gap, $E(x) = E_{\text{GaN}} + 2.7 \cdot x$. The PL-peak intensity showed a minimum FWHM at 0.17% Al with 17 meV. The PL-peaks were deconvoluted into the (D_1°, X) , (D_2°, X) , (A°, X) and shallow oxygen donor related peaks. High-resolution SEM analysis of the surfaces showed slightly improved morphology for alloy concentrations around 0.10%. This was confirmed by decreased PL intensities attributed to excitons bound to dislocation sites.

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