MBE Growth of Nitride-Arsenide Materials for long Wavelength Opto-electronics

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ABSTRACT

Nitride-Arsenide materials were grown by molecular beam epitaxy (MBE) using a radio frequency (rf) nitrogen plasma. The plasma conditions that maximize the amount of atomic nitrogen versus molecular nitrogen were determined using the emission spectrum of the plasma. Under constant plasma source conditions and varying group III flux, the nitrogen concentration in the film is inversely proportional to the group III flux (i. e. the nitrogen sticking coefficient is unity). The relationship between nitrogen concentration in the film and lattice parameter of the film is not linear for nitrogen concentrations above 2.9 mole % GaN, indicating that some nitrogen is incorporated on other locations than the group V lattice sites. For films with these higher nitrogen concentrations, XPS indicates that the nitrogen exists in two configurations: a Gallium-Nitrogen bond and another type of nitrogen complex in which nitrogen is less strongly bonded to Gallium atoms. Annealing removes this nitrogen complex and allows some of the nitrogen to diffuse out of the film. Annealing also improves the crystal quality of GaAsN quantum wells.

INTRODUCTION

Group III-Nitride-Arsenides are promising materials for 1.3μm and 1.55μm telecommunications optoelectronic devices grown on GaAs substrates[1,2,3]. The role of nitrogen is two fold: the nitrogen causes the bulk bandgap to decrease dramatically and the smaller lattice constant of GaN results in less strain in InGaNAs compared to InGaAs. However, the growth of such nitride-arsenides is complicated by the difficulty of generating a reactive nitrogen source and the divergent properties of nitride and arsenide materials. The luminescence properties of InGaNAs deteriorate rapidly with increasing nitrogen concentration[4]. It is common to increase the luminescence efficiency of these InGaNAs quantum wells by a short high temperature anneal[3].

In the present study, growth of nitride-arsenides was performed by elemental source MBE using a rf nitrogen plasma. We have investigated the incorporation of nitrogen using X-Ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), high resolution X-ray diffraction (HRXRD), and electron microprobe. The effect of thermal annealing on crystal quality and nitrogen incorporation was studied using XPS and HRXRD.

DETAILS OF MBE NITRIDE-ARSENIDE GROWTH

The growth of Nitride-Arsenides was performed in a Varian Gen II system by elemental source MBE. Group III fluxes are provided by thermal effusion cells, dimeric arsenic is provided by a thermal cracker, and reactive nitrogen is provided by an rf plasma cell. The plasma cell is operated at 250-350 W with a nitrogen gas flow of 0.1-0.5 sccm. Typical growth rates are 0.4-4 Å/s. These conditions allow to add up to 5 atomic percent nitrogen to III-V materials.

To minimize ion damage to the surface of the growing film, an rf plasma is used to generate atomic nitrogen[5]. The exit aperture of this source was custom designed so that the plasma can operate with low nitrogen flow rates without compromising the uniformity of the generated atomic nitrogen. The plasma conditions that maximize the amount of atomic nitrogen versus molecular nitrogen were determined using the emission spectrum of the plasma (see Figure 1). The intensity of the first set of bands at approximately 550, 580, and 650 nm is a measure of the amount of molecular nitrogen; the intensity in the bands at 740, 820 and 870 nm is proportional to the amount of atomic nitrogen present in the plasma[6]. Both the ratio of atomic nitrogen versus molecular nitrogen and the total amount of atomic nitrogen created, increase with increasing plasma power. For our plasma source design, the plasma power is more effective than the nitrogen flow rate to control the generation of atomic nitrogen. We optimized the start-up procedure of the plasma to maximize the generation of atomic nitrogen.

We have verified with SIMS that the impurity concentration (H, O, C and B) in our films is below $2.10^{17}/cm^3$.

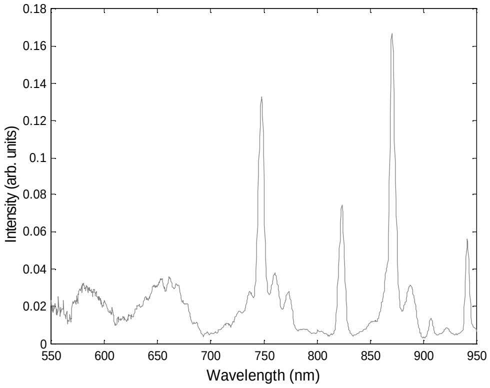

Figure 1. *Emission spectrum of the rf nitrogen plasma for an nitrogen supply of 0.25 sccm and power of 300 W.*

STUDY OF NITROGEN INCORPORATION

For the plasma operating with 300 W power and 0.25 sccm nitrogen flow, the nitrogen concentration in the film is dependent on the gallium arsenide (GaAs) growth rate as shown in Figure 2. The nitrogen concentration is inversely proportional to the GaAs growth rate because the atomic nitrogen is so reactive that all the supplied atomic nitrogen is consumed to form GaNAs. N_2 formation is limited because the generated amount of atomic nitrogen is small compared to the As_2 and Gallium overpressures in the MBE system[7]. As the films are grown under an As_2 pressure of twenty times the gallium pressure, the GaAs growth rate is only dependent on the Gallium flux. Therefore, the nitrogen concentration of the InGaNAs films can be controlled solely by the group III flux. This indicates that the InGaNAs system might have some advantages in terms of yield and reproducibility compared to the arsenide-phosphide system where the group V flux control is very critical and strongly temperature dependent [8,9].

We have observed that the relation between lattice parameter and nitrogen concentration in GaNAs films is not linear for nitrogen concentration above 2.9 mol % GaN (see Figure 3). This indicates that at high nitrogen concentration, some nitrogen is being incorporated on other locations than the group V lattice sites. The fact that nitrogen is such a small atom compared to gallium and arsenic makes this incorporation on other sites than the group V lattice sites more likely.

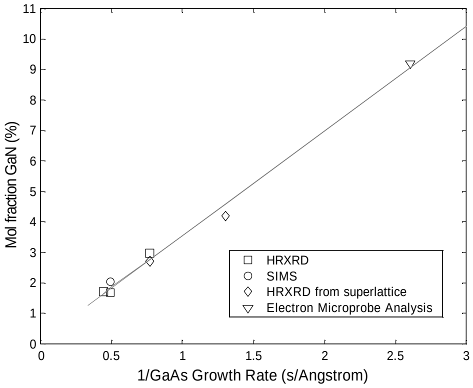

Figure 2. *Concentration of nitrogen in GaNAs films as function of the GaAs growth rate. The nitrogen concentration was measured by HRXRD, SIMS, and electron microprobe analysis. The nitrogen plasma was operated with a power of 300 W and a nitrogen flow of 0.25 sccm.*

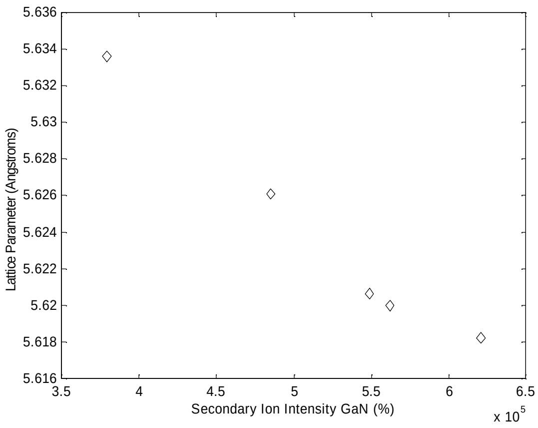

Figure 3. *Lattice parameter of different GaNAs films as function of nitrogen concentration The lattice parameter of the films was determined using HRXRD in a Philips Materials Research Diffractometer. The nitrogen concentration was measured by SIMS in an CAMECA IMS 4.5f instrument.*

XPS analysis was done to confirm this hypothesis. The N(1s) spectrum for a $GaN_{0.06}As_{0.94}$ film covered with GaAs cap (see Figure 4) indicates that the nitrogen exists in two configurations: a Ga-N bond and another nitrogen-complex in which N is less strongly bonded to Ga atoms. As the GaNAs layer is buried, surface contamination should have no influence on the shape of the nitrogen peak. Rapid thermal annealing (30 seconds at 775 ºC) removes this nitrogen complex but also results in out-diffusion of the nitrogen.

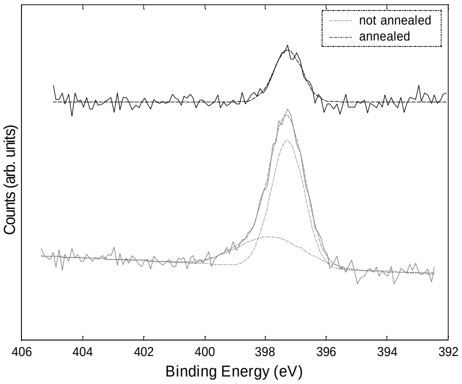

Figure 4. *XPS signal from N(1s) peak from an annealed and an not annealed $GaN_{0.06}As_{0.94}$ film measured in an PHI 5800 instrument. The Gallium Auger peak around 398 eV was removed by dividing the obtained spectrum by the spectrum of a GaAs reference sample. Annealing was done for 30 seconds at 775 ºC in an AG heatpulse 310.*

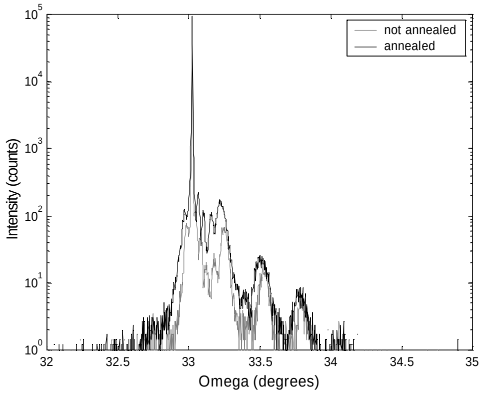

Figure 5. *HRXRD rocking curve from an annealed and not annealed 6 period 70 Å* $GaN_{0.05}As_{0.95}$*/130 Å GaAs superlattice. Annealing was done for 10 seconds at 775 ºC in an AG heatpulse 310.*

Rapid thermal annealing and the resulting disappearance of this nitrogen complex also improves of the crystal quality of $GaN_{0.05}As_{0.95}$ quantum wells as indicated by the increased X-ray intensity diffracted from an annealed 6 period 70 Å $GaN_{0.05}As_{0.95}$/130 Å GaAs superlattice (see Figure 5). The out-diffusion of the nitrogen is responsible for the slight shift of the peaks.

CONCLUSION

Growth of Nitride-Arsenides was performed by MBE using an rf plasma to generate atomic nitrogen. We have demonstrated that the nitrogen concentration can be controlled accurately by the group III growth rate as the nitrogen concentration is inversely proportional to the group III growth rate. Nitrogen exists in two binding configurations in as grown Nitride-Arsenides. We have investigated the effect of anneal on crystal quality and nitrogen binding configuration using HRXRD and XPS.

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