INFLUENCE OF DEPOSITION CONDITION ON ALN GROWTH BY MOVPE

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Abstract

AlN is a very perspective substrate material for $A^{III}N$ semiconductor growth. The AlN growth was performed in horizontal RF heated MOVPE reactor using trimethylaluminium (TMAl) and ammonia. The influence of V/III ratio and carrier gas composition on the structure and morphology of the layers were investigated. A significant effect of V/III ratio on layer structure and morphology was observed. High V/III ratio led to deterioration of surface morphology due to the pre-reaction of precursors in the gas phase. A positive effect of high nitrogen concentration in the carrier gas on the surface morphology was observed. Finally the influence of substrate treatment by high temperature annealing in ammonia atmosphere (nitridation) as well as deposition of low temperature buffer layer on the properties of deposited layers were investigated. The results show crucial importance of substrate nitridation on the layer structural and morphological properties. Also the low temperature buffer layer of AlN significantly improves the quality of the layer.

Keywords: A^{III} Nitrides, Aluminum nitride, MOVPE, Thin films

1. INTRODUCTION

AIII nitrides have attracted great attention due to its unique properties in the last decades. A^{III} nitrides like GaN and its ternary alloys are used in modern opto-electronic and microelectronic devices [1]. Substrates with large lattice mismatch are broadly used for the growth of $A^{III}N$ heterostructures applied in these devices [2]. Most commonly used substrates like sapphire exhibit 16% lattice mismatch and also lower thermal conductivity compared to aluminum nitride [3,4]. Another broadly used substrate, 6H-SiC, has lower lattice mismatch and higher thermal conductivity compared to sapphire [5]. However, extremely high cost of semi-insulating substrates represent a significant disadvantage for broad commercial application. The heat management in high power devices is one of the crucial topics [6]. Compared to most broadly used substrates like sapphire and silicon carbide, aluminium nitride exhibits higher thermal conductivity and a substantially lower lattice mismatch [7]. Currently available AlN substrates are usually produced using PVD methods. Such substrates are notably more expensive compared to standard substrates and these materials are also available only in a limited size.

In this work we investigated the influence of basic deposition parameters on the structure and morphology of the AlN layers. The AlN/c-plane sapphire pseudosubstrates can be applied for the deposition of $A^{III}N$ nitride heterostructures for electronic and opto-electronic applications. The deposition was performed using metal-organic vapor phase epitaxy (MOVPE) technology in horizontal inductively heated reactor. The basic growth parameters like precursor ratio (V/III ratio) and carrier gas composition was investigated. The deposition was performed at high temperatures (1100 - 1150 °C) in order to increase the surface diffusion and improve morphology of the layer. The optimization of deposition parameters led to high quality epitaxial layers suitable for application in electronic devices. In addition the influence of substrate pretreatment and low temperature AlN buffer layer on the properties of AlN layer were investigated in detail.

2. EXPERIMETAL

2.1. Procedures

The deposition of AlN layers was performed in horizontal inductively heated quartz reactor. The separated inlets for AIII precursor (trimethylaluminium) and nitrogen precursor (ammonia) were used. The c-plane sapphire substrates (0001) with the 0.2° misorientation were used for deposition of AlN layers. Trimethylaluminum (TMAl) was used as an Al precursor and ammonia was used as a nitrogen source. Hydrogen was used as a carrier gas for TMAl. Before the deposition the sapphire substrates were annealed in the deposition reactor in hydrogen atmosphere at 1050 °C and 50 mbar pressure for 10 minutes. Subsequently the sapphire substrates were annealed in ammonia atmosphere at 1100 °C and 50 mbar pressure for 3 minutes. This step is called substrate nitridation, since monolayer of AlN is formed on the sapphire substrate. The deposition of AlN layers was preformed using the total gas flow of 3500 ml/min and the deposition pressure of 100 mbar. The hydrogen carrier gas flow through TMAl bubbler was 15 mL/min at the pressure of 1000 mbar and temperature of 17 °C which corresponds to the molar mass flow of TMAl 13.1 μmol/min. The deposition temperature was in the range of 1100 - 1150 °C. The concentration of nitrogen was varied in the range up to 40 % by changing the composition of ammonia carrier gas from 100% hydrogen up to 100% nitrogen. In the next series the V/III ratio was varied by changing the ammonia flow and keeping all other deposition parameters constant (total flow 3500 mL/min; pressure 100 mbar; temperature 1100 °C; hydrogen carrier gas). Finally the influence of high temperature nitridation step on the layer properties as well as introduction of low temperature AlN layer deposited at 700 °C for 5 minutes were investigated.

2.2. Characterization

An inVia Raman microscope (Renishaw, England) was used for Raman spectroscopy measurements in backscattering geometry with a CCD detector. Nd-YAG laser (532 nm, 50 mW), with 50x VIS-NIR objective, was used as a radiation source. Instrument calibration was achieved using a silicon reference which gave a peak position at 520 cm^{-1} and a resolution of less than 1 cm^{-1}. To ensure a sufficiently strong signal and to avoid radiation damage of the samples, the laser power used for these measurements ranged from 0.05 to 5 mW. Characterization by Atomic Force Microscopy (AFM) was performed on NT-MDT Ntegra Spectra (NT-MDT) in tapping mode. The layer thickness was measured by optical reflectance spectroscopy. X-ray diffraction was performed with Bruker D8 Discoverer diffractometer.

3. RESULTS AND DISCUSSION

Several parameters strongly influence the growth of AlN layers. One of the crucial parameters is the molar mass ratio of trimethylaluminum and ammonia. This value was varied in the rage of 543 to 1630 showing strong influence on the layer properties like dislocation density represented by full width at half maximum of (0002) reflection rocking curve. The sample notation involves the actual V/III value used for the deposition. The depositions were performed at 1100 °C and total pressure of 100 mbar. The V/III ratio variation was performed by keeping constant flow of trimethylaluminum and varying ammonia flow at a constant total flow of 3500 mL/min in all experiments. For the V/III ratio of 931 the influence of reduction of total precursor flow on the investigated parameters was also investigated by reducing the flow of ammonia and trimethylaluminum on half in comparison with the other experiments. At high V/III ratio the pre-reaction in gas phase took place and the formed nanoparticles can significantly influence the morphology of the layers. This was clearly visible on the layer roughness represented by RMS value for 3x3 μm scan obtained by atomic force microscopy. The surface morphology is shown in **Figure 1**. The dependence of surface roughness on V/III ratio is shown in **Figure 2a**. The results show a strong impact of precursor ratio in the gas phase on the layer roughness with optimal values below 1200. The reduction of reactant flow also did not have significant impact on the layer morphology in comparison with other experiments performed at low V/III ratio. The dislocation density was determined by measuring FWHM of (0002) rocking curve. In this direction the measurement is sensitive towards screw and mixed type of dislocations. A significant narrowing of FWHM was observed with the reduction of V/III ratio showing optimal value around 800 - 1200. The experiment performed with reduced precursor flow revealed a substantial reduction of dislocation density with the layer thickness reduction. The results are summarized in **Figure 2b**. The growth rate was strongly dependent on the V/III ratio showing almost linear increase of growth rate with V/III ratio. However, compared to other nitrides like GaN the growth rate was relatively low ranging from 300 to 500 nm/hour. The decrease of precursor flow by 50% led to the growth rate reduction by about only 35%. The dependence of growth rate on the V/III ratio is shown in **Figure 2c**.

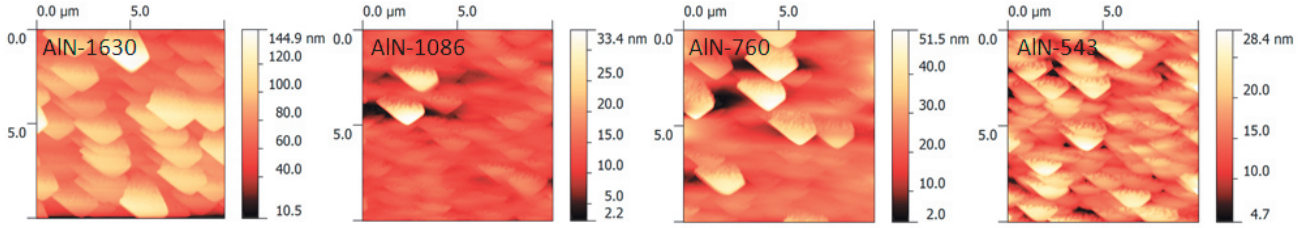

Figure 1 The surface morphology of the AlN layers growth with different V/III ratio

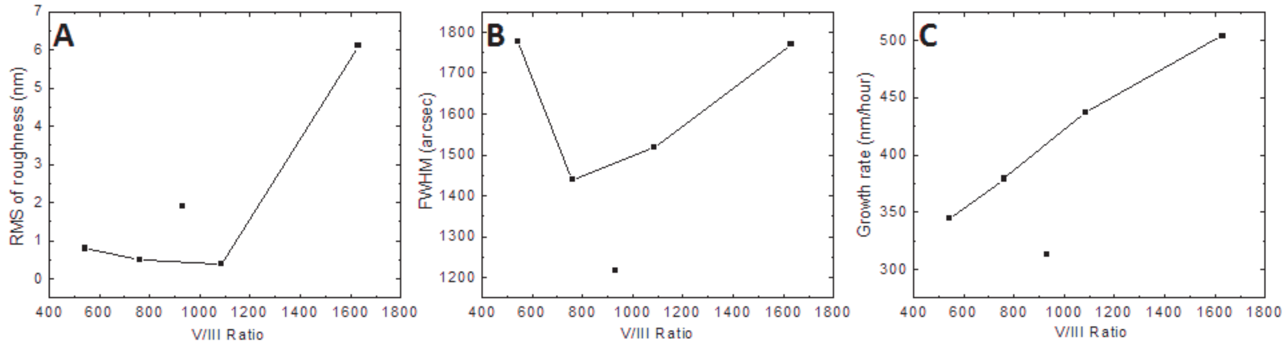

Figure 2 The dependence of surface roughness (A), FWHM of (0002) rocking curve (B) and growth rate on the V/III ratio

The layers were further characterized by Raman spectroscopy. Due to the relatively low thickness of the layers, a strong signal from the supporting sapphire substrate was observed. The bands observed at 379 cm ^{1}, 418 cm^{-1}, 431 cm^{-1}, 450 cm^{-1}, 578 cm^{-1} and 751 cm^{-1} originate from sapphire substrate. In the AlN up to 6 Raman active phonon modes can be observed, however for the excitation perpendicular to the c-plane direction only few of them are clearly visible (E_2(low); E_2(high) and A_1(LO)). Due to the low thickness only a weak band of E_2(high) phonon mode at 656.3 cm^{-1} can be seen on the AlN layers. On the sample deposited with V/III ratio of 543 (Sample AlN-543) an extremely weak E_1(TO) phonon mode at 670.4 cm^{-1} can be also found. Raman spectra are shown in **Figure 3**.

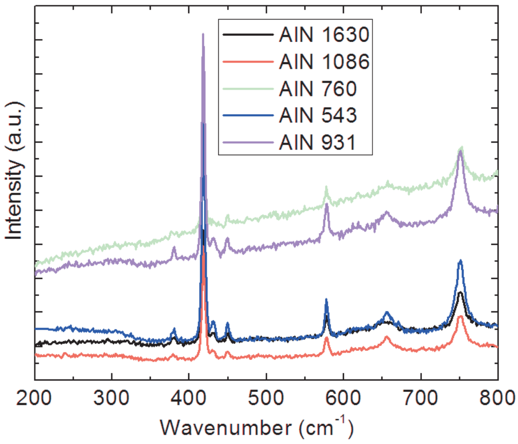

Figure 3 The Raman spectra of AlN layers prepared using various V/III ratios

Furthermore the influence of nitrogen concentration in the carrier gas on the layer properties was investigated. The presence of nitrogen in the carrier gas can considerably influence the layer growth due to its different heat conductivity and also diffusion process of the precursor to the substrate surface. The experiments were performed using the V/III ratio 1086 and the deposition pressure 100 mbar. The deposition was performed at 1150 °C keeping the total flow at 3500 mL/min. The concentration of nitrogen in the hydride line was varied from 0 to 100% corresponding to the variation of nitrogen concentration in gas phase from 0 up to 40 %. In comparison with the layer deposited at 1100 °C a sizable suppression of the growth rate was observed. The surface roughness investigated by AFM shows only minimal differences in the surface morphology of the layers deposited with different nitrogen concentration in the gas phase. The corresponding AFM images are shown in **Figure 4**. The surface roughness represented by the RMS value for 3x3 µm scan were in the range of 0.5 to 2 nm for all experiments without any evidence of systematic dependence of surface roughness on the concentration of nitrogen in the gas phase. Also in comparison with samples deposited at 1100 °C no significant difference was observed. The dependence of roughness on the concentration of nitrogen in the gas phase is shown in **Figure 5a**. The structure quality of the layer represented by FWHM of (0002) rocking curve was notably improved using higher deposition temperature. This result shows high influence of deposition temperature on the structural quality of the layer. On the other hand, the concentration of nitrogen in carrier gas did not have any significantly impact on the structural characteristic like screw and mix-type dislocation density and the values were in the range of 400 - 500 arcsec. The dependence of FWHM of (0002) rocking curve on the concentration of nitrogen in the gas phase is shown in **Figure 5b**. The increased nitrogen concentration in the gas phase mostly influences the growth rate. Compared to previous set of experiment, the increase of deposition temperature led to a substantial reduction of growth rate. Also the introduction of nitrogen in the gas phase led to further reduction of growth rate from about 280 nm/hour in pure hydrogen down to about only 170 nm/hour for 40% nitrogen. The results are shown in **Figure 5c**.

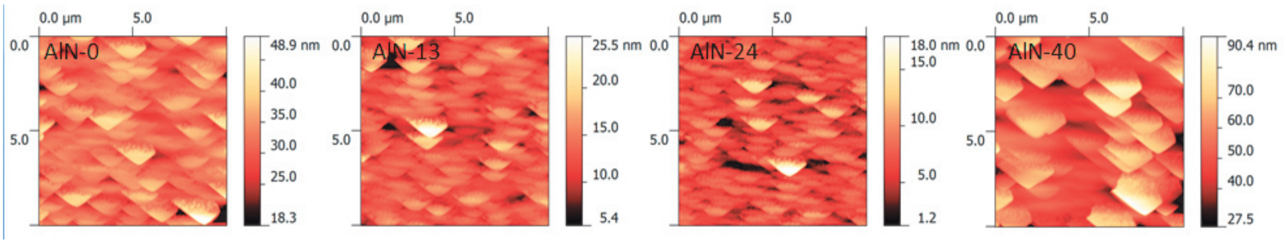

Figure 4 The surface morphology of AlN layers deposited using different concentration of nitrogen in carrier gas

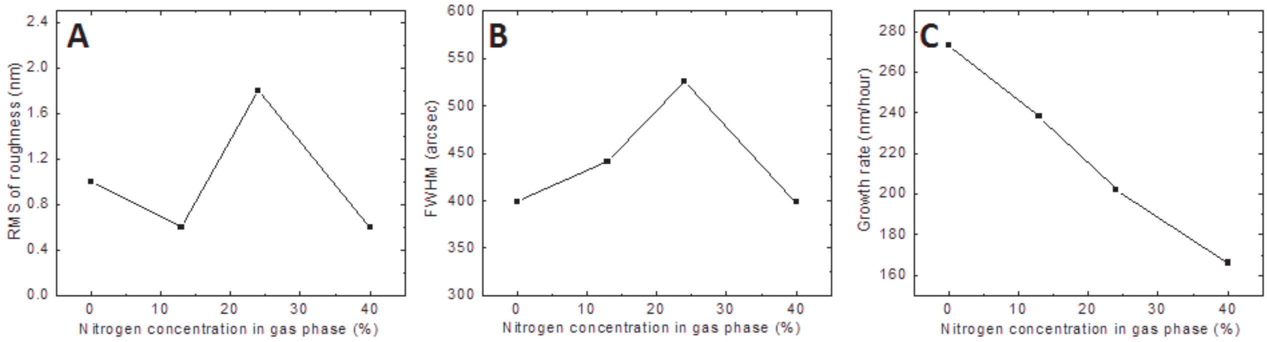

Figure 5 The dependence of surface roughness (A), FWHM of (0002) rocking curve (B) and growth rate on concentration of nitrogen in gas phase

Finally the influence of inserting a nitridation step in the growth process and the deposition of low temperature AlN interlayer on the obtained AlN layers properties were investigated. These experiments were performed using V/III ratio of 1086 and deposition temperature of 1100 °C and hydrogen as a carrier gas. The results show a crucial effect of nitridation step in the growth process on the quality and morphology of the obtained layers. Noticeable differences can be seen on the layer morphology of the obtained by AFM (**Figure 6**). The absence of surface monolayer on sapphire led to an induction of 3D growth and a significant increase of layer roughness. Also the application of low temperature AlN layer led to highly rough surface. The surface roughness increased from 3.4 nm for the layer deposited with nitridation step to 13.0 nm for the layer without including it. Similarly the application of low temperature AlN buffer layer increased the surface roughness to 15.0 nm (10x10 μm scan).

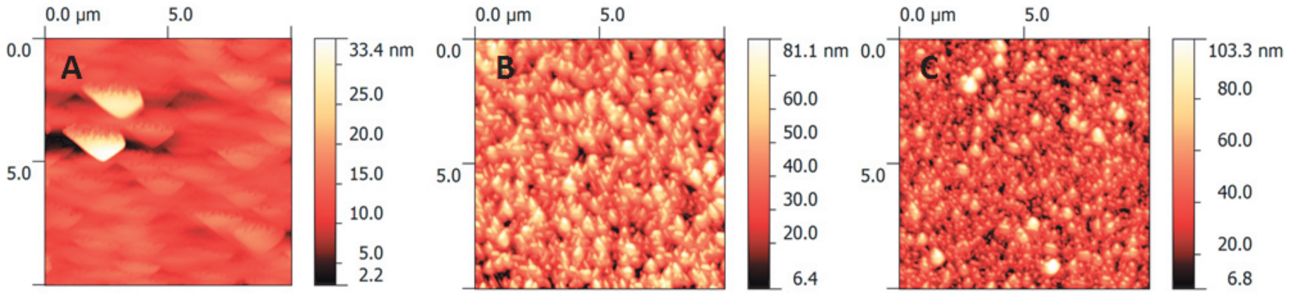

Figure 6 The surface morphology of the layer deposited with nitridation buffer layer (A) and without (B) and with application of low temperature AlN buffer layer (C)

The impact of nitridation step on the layer structure was further investigated using X-ray diffraction. The significant differences of the FWHM of the rocking curve for (0002) reflection were observed. The introduction of substrate nitridation step to the AlN growth process led to the reduction of FWHM from 2800 arcsec on 1519 arcsec showing an important improvement of layer structural quality and reduction of dislocation density. This was further deduced by application of low temperature AlN buffer layer, which led to further reduction of FWHM value to 921 arcsec. However this improvement was accompanied by a considerable increase of layer roughness. The growth rate was influenced by the application of nitridation step only slightly increasing from 438 nm/hour to 446 nm/hour for the layer growth with and without nitridation step. On the other hand, the application of low temperature AlN buffer layer significantly improved the growth rate which reaches 703 nm/hour.

4. CONCLUSION

In our contribution we showed a significant influence of growth parameters on the structural and morphological properties of AlN epitaxial layers prepared on sapphire substrates. The deposition by MOVPE using trimethylaluminium and ammonia as Al and N precursors was performed at temperatures in the range of 1100-1150 °C and pressure of 100 mbar. The V/III ratio (molar ratio of ammonia and aluminum in gas phase) has a strong impact on the layer morphology, structural properties as well as growth rate. High V/III ratio led to an increase of growth rate, however also to higher surface roughness and dislocation density (represented by FWHM of (0002) rocking curve). The influence of deposition temperature was also significant, especially on the structural properties of the layers. The increase of deposition temperature by 50 °C considerably reduced the FWHM of rocking curve of (0002) reflection. The influence of carrier gas composition with up to 40 % of nitrogen has a significantly lower effect on the surface morphology and structural properties. The increase of nitrogen concentration in the hydrogen carrier gas led to an increase of growth rate. Further experiments showed crucial importance of substrate annealing in ammonia (nitridation step) on the structure as well as on the surface roughness of AlN layers. The application of low temperature AlN buffer layer significantly suppressed the FWHM of rocking curve of (0002) reflection, but it simultaneously resulted in an increase of surface roughness.

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