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Sublimation Epitaxy of AlN layers grown by different conditions on 4H-SiC substrates

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Epitaxial layers of aluminium nitride were grown at temperature 2100 °C on 10x10 mm^2 4H-SiC substrates via a sublimation-recondensation method in an RF heated graphite furnace. The source material was polycrystalline sintered AlN. Growths of AlN layers in vacuum and pure nitrogen at 20 mbar were compared. MA maximum growth rate of 70 μm/h was achieved in a pure N_2 atmosphere. The surface morphology reveals the hexagonal symmetry of the seeds, suggesting an epitaxial growth. This was confirmed by High-Resolution X-Ray Diffraction. The spectra showed a strong and well defined (0002) reflection positioned at 36.04° in a symmetric θ-2θ scan for both samples. Micro-Raman spectroscopy revealed that the films had a wurtzite structure. Rutherford Backscattering Spectrometry indicated the quality with a relative χ_{min} parameter 0.68.

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1. Introduction

Aluminium nitride is a wide-band gap material, with a direct band gap of 6.2eV (at 300 K) [1]. This material can be proposed as an alternative dielectric material for high – temperature and high-power electronic applications, due to good thermal stability in SiC-based devices [2,3]. The direct band gap transition of the material is in the ultra violet (UV) region, which makes AlN a candidate material for UV-optoelectronic applications [4,5].

Sublimation growth of AlN crystals in the sandwich system has been studied by Segal et al. [6], the effect of contamination from the crucible has been investigated by Balkas et al. [7, 8] and in our previous work [9].

In this study, we investigated AlN growth on 4H-SiC (0001) Si at a source temperature 2100 °C in vacuum and pure nitrogen at 20mbar.

2. Experimental

Sublimation growth experiments were conducted in a RF heated graphite furnace. A sketch of the experimental configuration of the crucible and growth assembly is shown in Fig. 1.

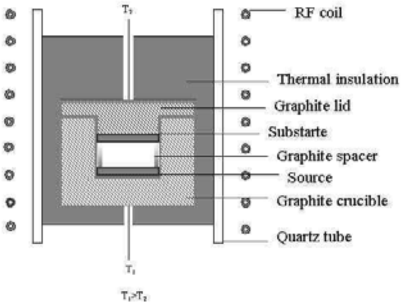


Fig. 1. Sublimation growth set-up.

As a source material, polycrystalline sintered AlN was used. It was chosen over loose powder to reduce contamination from the surface oxide and hydroxide, and to allow precise separation between the source and the seed.

Single crystal, Si face 4H-SiC(0001) wafers (10mm × 10mm), 8° vicinal cut toward $[11\bar{2}0]$, were used as seeds. All the wafers and source were degreased in boiling organic solvents for 5 min, H_2SO_4:H_2O (3:1), HCl:H_2O:H_2O_2 (1:1:1) for 10min, dipped in HF:H2O (1:1) for 20s and blown in nitrogen before loading into the furnace. The separation distance between the source and seed was, and the temperature difference was about 7°C.

The growth temperature was measured in-situ by an optical pyrometer focused on the top and bottom lid of the graphite crucible. The backside of the seed was covered by a graphite cap to reduce SiC dissociation. The source temperature was 2100 °C and was kept constant during the growth process by controlling the furnace output power. The deposition time was 1h for the both samples grown in vacuum at 2×10^{-5} mbar and grown at a fixed nitrogen pressure of 20 mbar. The thickness of the sample was measured with a mechanical indenter, the accuracy being about 1μm.

The AlN crystals were first characterized by Nomarski interference contrast microscopy at a magnification of 20×.

The structural properties were investigated by high resolution x-ray diffraction using a Philips MRD triple-axis diffractometer equipped with a symmetric or asymmetric four crystal Ge220 monochromator and double and triple bounce Ge220 analyzer crystals.

Micro-Raman measurements were carried out using a Microdil 28 (DILOR) triple spectrometer equipped with an optical microscope. A 100× objective was used to focus the incident laser beam to a spot of a 1-2μm diameter and to collect the scattered light in a backscattering geometry. A 488nm Ar^+ laser line was used for excitation. The laser power on the sample was 15 mW.

The crystal quality was studied by Rutherford Backscattering Spectrometry (RBS), using 2.4 MeV He^4 ions. All the spectra were taken in random geometry.

3. Results and discussion

AlN layers with thicknesses of 20 μm and 70 μm thick were obtained in vacuum and nitrogen ambient respectively. The growth rates were determined to be 20 and 70 μm/h respectively. The lower growth rate in vacuum could be explained with the critical pressure (P_c) which should be higher than the total pressure (P). The total pressure could be expressed as:

$$P = P_{Al}^{0} + P_{N_2}^{0} \tag{1}$$

where P_i^o is the partial pressure of the species whereas the critical pressure P_c can be calculated as:

$$P_c(T) = \frac{3}{2}\left[2K(T)\right]^{\frac{1}{3}} \tag{2}$$

where K(T) is the equilibrium constant of the heterogeneous reaction of AlN formation from the vapor phase.

At $P \ll P_c$, the gas flow pattern had a more pronounced two-dimensional (2D) form (both the source and seed sublimed. Under these conditions, the gas mixture had to flow out of the growth cell region which resulted in a reduced growth rate.

Fig. 2 shows optical micrographs of AlN layers grown in vacuum (a) and at a nitrogen pressure of20 mbar (b). The morphology reflects a hexagonal symmetry of the seed, suggesting epitaxial growth.

AlN layer grown in vacuum had lateral grown crystallites (2a) since the higher difference between P_c and P favors more pronounced two-dimensional (2D) growth. Island growth was achieved in a nitrogen ambient (2b).

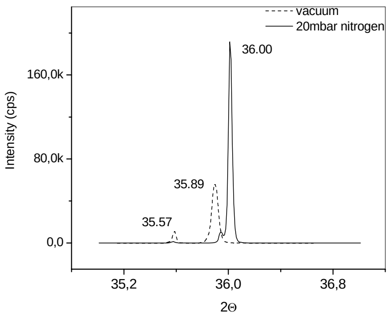
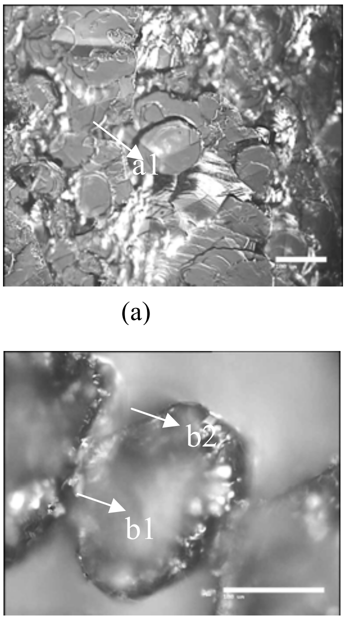


Fig. 3. θ-2θ scan taken from the samples grown at 2100 °C in vacuum and 20 mbar nitrogen ambient. The peak at 35.57 ° is due to the SiC substrate.

Both AlN crystals showed strong and well defined single crystalline XRD patterns. Only the (0002) reflection positioned at around 36° was observed in a symmetric θ-2θ scan, as shown in Fig. 3.

On the other hand, the difference in the sticking probabilities of Al and N_2 (1 and 10^{-4} respectively) [10, 11] results in the fact that the small deviation of 2θ from published data of JCPDS [12] (36.04°) can be reached for an AlN sample grown in nitrogen ambient.



(a)

(b)

Fig. 2. Optical micrograph of an AlN crystal grown: (a) in vacuum 2 × 10^{-5} mbar: a1- rounded hexagonal crystallite (b) in nitrogen ambient of 20 mbar: b1- hexagonal crystallite, b2 – SiC substrate. The scale bar corresponds to 100 μm.

The Raman spectra were obtained with an incident beam parallel to the film surface (the cross section of the sample). In the $Y(ZZ)\overline{Y}$ geometry, where the incident and the scattered polarization are parallel, only the A_1(TO) mode can be detected by Raman spectroscopy. There was no detectable contribution from the forbidden modes, which showed that the AlN layers had a well defined (0001) face of the wurtzite structure - Fig 4a.

Both A_1(TO) lines were shifted to low frequencies compared to published data [13-14], as well as the measured spectra of the AlN source used in our growth process - Fig. 4b. The shift of the A_1(TO) line was smaller for the sample grown in nitrogen ambient.

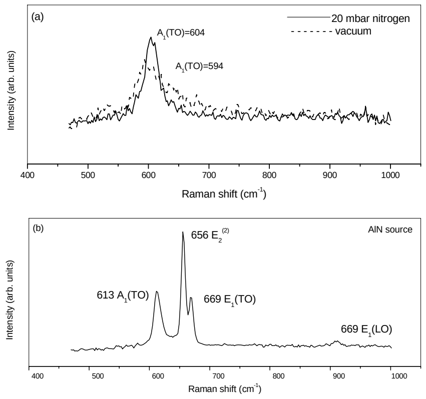


Fig. 4. (a) Raman spectra of wurtzite AlN grown at a source temperature 2100 ℃ in vacuum and a nitrogen pressure of 20 mbar, (b) Raman spectra of the AlN source.

The more pronounced shift of the A_1(TO) line for the sample grown in vacuum could be explained by an insufficiency of nitrogen molecules on the growth seed, which favors carbon and/or oxygen acting as highly soluble impurities in AlN by substituting nitrogen. The higher intensity of the A_1 (TO) line grown in nitrogen confirms the better crystalline quality.

The Rutherford backscattering spectra of both compared materials are displayed in Fig. 5.

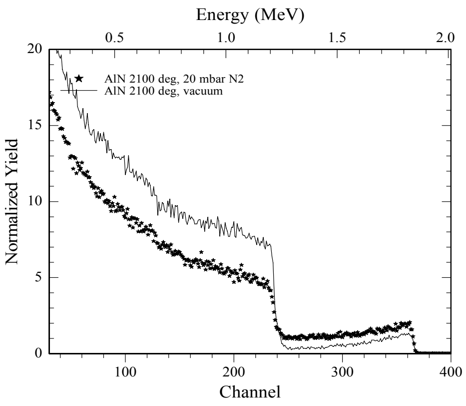


Fig. 5. The Rutherford backscattering spectra of AlN grown at source temperature 2100 ℃ in vacuum and in nitrogen, pressure 20 mbar.

Since the spectra were taken with the same position and geometry of the detector, the line with dots corresponds to AlN grown in nitrogen ambient suggests better crystallinity (a better channelling effect) and a relatively low level of impurities. The relative minimum yield χ_{min} is used as a measure of crystal quality, and is defined as the ratio between the backscattering ion yields for both samples. The relative χ_{min} parameter in this case was equal to 0.68, suggesting a reduced defect density for the sample grown in nitrogen ambient. High-precision spectra simulation (not shown here) showed a homogeneous elemental depth distribution, where the Al/N ratio was equal to unity for the sample grown in N_2 ambient.

4. Conclusion

In this work, we have studied the effect of vacuum and nitrogen ambient on the growth rate and crystal structure of AlN layers grown by a sublimation technique. We established that a nitrogen pressure favors the growth rate (70 μm/h). The results of optical microscopy revealed a hexagonal symmetry that suggests epitaxial growth. High-resolution XRD and Raman spectroscopy confirmed a better monocrystalline wurtzite structure for samples grown in nitrogen ambient. Rutherford backscattering spectroscopy showed a relative χ_{min} parameter equal to 0.68, proving the improvement of the crystal quality for the layer grown in nitrogen ambient. The results obtained in this study showed that nitrogen ambient is crucial in the growth of monocrystalline AlN.

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