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Atomic Layer Epitaxy Growth of AlN Thin Films

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ABSTRACT. AlN thin films were grown by the Atomic Layer Epitaxy (ALE) technique employing AlCl_3 and NH_3 as precursors. A growth rate of $1.0 \text{ \AA}/\text{cycle}$ was obtained in experiments carried out at $500 \text{ }^\circ\text{C}$. The films deposited onto soda lime glass substrates were polycrystalline exhibiting a strong preferred orientation in the $[001]$ direction. X-ray Photoelectron Spectroscopy (XPS) measurements revealed that the films contained oxygen and chlorine as impurities.

1. INTRODUCTION

Owing to its large band gap, thermal and chemical stability, high thermal conductivity and thermal expansion coefficient well matched to those of Si and GaAs, AlN has been considered as a potential material for dielectric and passivation layers for microelectronic devices, particularly for high temperature applications. Transmission over a broad wavelength region, relatively high refractive index and high hardness make AlN an interesting material for optical coatings. In addition, considerable research effort has been devoted to epitaxial AlN films, especially to $\text{Al}_{1-x}\text{Ga}_x\text{N}$ for optoelectronic devices being active in the blue and UV wavelengths, and to the pure piezoelectric epitaxial AlN films for surface acoustic wave devices.

The most commonly employed precursors in CVD growth of AlN have been AlCl_3 or $\text{Al}(\text{CH}_3)_3$ in combination with NH_3 [1]. Most of these processes have, however, suffered from a need of unpractically high growth temperatures, typically above $700 \text{ }^\circ\text{C}$, which has usually been attributed to the thermal stability of NH_3 or to a formation of relatively stable adducts, e.g. $\text{AlCl}_3 \cdot \text{NH}_3$. Recently, Yu *et al.* [2] demonstrated that in the $\text{Al}(\text{CH}_3)_3 - \text{NH}_3$ CVD process the growth temperature can be lowered down to $400 \text{ }^\circ\text{C}$ by confining all the film forming reactions on the substrate surface, thus eliminating possible gas phase reactions including the adduct formation. Likewise, Asif Khan *et al.* [3] reported that while temperatures exceeding $700 \text{ }^\circ\text{C}$ were needed in a conventional CVD to grow epitaxial AlN films from $\text{Al}(\text{C}_2\text{H}_5)_3$ and NH_3 , the Atomic Layer Epitaxy (ALE) technique was capable of producing films with a high quality already at $450 \text{ }^\circ\text{C}$. As distinct from CVD, in ALE the precursors are led onto the substrate alternately [4,5]. The reactant pulses are separated by a purging period to remove all the other precursor molecules except those chemisorbed on the surface of the growing film. Therefore, instead of forming gas phase adducts, the incoming precursor will encounter a reactive surface consisting of species left behind from the preceding reaction step. In the present work we have examined the possibility to employ the ALE method in growing AlN films from AlCl_3 and NH_3 at temperatures compatible with glass and other temperature sensitive substrates.

2. EXPERIMENTAL

The AlN films were grown on $5 \times 5 \text{ cm}^2$ soda lime glass substrates in a commercial flow type reactor F-120 (Microchemistry Ltd, Espoo Finland) [4] operated under a pressure of 10 mbar. Nitrogen served both as a carrier and purging gas. A characteristic feature of the F-120 reactor is that the two substrates to be coated are located face to face within a distance of 2 mm (Fig. 1). This arrangement provides that when travelling through the narrow flow channel the precursor molecules undergo a large number of collisions with the substrates which both increases the precursor utilization efficiency and facilitates the use of short pulsing and purging periods.

AlCl_3 (99.99 %, Aldrich) was evaporated from an open boat held at 90°C inside of the reactor. The pulsing of AlCl_3 was accomplished by means of inert gas valving (Fig. 1). Ammonia (99.999 %, Messer Griesheim) was introduced into the reactor through a mass flow meter and needle and solenoid valves. The ammonia flow rate was adjusted to $8 \text{ std. cm}^3 \text{ min}^{-1}$ during a continuous flow.

Film thicknesses were determined by fitting transmittance spectra using a procedure developed and described by Ylilammi and Ranta-aho [6]. The transmittance spectra were measured in a wavelength region of 380 - 1100 nm with a Hitachi U-2000 spectrophotometer. Film composition was analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI Small Spot ESCA 5400 electron spectrometer. XPS spectra were excited by non-monochromatized $\text{MgK}\alpha$ radiation and measured using 89 eV analyzer energy and 0.5 eV channel width. Depth profiling was accomplished with argon ion sputtering using a PHI 04-300 ion gun with 3.0 kV acceleration voltage, 25 mA current, 10 mPa

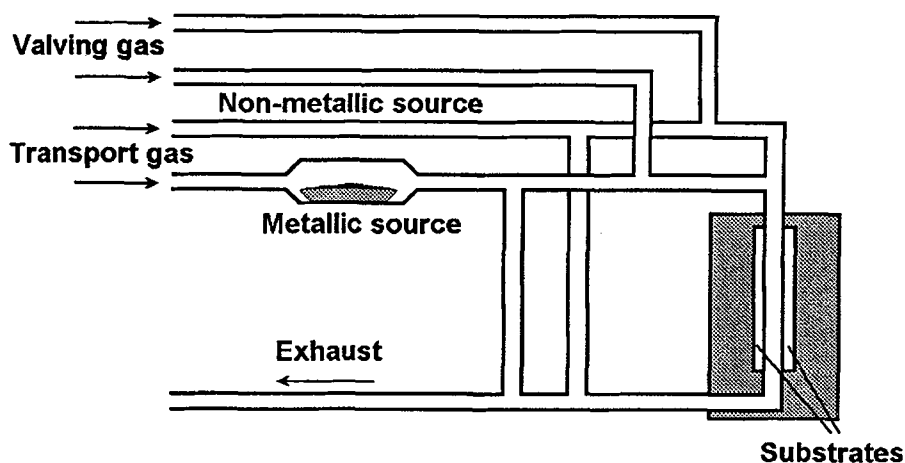


Figure 1: A schematic diagram of the central part of the F-120 ALE reactor.

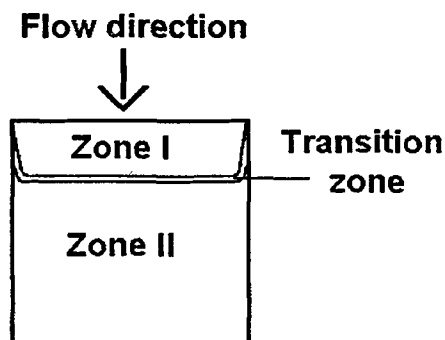


Figure 2: A sketch of a typical outcome of the films prepared. See text for further discussion.

argon pressure and 50 % raster. The sputtering rate was approximated to be roughly 2 nm/min by means of calibration measurements on a SiO_2/Si system. Film morphology was examined with a Zeiss DSM 962 scanning electron microscope (SEM). A Philips MPD 1880 powder X-ray diffractometer using $\text{CuK}\alpha$ radiation was employed in crystal structure determination.

3. RESULTS AND DISCUSSION

3.1. Film growth.

The films exhibited an interesting outcome being divided into two distinct zones in the flow direction (Fig. 2). The first zone (Zone I) located at the leading edge of the substrate became covered with a uniform amorphous film having a refractive index of 1.8 - 1.9. This was followed by the Zone II, the larger one of the two zones, covered uniformly with a crystalline AlN. Between the major zones there was a sharp transition zone whose length in the flow direction did not exceed 3 mm. Typically, the thickness of the film deposited on the Zone I was about half of that deposited on the Zone II.

The amorphous structure of the film deposited on the Zone I together with its low refractive index implied that the film consisted of a mixture of aluminium oxide and nitride, represented as AlO_xN_y . The reason for the formation of the AlO_xN_y phase at the leading edge of the substrate was apparently the existence of O_2 and H_2O residues in the nitrogen carrier gas and in ammonia. Indeed, when the purity of nitrogen was changed from 99.999 % to 99.9999 %, the length of the Zone I decreased from about 1.8 to 1.0 cm.

The sharpness of the transition zone between the major zones indicates that the O_2 and H_2O residues have a high sticking coefficient on the AlN surface. As a consequence, they become rapidly exhausted once they encounter the AlN surface, *i.e.* the fresh AlN surface on the Zone I acts as an effective internal getter. Nevertheless, since the flow routes of AlCl_3 and NH_3 merge only about 1 cm ahead of the substrates (Fig. 1), the AlO_xN_y phase extends partially also over the substrates. Evidently, the substrates could be covered uniformly with AlN if they were moved further off the crossing point of the flow routes. However, rather than redesigning the flow arrangements of the presently employed reactor, a simpler strategy was adopted by concentrating all the experiments on the Zone II, thereby decreasing the effective substrate area upon which AlN was deposited to about $3 \times 5 \text{ cm}^2$.

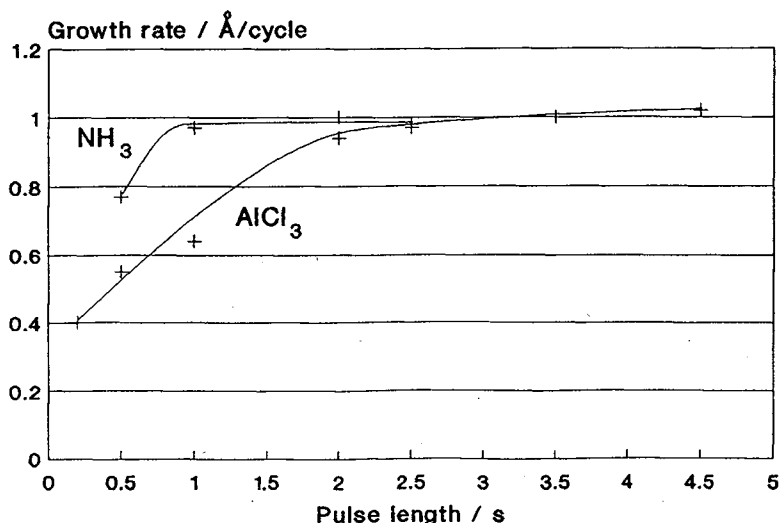


Figure 3: Growth rate as a function of AlCl_3 and NH_3 pulse lengths. While varying the AlCl_3 pulse lengths, the NH_3 pulse lengths were fixed to 1.0 s. Likewise, while the NH_3 pulse lengths were varied, the lengths of AlCl_3 pulses were kept constant at 2.5 s.

Figure 3 depicts how the growth rate varied as a function of AlCl_3 and NH_3 pulse lengths at 500 °C. In both cases the growth rate was observed to saturate to a constant value of about 1.0 Å/cycle, thus giving an evidence of a self-limiting ALE growth process. The saturation of the growth rate as a function of the AlCl_3 pulse length indicates also that AlCl_3 does not react with nitrogen, thereby validating the use of nitrogen as an inert carrier gas. The time needed to reach the saturation level was shorter for NH_3 , 1.0 s, than for AlCl_3 , 2.0 s. The elongation of the purge times from 0.5 to 1.0 s had no effect on the growth rate indicating that the surface species acting as intermediates in the film growth were stable against desorption - another feature which is essential for a truly self-limited ALE process.

One of the attractive features of ALE is the easy and accurate film thickness control accomplished simply by counting the deposition cycles repeated. This was verified also in the present study as demonstrated in Figure 4.

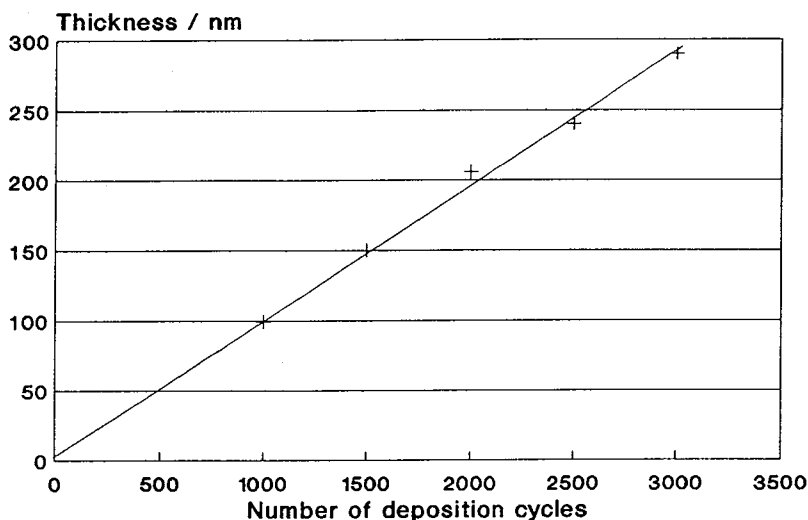


Figure 4: Film thicknesses vs. the number of deposition cycles used.

When the film growth was attempted at 450 °C using the parameters optimized at 500 °C, the growth rate decreased sharply to a level below 0.4 Å/cycle. Such a strong temperature dependence implies that at least one of the surface processes taking part in the film growth has a high activation energy. Fortunately, reasonably short pulse times could be employed at 500 °C which is still within the temperature limits where soda lime glass substrates can be processed.

Comparison of the growth rate obtained, 1.0 Å/cycle, with the distance between the subsequent Al layers in the [001] direction of AlN, 2.49 Å [7], reveals that about 40 % of the complete monolayer was deposited during one cycle. The most evident reason for the submonolayer growth is steric hindrances between the chlorine ligands.

3.2. Film structure, composition and properties

The film composition was analyzed with XPS and depth profiling (Fig. 5). Besides Al and N, also O and Cl impurities were detected in the films. In addition, about 30 at.% carbon was detected at the outermost surface. However, since the carbon content decreased to below 4 at.% already after a brief sputtering it was ascribed to a contamination of the film surface after removing from the reactor and, thus, it was neglected in constructing Fig. 5.

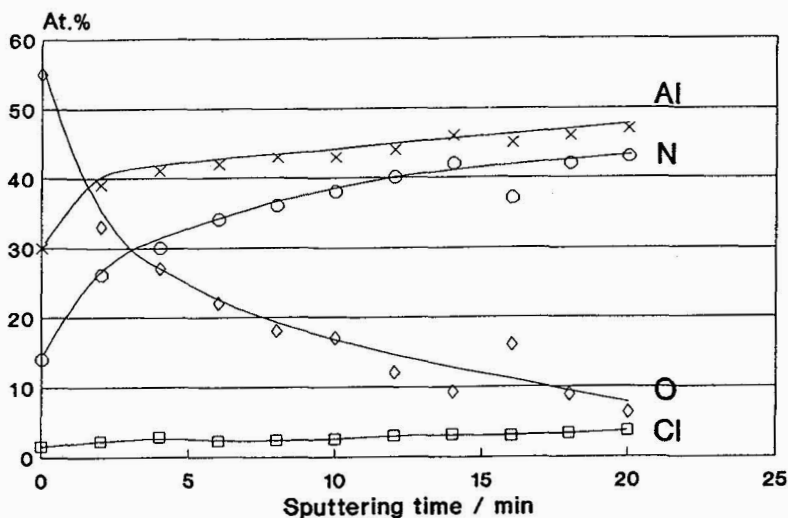


Figure 5: XPS depth profiles of the AlN film surface.

The content of chlorine residues increased slightly with increasing depth being in average about 3 at.%. Obviously, the chlorine residues indicate that the the surface reactions between the sequentially dosed AlCl_3 and NH_3 are not totally complete.

Since the oxygen content decreased and nitrogen content increased when going deeper into the film, the origin of oxygen was ascribed to a post deposition oxidation of the film surface. It is known that a passivating oxide layer with a thickness of 5 - 10 nm is formed on an AlN surface when exposed to air for one day [8]. However, in the present case about 6 at.% oxygen was found still after 20 min sputtering corresponding to a thickness of roughly about 40 nm. The reason for such a high oxidation depth is most probably that the surface got oxidized already while cooling from 500 °C to room temperature under the flow of nitrogen containing O_2 and H_2O as residues. Owing to the high temperature, the diffusivity of oxygen was increased resulting in a thicker oxide layer as compared with films oxidized at room temperature.

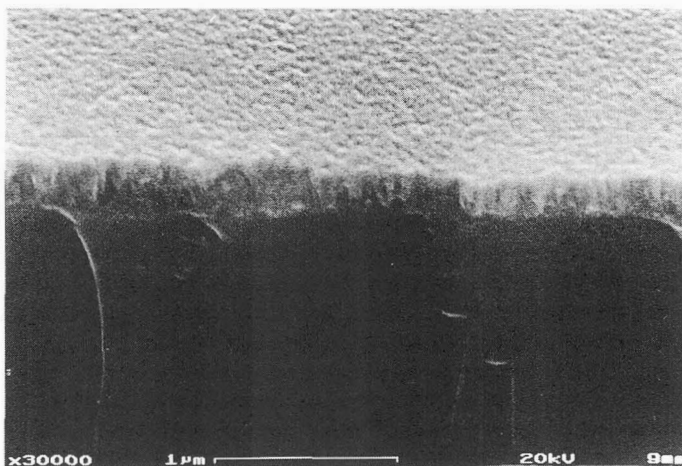


Figure 6: SEM image of a fractured film cross section.

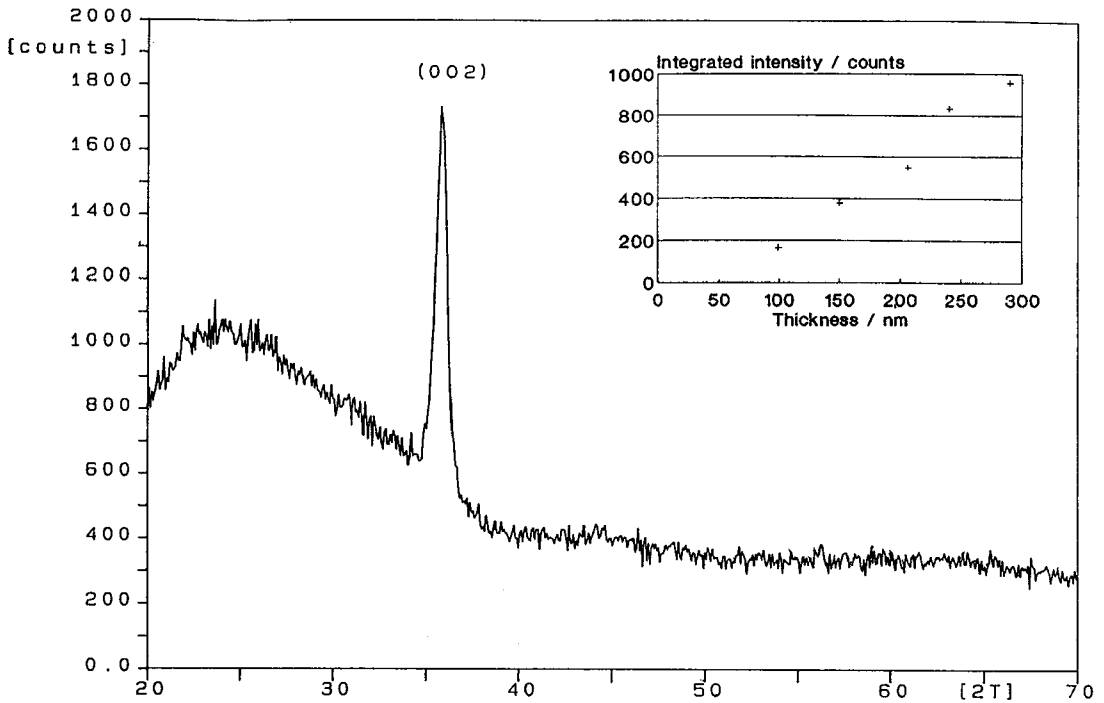


Figure 7: An XRD pattern of a 290 nm thick AlN film. The inset depicts the integrated intensities as a function of film thicknesses.

Examination with SEM revealed that the films were built up of densely packed columnar grains (Fig. 6). In all the XRD measurements only a single reflection was observed (Fig. 7). The d -value of this reflection, 2.50 \AA , was in a fairly good agreement with the reference value of the (002) reflection of hexagonal AlN, 2.490 \AA [7]. In randomly oriented AlN powder the relative intensity of the (002) reflection, 60, is exceeded by those of the (100) and (101) reflections, 100 and 85, respectively [7]. Since the latter reflections were not detected from the films it can be concluded that even though no complete monolayer-by-monolayer growth took place, the films still exhibited a strong preferred orientation in the [001] direction where the AlN structure is built up of alternating Al and N planes. As the inset in Fig. 7 reveals, the integrated intensity of the (002) reflection increased linearly along with film thickness. However, if the intensities are extrapolated with a line this line does not intercept the film thickness axis at origo but, instead, at about 50 nm. This may be explained either in terms of an amorphous interface layer between the amorphous substrate and the crystalline film, or in terms of a formation of an amorphous surface layer as a result of the post deposition oxidation of the film.

The films were highly transparent and their refractive index at $\lambda = 580 \text{ nm}$ was about 1.97. In general refractive indices of 1.99 - 2.25 have been measured for AlN [1]. The slightly lower values measured for the present films may be due to their low density which, in turn, is attributable to the relatively low growth temperature. On the other hand, the formation of the oxidation layer on the film surface may also have an effect on the refractive indices evaluated by the rather simple method, *i.e.* by fitting the transmittance spectra with a simplifying assumption that the refractive index would remain constant through the whole film thickness. Apparently, this assumption does not hold in the outermost oxidized surface layers, thus causing uncertainty to the fitting results. Indeed, when a two layer model was employed in fitting the spectra, an increased refractive index of 2.01 was evaluated for the film bulk.

To examine the chemical stability of the films they were etched with concentrated H_3PO_4 at 30 °C. An average etching rate of 20 nm min^{-1} was measured. Using an analogous etching procedure, results comparable with the present ones were obtained by Hagesawa *et al.* [9] for their AlN films prepared from $\text{Al}(\text{CH}_3)_3$ and NH_3 by plasma CVD at 300 °C. On the other hand, Gordon *et al.* [10] reported that their AlN films prepared from $\text{Al}_2(\text{N}(\text{CH}_3)_2)_6$ and NH_3 by atmospheric CVD in a temperature range 100 - 500 °C were dissolved with an approximate rate of 100 nm min^{-1} under identical etching conditions.

4. CONCLUSIONS

ALE growth of AlN thin films from AlCl_3 and NH_3 was studied. A self-limiting growth with a rate of 1.0 \AA/cycle was achieved at 500 °C. Despite the relatively low growth temperature and the fact that amorphous soda lime glasses were employed as substrates, the resulting films were polycrystalline and strongly oriented having the (001) planes as the growth planes. The films contained oxygen and chlorine as impurities. Since the oxygen content decreased steadily when the film was depth profiled, its origin was ascribed to post deposition oxidation of the surface. The chlorine content increased somewhat with increasing depth into the film being in average about 3 at.%. The refractive indices of the films were around 1.97.

Acknowledgments

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