Journal of the European Ceramic Society 17 (1997) 1807–1811
© 1997 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(97)00073-3
0955-2219/97/$17.00 + 0.00

UHV Reactive Sputtering of AlN(0 0 0 1) Single Crystals On Si(1 1 1) at High Temperature by a Two-Step Growth Method

F. Malengreau,[a,b] S. Hagège,[a] R. Sporken,[b] M. Vermeersch[b,*] and R. Caudano[b]

[a]Centre d'Etudes de Chimie Metallurgique — CNRS, 15 rue Georges Urbain, F-94407 Vitry Sur Seine Cedex, France.
[b]LISE-FUNDP, 61, rue de Bruxelles, B-5000 Namur, Belgium.

Abstract

The growth of large-size single crystals of aluminium nitride has been obtained by UHV reactive rf-sputtering at high temperature (1050°C). The growth mode was studied in situ *by electron spectroscopy (HREELS, LEED) and by* ex-situ *High Resolution Transmission Electron Microscopy (HRTEM). The deposition of a buffer layer at lower temperature (700°C) yielded a thick mosaic layer with a very low surface roughness. Electron microscopy has evidenced the presence of a thin interfacial layer composed of small and slightly misoriented domains, suggesting therefore a 3-D growth of the layer before the temperature transition; it has also confirmed the very good crystalline quality of the final thick film: the constituent domains of the film are large (100 nm) and their respective misorientation is less than 0·1 degree. © 1997 Elsevier Science Limited.*

Résumé

La croissance de monocristaux de nitrure d'aluminium de grande taille a été obtenue par pulvérisation cathodique réactive (rf) en ultra haut vide et à haute température (1050°C). Le mode de croissance de ces films a été étudié in situ *par spectroscopie électronique (HREELS, LEED) et* ex-situ *en microscopie électronique en transmission à haute résolution (HRTEM). Le dépôt préliminaire d'une couche tampon à plus basse température (700°C) permet d'obtenir un film présentant une faible mosaïcité ainsi qu'une rugosité de surface réduite. La microscopie électronique a mis en évidence la présence d'une couche interfaciale constituée de domaine de taille réduite et légèrement désorientés, suggérant une croissance tridimensionnelle du film avant la transition en température. Elle a en outre permis de confirmer la bonne qualité cristalline du film complet: les domaines constitutifs du film sont de grande taille (100 nm), et leur désorientation respective est inférieure à 0·1 degré.*

1 Introduction

Aluminium nitride is a wide band gap semiconductor which exhibits properties (high melting point, very good thermal conductivity, thermal expansion coefficient similar to Si, piezoelectricity...) that are very interesting for numerous electronic applications.[1] Epitaxial growth of AlN has already been achieved by CVD[2] or reactive MBE[3], but reactive sputtering has only, up to now, resulted in highly oriented films[4] or in epitaxial films containing a high density of dislocations as observed by Meng *et al.*[5] These authors evidenced the growth of wurtzitic AlN and an epitaxial orientation relationship for films grown at temperatures ranging from 600 to 1000°C. They also showed that although it is often assumed that misfit stresses relax during the first stage of growth by formation of misfit dislocations at the interface, this is not the case for AlN/Si, suggesting therefore a coincidence interface with a ratio of 5:4. Finally, real-time measurements of substrate bending during the deposition showed the presence of variation of intrinsic stresses resulting from the island growth mode.

A minimum growth temperature ($T/T_m \geq 0{\cdot}3$) is usually needed to obtain epitaxial growth and good quality single crystals. However, when the lattice misfit is too high (>20%) and results in the formation of strained layers, with high density of defects and dislocations,[5,6] the energy brought by the high temperature is not sufficient, with regards to the refractory nature of aluminium nitride, to

---

*To whom correspondence should be addressed.
Now at Glaceries de St-Roch — R&D Center, 169 Rue des Glaces Nationales, B-5060 Sambreville B.P.50 Belgium

overcome the strains and reorganise the film, resulting in a columnar growth as we have previously observed.[7] To overcome these problems that give rise to lower quality films, several authors have, in the case of the growth of gallium nitride, deposited a buffer layer of AlN[8–10] or GaN[11] at low temperature. It has been shown that with the presence of this buffer layer, the density of dislocations decreased rapidly with increasing thickness. Kuznia *et al.* have compared the use of AlN or GaN as a buffer layer for the growth of gallium nitride.[11] They showed that the use of a thin buffer layer improves the material quality, but they also showed that the total epilayer thickness must be of a minimum of 4 μm in order to obtain the best result. This minimum thickness is probably related to a poor quality of the buffer layer. It was grown at a temperature which was probably too low and at deposition rate which was probably too fast.

We have applied this procedure — called 'two-step growth' and used for semiconductors other than the III-V nitrides[12] — to the growth by rf-sputtering of AlN layers. The very good quality single crystalline films were grown on Si(1 1 1) and studied *in situ* by electron spectroscopy (LEED, HREELS) and *ex-situ* by High Resolution Transmission Electron Microscopy (HRTEM).

2 Experimental

The substrates were Si(1 1 1) resistively heated at a temperature of 1050°C during deposition. The films were grown by reactive rf-sputtering of a pure Al target in a mixed atmosphere of N and Ar. The base pressure of the sputtering chamber was 1×10^{-7} Pa. The total deposition pressure was $5{\cdot}5 \times 10^{-1}$ Pa. Precise control of the partial pressure of each gas in the chamber allowed us to obtain a higher stability of the plasma, giving access to very low deposition rates (500 Å h^{-1} at 1050°C).

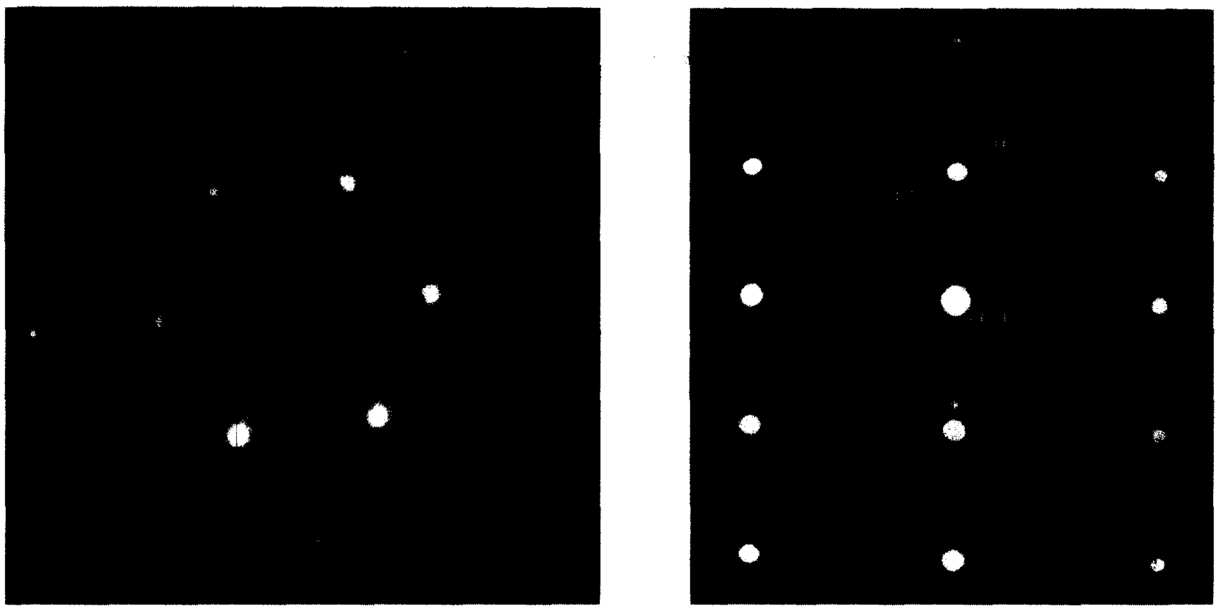
Ex-situ chemical preparation of the substrate is based on the RCA method of Ishizaka and Shiraki.[13] The growth procedure was basically as follows; after outgassing, clean Si(1 1 1) surfaces with a sharp (7 × 7) reconstruction were obtained and the growth started with the deposition of the buffer layer at 700°C during the first tens Å of growth. The temperature was then raised to 1050°C and the thicker part of the film deposited at constant temperature. After deposition, the sample was annealed at the growth temperature under nitrogen atmosphere (5×10^{-1} Pa) for 30 min and under UHV at 600°C for 15 min. The details of sample cleaning and deposition procedure have been presented in a previous paper.[7] The total deposition time was typically of the order of several hours.

Transmission Electron Microscopy (TEM) was carried out in cross section. Samples were mechanically thinned to 30 μm and then ion milled with Ar$^+$. Conventional and high resolution TEM were performed on a Topcon 0002-B operating at 200 kV. Surface diffraction patterns were obtained on a four-grid LEED optics. Auger measurements were performed with a cylindrical mirror analyser (CMA) and an axial electron gun ($0 < Ep < 10$ keV). HREELS spectrometer was a double hemispherical system (SEDRA-ISA Riber). The spectrum presented here was measured in the specular geometry and with an incidence angle of 45°. The primary energy of the electron beam was 7 eV. For the samples presented here, no charging of the film surface was detected, and the neutralisation gun has not been used.

3 Results and Discussion

Typical LEED patterns of thick AlN films obtained by this two-step growth method showed very sharp spots as can be seen in Fig. 1 (a). This pattern exhibits a hexagonal symmetry *a priori* compatible with both the cubic and hexagonal forms of AlN. Several films were grown with coverage ranging from 0·1 μm to 0·6 μm, giving the same surface electron diffraction pattern. Measurements of the lattice parameter on several of these LEED diagrams gave an average value of 3·1 Å, which is close to the bulk value, indicating fully relaxed films. A general overview in AES allowed checking of the contaminations; the only one found was residual oxygen which was determined to have concentrations lower than 1 atomic percent, which is difficult to quantify in that range. No carbon contamination was detected in the sensitivity range of AES. Preliminary PEELS results (to be published) have confirmed the very low concentration of oxygen contamination ($\sim$0·1 atomic percent).

HREELS spectra of a thick film also indicates a very good crystalline quality of the layer (Fig. 2). A high signal to noise ratio and a resolution close to the theoretical one for the configuration used are known to be a sign of high quality layers. This spectrum shows the well-known structures characteristic of aluminium nitride, the most important one being at 106 meV and a shoulder appearing at 80 meV easy to separate here thanks to the good resolution. The determination of the dielectric constants of AlN has been performed from this spectrum and is detailed in another paper.[14] At the interface, a measurement of the angular dispersion of the dipole lobe shows the following steps in the growth: before the temperature transition, the



(a) (b)

Fig. 1. (a)LEED pattern of the AlN(0 0 1) grown by the two step-growth method (Ep = 81 eV) and (b) cross-section diffraction pattern showing superimposition of AlN $(1\,0\,\bar{1}\,0)$ with Si(2 1 1) zone axis patterns.

roughness of the surface increases, indicated by the increasing angular dispersion (up to 20°); when the temperature is increased to 1050°C this dispersion slowly improves to become very sharp at high thickness ($\sim 6°$, insert of Fig. 2). The evolution of the roughness suggests a first step including three-dimensional growth of AlN at low temperature. This is in agreement with the results of Hiramatsu *et al.*, who have evidenced for the growth of AlN on sapphire[15] that below 600°C, the buffer layer is amorphous, and above it is constituted of three-dimensional crystallites and incorporates defects during the island growth process. In our case, the quality of the buffer layer is already quite good, needing less energy to reorganise when the temperature is increased. This improvement in our results is certainly due to a deposition at higher temperature, but also mainly to the much lower deposition rate that we were able to reach in our system.

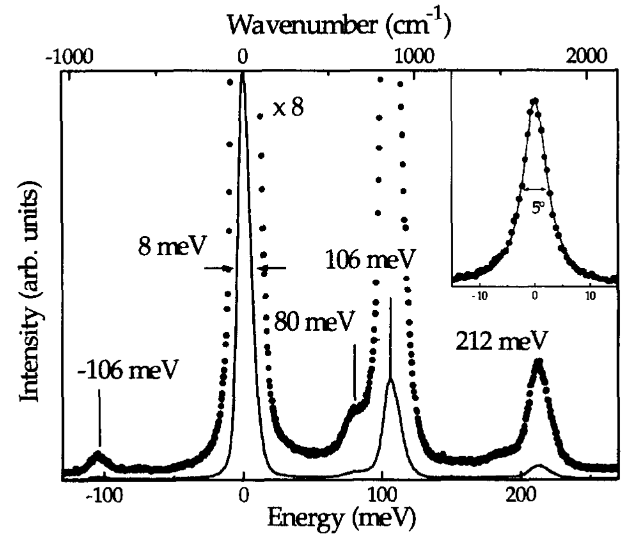


Fig. 2. HREELS spectrum of a 0·35μm thick film deposited by the two-step growth method on Si(1 1 1). The insert shows the angular dispersion of the dipole lobe.

The crystalline structure of the films and their orientation with respect to the substrate were specified using TEM. The diffraction patterns of the films, for a cross-section in the $(1\,0\,\bar{1}\,0)$ axis of the aluminium nitride confirms the hexagonal symmetry for the aluminium nitride (Fig. 1(b)). From the pattern, we can also determine that the orientational relationship between the film and the substrate is AlN(0 0 0 1)//Si(1 1 1) and Si$(1\,\bar{1}\,0)$// AlN$(\bar{1}\,2\,\bar{1}\,0)$, which is in agreement with the ones found in the literature.[5,16] We can also see from the pattern that we have a perfect epitaxy of AlN(0 0 0 1) on Si(1 1 1) in spite of the 20% misfit at the interface and for this orientation.

The quality of the film is also confirmed by TEM bright field imaging. At low resolution, we can see that the layer is homogeneous, and the interface abrupt (Fig. 3(a)). Relatively few extended defects were observed, and the film does not present a columnar growth as in the case of a deposition in one step at high temperature.[7] The homogeneity in the contrasts of the image suggests that the misorientation of the crystallites in the film remains very low. At higher resolution (Fig. 3(b)), we can distinguish an interfacial layer, about 100 Å thick, this layer is obviously to be correlated to the layer deposited during the first step of the growth. However, it is possible that after the temperature

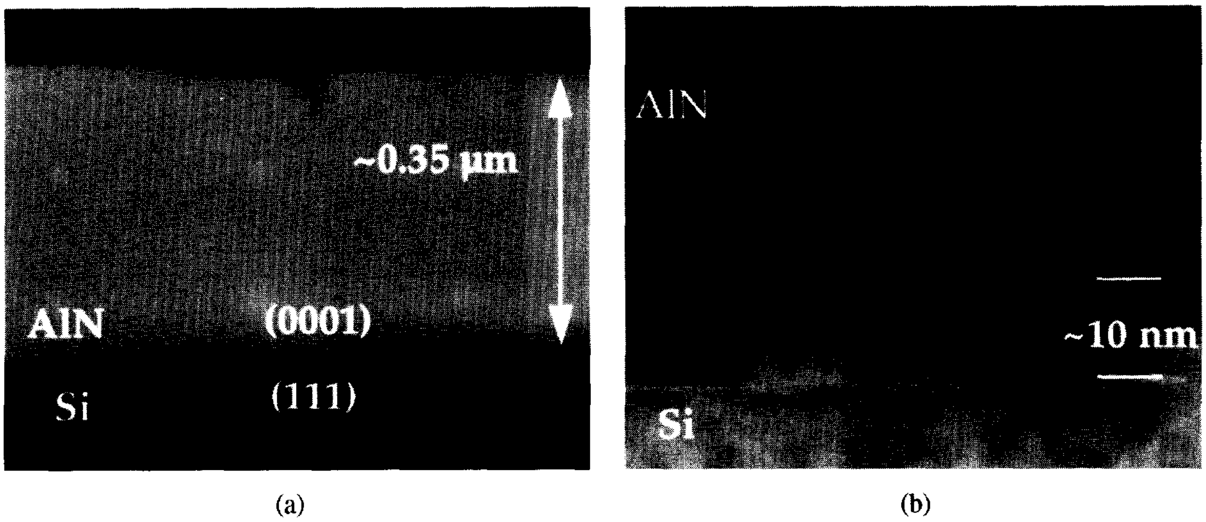


Fig. 3. (a)TEM images of a 0·35μm thick aluminium nitride formed by the two-step growth method. Image (b) shows the buffer layer of AlN deposited at lower temperature.

transition, the quality of the layer is slowly improving and that its thickness is higher than the one deposited before the transition. It is also possible that the increase in temperature results in a reorganisation of the buffer layer from the top through the substrate, in which case the thickness would be smaller. From the information we have up to now, it is not possible to decide which transformation is occurring, but as the interface between the interfacial layer and the main film is quite sharp, it is most probable that a front of reorganisation is moving towards the substrate and stops when the strains in the layer are too high to be overcome by the energy of the heating.

We can see stronger differences in the contrasts of this first layer than in the thick film, indicating that it is constituted of very small domains slightly misoriented and having a distribution of orientation (Fig. 4), but we did not detect the formation of clearly defined domains as was the case in the columnar growth. The misorientation of these crystallites is of the order of 1°. The presence of defects confirms the initial three-dimensional growth. The thick film deposited on top of the buffer layer is also composed of these domains, but with a much larger size (100 nm instead of 10 nm) and a smaller misorientation (~0·1° instead of 1°). This shows that the final layer deposited by the two-step growth method results in a well-organised film as was suggested by electron spectroscopy. We did not notice a strong difference in the quality of the layer with respect to its thickness as was the case for Kuznia *et al.*[11] The better quality of our buffer layer probably allowed us to obtain a very good epilayer for a much smaller thickness.

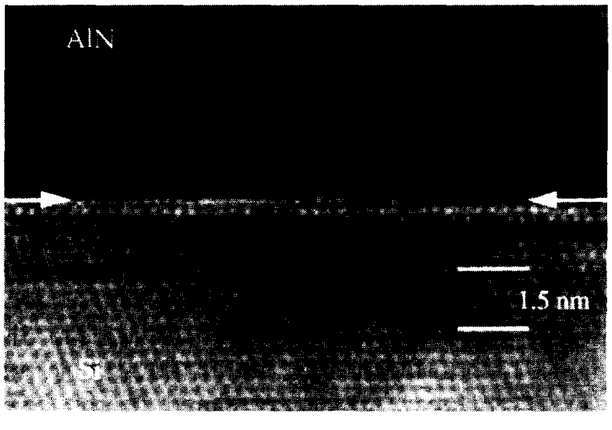


Fig. 4. HRTEM image of the interface between the buffer layer and the substrate.

Moreover, whilst the buffer layer seems to be less organised, it can be seen on Fig. 4 that the interface between the AlN and the substrate is structurally sharp and we can easily distinguish the interfacial arrangement of the first layer of AlN. This layer seems to be very little influenced by the presence of the substrate. We did not measure any significant relaxation at the interface in the interplanar distance nor in the arrangement of the first atomic layer.

During the growth of small crystallites in the buffer layer, we may assume that the epitaxial orientation with the substrate allows a lesser accumulation of global strains at the interface and this is possible thanks to the near 5 : 4 coincidence ratio at the interface and despite the large misfit (Fig. 5). For this orientation, the areas of good fit (labelled A in Fig. 5) are densely distributed within the interface and the structural relaxation of bad matching areas would be energetically unfavourable because they would affect the coherency of good matching areas. Then, during the growth of crystallites, the amount of strain which is accumulated in them may be relaxed at the low angle boundary between the crystallites. The very low

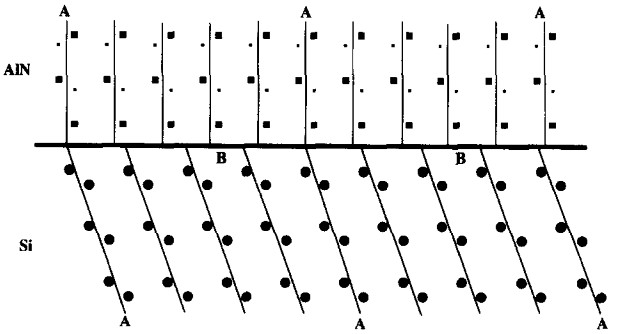


Fig. 5. Schematic representation of the 5 : 4 near coincidence orientation at the AlN/Si interface. Areas of good match are labelled (A), strain is concentrated in areas labelled (B).

deposition rate and the relatively high temperature we were able to use during our experiment is certainly critical for this mechanism to operate. Time and energy are necessary to let the film relax at different stages of its growth. We can also conclude from such a sharp interface that the chemical interaction at the interface probably remains small. PEELS measurements and a fine analysis of the interface structure are still in progress to obtain a chemical and structural information at the interface.

4 Conclusions

We have shown in this paper that it has been possible to grow large single crystalline films of aluminium nitride by reactive rf-sputtering at high temperature. A very good crystalline quality was achieved by the deposition of a buffer layer of AlN at low temperature (700°C) in order to avoid dislocations in the whole thick film. The sputtering conditions consisted of a low pressure and low power plasma that resulted in a good quality buffer layer for this deposition temperature and allowed to reorganise quicker at the temperature transition, facilitating the crystalline growth of the thick film. A combination of HREELS and HRTEM has shown that this buffer layer is growing in a 3-D mode and is constituted of slightly misoriented domains. It has also been shown that the resulting thick film showed a low surface roughness and large domains (100 nm) with a very small misorientation.

Acknowledgements

R. Sporken acknowledges financial support from the National Fund for Scientific Research (NFSR, Belgium). This work was supported by the EEC Human Capital and Mobility program, a research program on interfacial materials (Région Wallonne, Belgium), the NFSR (Belgium) and by the Belgian Prime Minister's Services - Science Policy Programming within the framework of the Interuniversity Attraction Pole in Interface Science and the Impulse Program on High Tc Superconductors.

References

1. Strite, S. and Morkoç, H., GaN, AlN, InN: a review. *Journal Vac. Sci. Technol. B*, 1992, **10**, 1237.
2. Morita, M., Tsubouchi, K. and Mikoshiba, N., Optical observation and cathodoluminescence of epitaxial aluminum nitride film. *Jpn. Journal Appl. Phys.*, 1982, **21**, 1102.
3. Rowland, L. B., Kern, R. S., Tanaka, S. and Davis, R. F., Epitaxial growth of AlN by plasma-assisted, gas-source molecular beam epitax. *Journal Mater. Res.*, 1993, **8**, 2310.
4. Meng, W. J., Heremans, J. and Cheng, Y. T., Epitaxial growth of aluminium nitride on Si(111) by reactive sputtering. *Appl. Phys. Lett.*, 1991, **59**, 2097.
5. Meng, W. J., Sell, J. A., Perry, T. A., Rehn, L. E. and Baldo, P. M., Growth of aluminum nitride thin films on Si(111) and Si(001): structural characteristics and development of intrinsic stresses. *Journal Appl. Phys.*, 1994, **75**, 3446.
6. Meng, W. J., Sell, J. A., Eesley, G. L. and Perry, T. A., Measurement of intrinsic stresses during growth of aluminum nitride thin films by reactive sputter deposition. *Journal Appl. Phys.*, 1993, **74**, 2411.
7. Malengreau, F., Vermeersch, M., Hagège, S., Sporken, R., Lange, M. D. and Caudano, R., Epitaxial growth of aluminum nitride layers on Si(111) at high temperature and for different thicknesses. *Journal of Materials Research*, 1997, **12**, 175.
8. Warren Weeks, T., Bremser Jr., M. D., Shawn Ailey, K., Carlson, E., Perry, W. G. and Davis, R. F., GaN thin films deposited via organometallic vapor phase apitaxy on a (6H)-SiC(0001) using high-temperature monocrystalline AlN buffer layer. *Appl. Phys. Lett.*, 1995, **67**, 401.
9. Khan, M. A., Kuznia, J. N., Olson, D. T. and Kaplan, R., Deposition and surface characterization of high quality single crystal GaN layers. *Journal Appl. Phys.*, 1993, **73**, 3108.
10. Qian, W., Skowronski, M., De Graef, M., Doverspike, K., Rowland, L. B. and Gaskil, D. K., Microstructural characterization of a-GaN films grown on sapphire by organometallic vapor phase epitaxy. *Appl. Phys. Lett.*, 1995, **66**, 1252.
11. Kuznia, J. N., Asif Khan, M., Olson, D. T., Kaplan, R. and Freitas, J., Influence of buffe layers on the deposition of high quality single crystal GaN over sapphire substrates. *Journal Appl. Phys.*, 1993, **73**, 4700.
12. Koch, S. M., Rosner, S. J., Hul, R. G., Yoffe, W. and Harris Jr., J. S., The growth of GaAs on Si by MBE. *Journal Crystal Growth*, 1987, **81**, 205.
13. Ishizaka, A. and Shiraki Y., *Journal Electrochem. Soc.* 1986, **133**, 667
14. Malengreau, F., Sporken, R., Vermeersch, M., Hagège, S. and Caudano, R., HREELS study of epitaxial aluminum nitride thick layers on Si(111) grown at high temperature, submitted to *Solid state commun.*
15. Kuwano, N., Shiraishi, T., Koga, A., Oki, K., Hiramatsu, K., Amano, H., Itho, K. and Akasaki, I., Growth mechanism of GaN grown on sapphire with AlN buffer layer by MOVPE. *Journal Crystal Growth*, 1991, **115**, 628.
16. Rössner, U., Ph. D. thesis, 1996.