ELSEVIER

Journal of Crystal Growth 230 (2001) 426–431

JOURNAL OF CRYSTAL GROWTH

www.elsevier.com/locate/jcrysgro

Hexagonal AlN films grown on nominal and off-axis Si(0 0 1) substrates

V. Lebedev[a,*], J. Jinschek[a], J. Kräußlich[b], U. Kaiser[b], B. Schröter[a], W. Richter[a]

[a] *Institut für Festkörperphysik, Universität Jena, Max-Wien-Platz 1, D-07743 Jena, Germany*
[b] *Institut für Quantenelektronik, Universität Jena, Max-Wien-Platz 1, D-07743 Jena, Germany*

Abstract

Nucleation and growth of wurtzite AlN layers on nominal and off-axis Si(0 0 1) substrates by plasma-assisted molecular beam epitaxy is reported. The nucleation and the growth dynamics have been studied in situ by reflection high-energy electron diffraction. For the films grown on the nominal Si(0 0 1) surface, cross-sectional transmission electron microscopy and X-ray diffraction investigations revealed a two-domain film structure (AlN^1 and AlN^2) with an epitaxial orientation relationship of $[0\,0\,0\,1]_{AlN} \parallel [0\,0\,1]_{Si}$ and $\langle 0\,1\,\bar{1}\,0\rangle AlN^1 \parallel \langle \bar{2}\,1\,1\,0\rangle AlN^2 \parallel [1\,1\,0]_{Si}$. The epitaxial growth of single crystalline wurtzite AlN thin films has been achieved on off-axis Si(0 0 1) substrates with an epitaxial orientation relationship of $[0\,0\,0\,1]_{AlN}$ parallel to the surface normal and $\langle 0\,1\,1\,0\rangle_{AlN} \parallel [1\,1\,0]_{Si}$. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 81.15.Hi; 61.14.Hg; 61.14.Qp

Keywords: A1. Interfaces; A1. Nucleation; A3. Molecular beam epitaxy; B1. Nitrides

AlN thin films are of increasing interest for a large number of applications in microelectronic field. Due to the wide direct band gap, AlN is a promising material for integrated optics in the UV region [1] and due to its piezoelectric properties, for fabrication of high frequency surface acoustic wave devices using different substrates such as sapphire, SiC and Si [2].

Silicon substrates offer important advantages for nitride devices over other substrate materials, because it is ideal for integrating nitride optoelectronics into the well-established Si technology. Despite the misfit of 23.4%, wurtzite AlN (2H-AlN) can be grown on Si(1 1 1) plane with good structural properties and smooth surface morphology [3–5]. This fact can be explained firstly by the coincident 6-fold symmetry of the Si(1 1 1) surface and 2H-AlN growing in $\langle 0\,0\,0\,1\rangle$ direction and secondly by the relaxation of the entire misfit via a large number of misfit dislocations at the Si/AlN interface [6].

The molecular beam epitaxy (MBE) of AlN on silicon (0 0 1) plane having 4-fold symmetry is much more difficult because of the meta-stable

*Corresponding author. Tel.: +49-3641-947448: fax: +49-3641-947442.

E-mail address: lvb@pinet.uni-jena.de (V. Lebedev).

PII: S 0 0 2 2 - 0 2 4 8 (0 1) 0 1 2 4 1 - 6

character of the cubic AlN polytype. Therefore, the growth of the thermodynamically stable 2H-AlN phase [7,8] on Si(0 0 1) might be an acceptable solution for the preparation of composite substrates for GaN-based optoelectronics.

In this paper, we report on single crystalline 2H-AlN films grown on nominal and off-axis silicon (0 0 1) substrates by plasma-assisted MBE. The nucleation processes and growth dynamics were studied in detail by in situ reflection high-energy electron diffraction (RHEED). Cross-sectional transmission electron microscopy (XTEM), high-resolution XTEM (HRTEM) and X-ray diffraction (XRD) methods were used for ex situ characterization.

The AlN films were grown in a MBE system (background pressure $\sim 9 \times 10^{-11}$ mbar) equipped with a radio-frequency plasma source (MPD21, Oxford Applied Research) to supply activated nitrogen. High purity aluminum (6N5) was evaporated from a standard effusion cell. The growth rate ranged from 100 to 120 nm h^{-1}. A 10 kV RHEED system was used for monitoring the epitaxial process.

Two types of Si(0 0 1) (B-doped, p-type, $\rho \cong 6.7\,\mathrm{K\Omega\,cm}$) wafers were used in the growth experiments: (i) nominal $\pm 0.5^\circ$ (0 0 1)-oriented substrates and (ii) off-axis substrates tilted by $5 \pm 0.5^\circ$ toward the [1 1 0] direction. The substrate surface was initially prepared by a wet chemical cleaning process proposed by Ishizaka and Shiraki [9] followed by annealing at 900°C to remove a thin surface oxide. The surface quality was monitored by RHEED pattern observations. The first annealing process was performed until obvious Kikuchi-lines became clearly visible. On the clean Si(0 0 1) surface, a pronounced, streaky (2×1)-reconstructed pattern was observed at 900°C. The subsequent preparation procedures were different for the nominal and off-axis substrates. Prior the epitaxy, one to two monolayers of Al were deposited on the substrate surface at 650°C leading to the transition from the 2×1 to the 6×4 surface reconstruction [10].

It is well known that well-oriented clean Si(0 0 1) surface exhibit a 2×1 reconstruction with two types of 2×1 domains, which are rotated by 90° with respect to each other [11]. The Si–Si dimers, which are responsible for 2×1 symmetry, have their dimer bonds directed alternately along the [1 1 0] and $[1\,\bar{1}\,0]$ directions on neighboring terraces which are separated by single-atomic step boundaries (SASB). Such surface domain assymetry leads to the formation of antiphase boundary (APB) defects in GaAs epilayers grown on the nominal Si(0 0 1) surface [11].

Likewise, the wurtzite AlN films grown on the nominal (0 0 1) plane of Si form a two-domain structure with the 2H-AlN domains rotated by 30° with respect to each other [12]. According to the model suggested, single atomic steps dominate on nominal Si(0 0 1) surfaces [13] and two terrace types exist which are separated by the SASBs (step height $= a_{Si}/4 \sim 0.1358$ nm). The neighboring terraces (1) and (2) have a 90° angular difference between surface dangling bonds directions existing along $[1\,\bar{1}\,0]_1$ and $[1\,1\,0]_2$. Thus, the nucleation of AlN^1 and AlN^2 nuclei rotated by 30° on neighboring terraces is energetically favorable due to the partial coincidence of the surface bond directions of Si surface and of 2H-AlN nuclei.

Consequently, if the SASB structure of the nominal Si(0 0 1) surface determines the two-domain character of the 2H-AlN films, the single-domain Si(0 0 1) surface structure (with either no steps or bilayer steps) may be an essential presumption for a single-domain AlN film heteroepitaxy.

According to the published experimental results, the single-domain Si(0 0 1) surface can be obtained either (i) with vicinal plane, which were intentionally misoriented by more than 4° towards [1 1 0] after a high-temperature annealing procedure, or (ii) by prolonged high-temperature annealing of nominal (0 0 1) surface [11,13,14].

In our experiments we used three methods of the substrate surface preparation (A, B, C) to determine the relationship between a substrate surface structure and the structural characteristics of the 2H-AlN epilayer: (A) well-oriented ($\pm 0.5^\circ$) nominal Si(0 0 1) substrates annealed at 900°C; (B) type A substrates followed by a prolonged (15 min) high-temperature anneal at 1000°C to establish the double stepped surface; (C) off-axis (0 0 1) Si substrates tilted by $5^\circ \pm 0.5^\circ$ toward the [1 1 0] direction and annealed at 1120°C for 3 min to reach the double stepped surface.

The nucleation and subsequent growth procedure consisted of three basic steps independently on the substrate type used: (1) pre-growth deposition of one to two Al monolayers on the (2×1)-reconstructed Si surface and AlN nucleation at 650°C, (2) growth of a low-temperature AlN buffer (<10 monolayers) and subsequent gradual increasing of the sample temperature to the normal growth point ranging from 860°C to 880°C, (3) AlN long-term epitaxy under stable growth conditions.

For the surface types A and B, the RHEED pattern at the nucleation stage demonstrates a superposition of $0\,1\,\bar{1}\,0$ and $\bar{2}\,1\,1\,0$ reflections of the 2H-AlN lattice together with the 110 reflections of Si. A 12-fold symmetry of the RHEED pattern indicates that at this stage the AlN film consists of two types of domains (marked AlN^1 and AlN^2) rotated by 30° with respect to each other. The obtained orientation relationship is $\langle 0\,1\,\bar{1}\,0\rangle AlN^1 \parallel \langle \bar{2}\,1\,1\,0\rangle AlN^2 \parallel [1\,1\,0]_{Si}$.

The nucleation on tilted single-domain Si(0 0 1) surface (type C) is peculiar by well-pronounced RHEED pattern streaks from two-dimensional single-domain AlN layer. The pattern has a 6-fold symmetry. The orientation relationship $\langle 0\,1\,\bar{1}\,0\rangle_{AlN} \parallel [1\,1\,0]_{Si}$ has been derived from the RHEED analysis.

The subsequent epitaxy on all types of the surfaces has a two-dimensional character and does not change the orientation of the domains (for A and B) as well as the ratio between the two domain types estimated from the rod intensity analysis of RHEED pattern. Thus, we can conclude that the substrate surface type determines either the two- or one-domain characters of the films and the orientation of 2H-AlN domains. No significant differences were found in the RHEED pattern evolution during the growth on the A and B substrate types.

It was evident from the post-growth characterization (XRD, TEM) that the AlN epilayers remain bonded to the Si(0 0 1) substrate over the complete epitaxial area. For the single crystalline films (type-C) with thickness up to 100 nm no stress-induced cracks were observed.

XRD 2Θ-scans demonstrate the high structural quality of the grown films. For a 500 nm thick AlN film (type A), the FWHM of the $\{0\,0\,0\,2\}_{AlN}$ peak is 0.54°. The preferred growth direction is $\langle 0\,0\,0\,1\rangle_{AlN} \parallel [0\,0\,1]_{Si}$. For a 200 nm thick AlN film grown on the C type surface, the FWHM of the $\{0\,0\,0\,2\}_{AlN}$ peak is 0.273°. The preferred growth direction is $\langle 0\,0\,0\,1\rangle$ and parallel to the surface normal resulting in a 5° angular difference between $\langle 0\,0\,0\,1\rangle_{AlN}$ and $[0\,0\,1]_{Si}$. No peaks related to the cubic phase were observed in both cases.

For the A-type substrate, the XRD Φ-scan of 2H-AlN film demonstrates the expected 12-fold symmetry of the crystal (Fig. 1a). The epitaxial relationship is fully in accordance with the RHEED pattern observations. The measured lattice constants for the epitaxial 2H-AlN ($a_{AlN}=0.3050$ nm, $c_{AlN}=0.4973$ nm) are slightly different from the referenced values ($a_{AlN}=0.3112$ nm, $c_{AlN}=0.4979$ nm) [7,8].

From the Φ-scan of 2H-AlN film grown on B-type surface (Fig. 1b), it is evident that this type of the substrate preparation is not sufficient to establish a pure single-domain Si surface and on such surface terraces of both orientations exist determining the two-domain character of the epilayer with a domination of one 2H-AlN domain type. Thus, after a 15-min annealing of nominally oriented Si(0 0 1) surface at 1000°C the formation of the double-stepped surface structure is not complete. A longer annealing procedure (30–60 min) leads to a partial carbonization of the Si surface from the residual carbon-containing species resulting in a columnar growth of AlN.

The XRD Φ-scan of the film grown on C-type substrates (Fig. 2c) shows the 6-fold symmetry of the AlN epilayer and proves the single-domain character of the Si surface. The measured lattice parameters of epitaxial 2H-AlN are equal to the two-domain films grown on nominal surface.

In Fig. 2 the results of TEM and HRTEM studies of the films grown on A- (Figs. 2a, c and e) and C-type (Figs 2b, d and f) surfaces are presented. The two-domain structure of the film grown on the nominally oriented Si(0 0 1) substrate with SASB surface structure is clearly seen on the bright-field XTEM image (Fig. 2a). The corresponding diffraction pattern shows the reflections

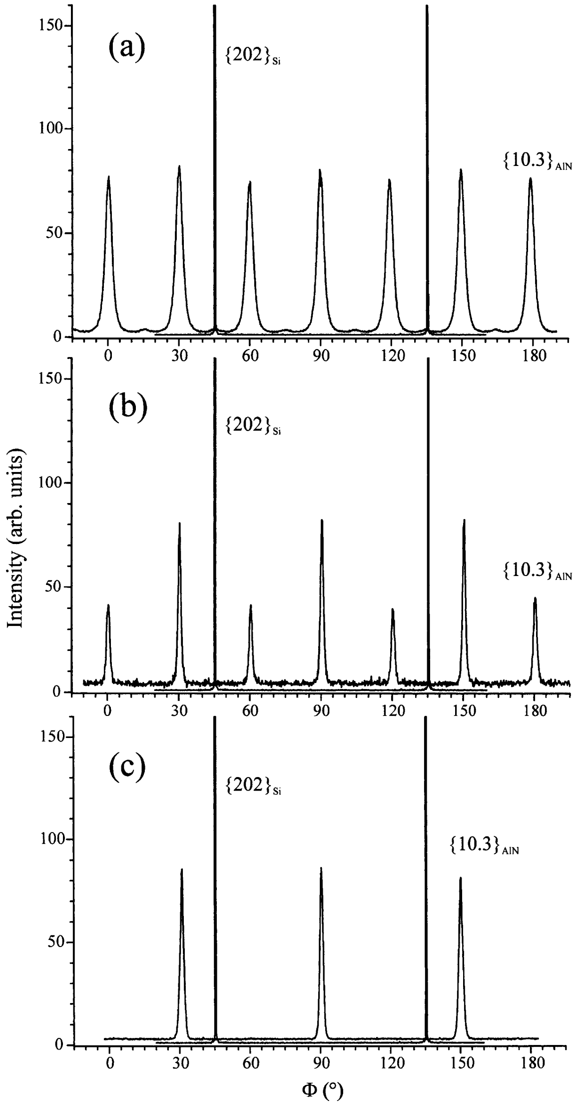

Fig. 1. The XRD Φ-scans of 2H-AlN film grown on (a) nominal type A surface, (b) nominal type B surface, (c) tilted type C surface of silicon.

from both domain types (AlN^1 and AlN^2). Within one domain the interface between the substrate and epilayer is extremely sharp and each AlN domain has a nearly perfect crystal structure as it has been proven by XRD (Fig. 1a) and HRTEM (Fig. 2c).

Fig. 2b presents a bright-field XTEM image of AlN epilayer grown on tilted (0 0 1) surface of Si. The epilayer has a single-domain character and consequently, the diffraction pattern shows only one type of AlN reflections. In Fig. 2d, a HRTEM image of the interface between the substrate and the epilayer in the area of double atomic step on the Si surface is shown. A corresponding schema of a possible atomic arrangement at 2H-AlN/Si(0 0 1) interface in this area is shown in Fig. 2f. From the scheme, one can expect that AlN/Si interface should have a very high density of misfit dislocations.

The interesting finding is that the preferred AlN growth direction is $\langle 0001 \rangle$ parallel to the substrate surface normal. The 5° tilt of the Si(0 0 1) surface toward the [1 1 0] direction results in 5° difference between Si[0 0 1] and AlN[0 0 0 1] directions in the $(0\,1\,\bar{1}\,0)$ plane. As it has been discussed by Hellman et al. [15], the film tilt may accommodate lattice mismatch and in our case, such "coherent tilt" of the film partly accommodates one-dimensional mismatch along the $\langle 0\,1\,\bar{1}\,0 \rangle$ direction with a corresponding reduction in the misfit of $\sim 0.4\%$.

In summary, it was found that the properties of the 2H-AlN epilayers strongly depend on the Si(0 0 1) surface geometry and the initial growth conditions. 2H-AlN films grown on the nominal Si(0 0 1) surface have a two-domain structure with the epitaxial orientation relationship of $[0\,0\,0\,1]_{AlN} \parallel [0\,0\,1]_{Si}$ and $\langle 0\,1\,\bar{1}\,0 \rangle AlN^1 \parallel \langle \bar{2}\,1\,1\,0 \rangle AlN^2 \parallel [1\,1\,0]_{Si}$ confirming that the SASB structure of the nominal Si(0 0 1) surface determines the two-domain character of the epilayer. Single domain 2H-AlN films have been grown on off-axis Si(0 0 1) substrates having double-stepped surface structure. The observed epitaxial orientation relationship is $\langle 0\,1\,\bar{1}\,0 \rangle_{AlN} \parallel [1\,1\,0]_{Si}$. The preferred AlN growth direction is $\langle 0001 \rangle$ parallel to the substrate surface normal. We may assume that the film tilt is favorable due to the corresponding reduction in the interface energy.

In addition, for both, nominal and off-axis Si(0 0 1) substrates, there is no topological compatibility between substrate and epilayer lattices. Therefore the tendency to form the perfect wurtzite structure of AlN on such surfaces might be explained by a thermodynamical stability of the wurtzite AlN polytype and a large number of

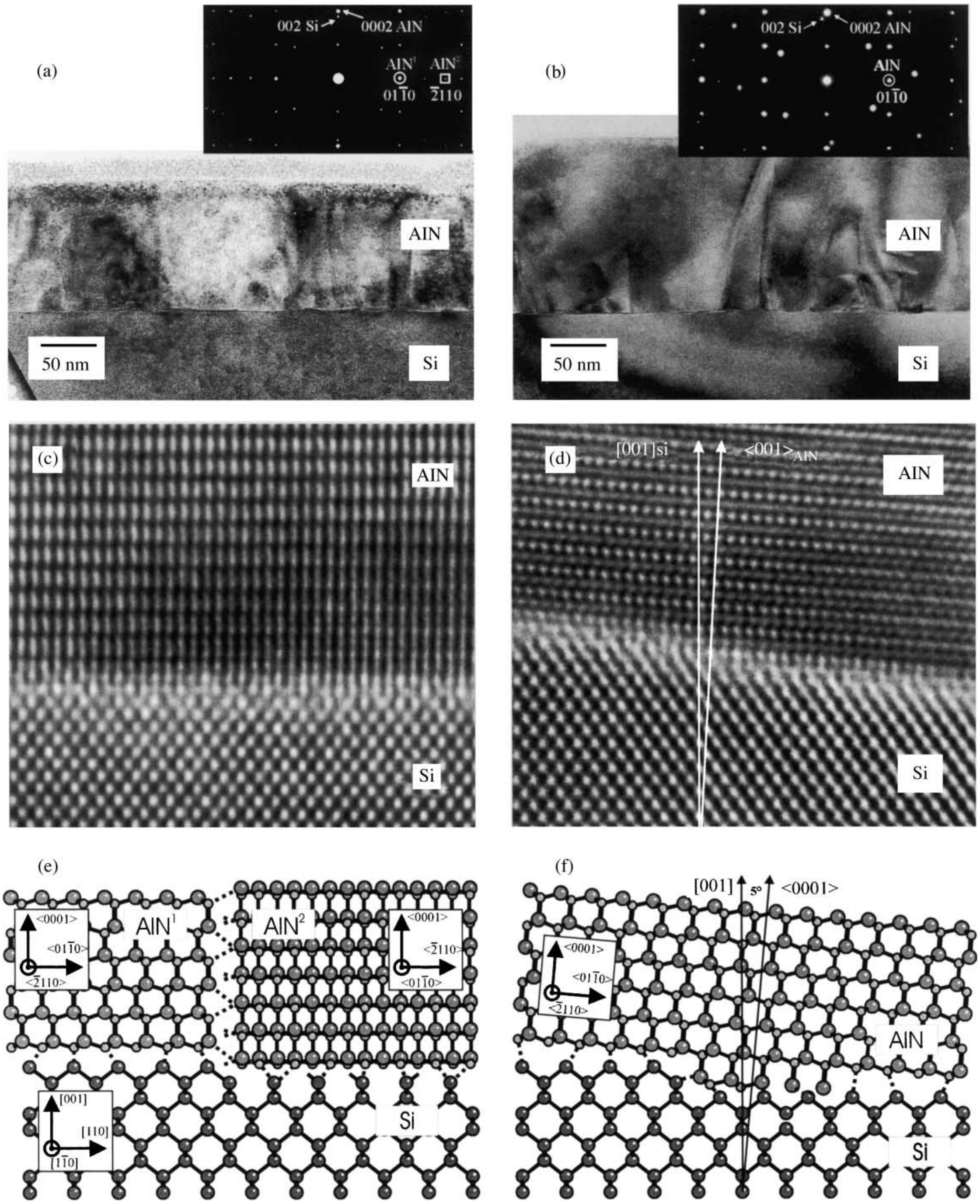

Fig. 2. (a,b) Bright-field XTEM image of 2H-AlN thin films: (a) grown on nominal Si(0 0 1) substrate, and (b) grown on 5°-tilted Si(0 0 1) substrate (insets: diffraction patterns taken at $[1\ \bar{1}\ 0]_{Si}$ zone axis, AlN^1 and AlN^2 reflections marked by cycle and square, respectively). (c,d) HRTEM images of the interface area; (c) between nominal Si(0 0 1) substrate and two-domain AlN epilayer in the domain-boundary-free area and (d) between 5°-tilted toward [1 1 0] Si(0 0 1) substrate and single-domain AlN epilayer (double-stepped Si surface). (e,f) Schematic view of the possible atomic arrangement at the interface between the epilayer and the substrate; (e) for a two-domain AlN film grown on the nominal, single-stepped Si(0 0 1) surface and (f) for a single-domain AlN film grown on the double-stepped Si(0 0 1) surface.

well-ordered nucleation sites on (0 0 1) surface of silicon.

This work was supported by grant of the Deutsche Forschungsgemeinschaft (contract No. RI 650/5-1).

References

[1] S.J. Peatron, J.C. Zolper, R.J. Shul, F. Ren. J. Appl. Phys. 86 (1999) 1.

[2] C. Deger, E. Born, H. Angerer, O. Ambacher, M. Stutzmann, J. Hornsteiner, E. Riha, G. Fischerauer, Appl. Phys. Lett. 72 (1998) 2400.

[3] V. Lebedev, B. Schröter, G. Kipshidze, Wo. Richter, J. Crystal Growth 207 (1999) 266.

[4] A.T. Schremer, J.A. Smart, Y. Wang, O. Ambacher, N.C. MacDonald, J.R. Shealy, Appl. Phys. Lett. 76 (2000) 736.

[5] S.I. Molina, A.M. Sanchez, F.J. Pacheco, R. Garcia, M.A. Sanchez-Garcia, F.J. Sanchez, E. Calleja, Appl. Phys. Lett. 74 (1999) 3362.

[6] H.P.D. Schenk, U. Kaiser, G. Kipshidze, A. Fissel, J. Kräußlich, H. Hobert, J. Schulze, W. Richter, Nat. Sci. Eng. B 59 (1999) 84.

[7] J.H. Edgar (Ed.), Properties of group III nitrides, EMIS Datareview, Vol. 11, INSPEC, London, 1995.

[8] D. Gerthsen, B. Neubauer, Ch. Dieker, R. Lantier, A. Rizzi, H. Lüth, J. Crystal Growth 200 (1999) 353.

[9] A. Ishizaka, Y. Shiraki, J. Electrochem. Soc. 133 (1986) 666.

[10] C. Zhu, A. Kawazu, S. Misawa, S. Tsukahara, Phys. Rev. B 59 (1999) 9760.

[11] R.D. Bringans, R.I.G. Uhrberg, M.A. Olmstead, R.Z. Baxhrach, Phys. Rev. B 34 (1986) 7447.

[12] V. Lebedev, J. Jinschek, U. Kaiser, B. Schröter, W. Richter, J. Kräußlich, Appl. Phys. Lett. 76 (2000) 2029.

[13] R. Fischer, H. Morkoc, D.A. Neumann, H. Zabel, C. Choi, N. Otsuka, M. Longerbone, L.P. Erckson, J. Appl. Phys. 60 (1986) 1640.

[14] T. Sakamoto, G. Hashiguchi, Jpn. J. Appl. Phys. 25 (1986) 78.

[15] E.S. Hellman, Z. Liliental-Weber, D.N.E. Buchanan, MRS Internet J. Nitride Semicond. Res. 2 (1997) 30.