



Growth of *M*-plane GaN on (100) LiGaO₂ by plasma-assisted molecular beam epitaxy

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ABSTRACT

Growth of *M*-plane GaN on (100) LiGaO₂ was achieved using plasma-assisted molecular beam epitaxy. Thermal annealing of the LiGaO₂ wafer was found to lead to a substrate surface suitable for growth. Structural and morphological analysis was performed using x-ray and reflective high energy electron diffraction, scanning electron and atomic force microscopy. X-ray diffraction results show very high phase purity and a relaxation state of the GaN film close to 80%. The surface morphology, showing characteristic *M*-plane streaks, is flat and smooth.

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1. Introduction

GaN, as one of the most important compound semiconductors today, has been under vivid investigation over the past years. Special interest is given to the growth of non-polar *M*-plane GaN, which presents a way to circumvent unwanted effects due to its intrinsically built-in electric fields [1]. Since GaN substrates are not readily available for homoepitaxy, various alternative substrates have been examined for growth of high quality GaN crystals [2].

LiGaO₂ (LGO) presents the closest lattice matched substrate that has been considered for GaN heteroepitaxy. Its structure was determined as orthorhombic, space group Pna2₁, with lattice parameters $a = 5.402 \text{ \AA}$, $b = 6.372 \text{ \AA}$, $c = 5.007 \text{ \AA}$ [3]. Earlier reports on the epitaxial relationship between GaN and LGO noted the small lattice mismatch between *M*-plane GaN on (100) LGO, *A*-plane GaN on (010) LGO and *C*-plane GaN on (001) LGO [4,6].

Fig. 1 shows a ball and stick model of the (100) LGO surface with its unit cell as a dotted rectangle. The gray rectangles display possible nucleation sites for *M*-plane GaN growth. The lattice mismatch for the relationship [010]LGO||[11 $\bar{2}$ 0]GaN and [001]LGO||[0001]GaN is only 0.07% and 3.58%, respectively. Growth on the (100) plane of LGO also benefits from the lack of a metal–non-metal polarity, which is an issue that has to be taken into account when growing on (001) LGO. While several groups have put effort in growing *C*-plane GaN on (001) LGO [4,5,7–11], there has only been one report about non-polar *A*-plane GaN growth on the (010) orientation of LGO [17] and no report on GaN

growth on (100) LGO. Here we demonstrate the growth of *M*-plane GaN on (100) LGO by plasma-assisted molecular beam epitaxy (MBE).

2. Experimental procedure

The (100) LGO substrates were grown at the National Sun Yat-sen University in Taiwan and polished by a commercial vendor. The crystal growth experiments were carried out in a Czochralski pulling furnace. The starting raw materials (Li₂CO₃ and Ga₂O₃ powders with a purity of at least 99.99%) were mixed mechanically according to 99.99% stoichiometric ratio. After placing the raw materials in an iridium crucible covered with an iridium lid to reduce the temperature gradient, the crucible was heated to approximately 1650 °C to melt the raw materials. During growth, nitrogen gas was continuously supplied to prevent the oxidation of the Ir crucible. The seed had a (001) *c*-axis orientation. A rotation rate of 10–20 rpm was used to control the growth conditions. Because of the high vapor pressure of the LGO melt, a high crystal pulling rate of 2–4 mm/h was applied in order to avoid loss of the melt. Our sample shows a small inclusion at the bottom of the crystal. No twin boundaries are found. However, dislocations definitely exist and we estimate their density to be 10⁴–10⁵. We have tried to prepare TEM samples for further characterization but have failed a couple of times.

The samples were grown in a RIBER Compact 21 MBE system. Due to transparency of the substrate in the visible and near infrared wavelength range the substrate was mounted onto a Si wafer using a thin layer of In to provide a homogeneous thermal coupling. The substrates, inserted into molybdenum holders, were first outgassed for 60 min at 130 °C in a load lock chamber and thereafter transferred into the growth chamber. Activated nitrogen was supplied by an Oxford

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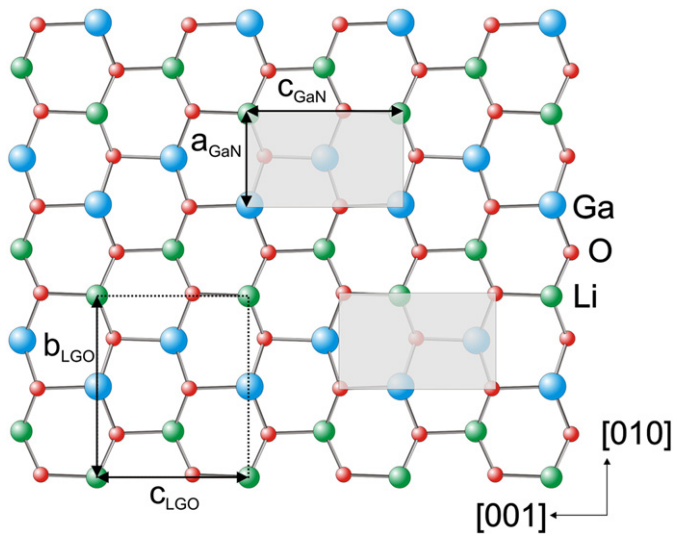


Fig. 1. Ball and stick model of the (100) LGO surface. The dotted rectangle signals the size of the LGO unit cell, while the rectangles with continuous lines indicate possible nucleation sites for (1 $\bar{1}$ 00) GaN.

HD25 RF plasma cell operated at a steady gas flow of 0.3 sccm and 450 W forward power. A growth rate of roughly 100 nm/h was used. Growth was monitored *in-situ* using reflective high energy electron diffraction (RHEED). To prevent damage to the sample, care was taken to not irradiate the sample for too long with the electron beam.

Initial growth showed almost complete peeling off of the epitaxial film from the substrate. This may have a number of reasons such as damage caused to the substrate by its irradiation with highly energetic electrons from RHEED measurements. Moreover, an enhanced misfit of the anisotropic coefficients of thermal expansion (CTE) between LGO and GaN at high temperature could facilitate the lift-off of the epitaxial film from its substrate. The exact direction dependent amount of stress caused by this mechanism is difficult to calculate as there is a large scatter of experimental data on the determination of the CTE for LGO [12–15]. However, from the data reported it is apparent, that there is a strong anisotropy in the LGO values for the CTE. In addition, the CTE in a temperature range of 700 K are not constant and as pointed out by Neumann et al. [13] each of the 3 different CTE in LGO shows a different non-linear behaviour in the

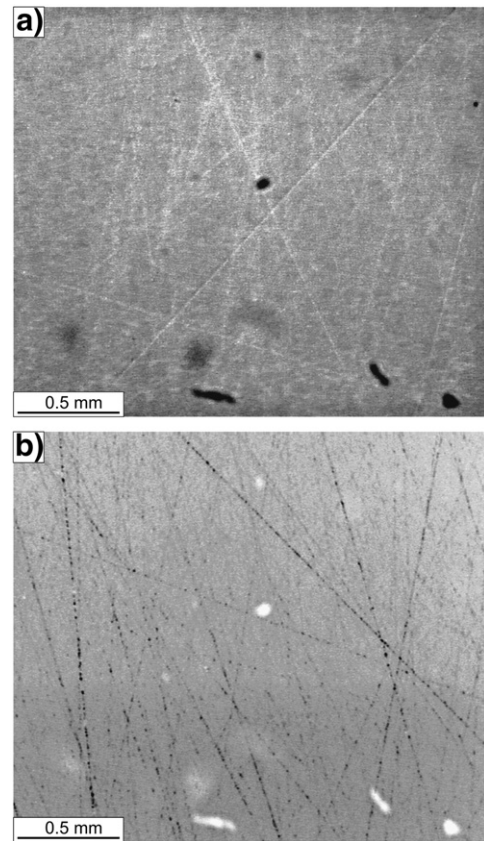


Fig. 3. Images of the substrate surface before growth (a) and of the sample surface after growth (b) taken through an optical microscope at a magnification of 100. The scratches on the substrate, probably caused by mechanical polishing, are clearly visible in both cases. The spots occurring mostly in the lower part of both pictures are due to impurities on the microscope lens.

temperature range between 293 K and 1100 K. We therefore believe the calculation of the stress caused using the CTE to be inexact.

We consider a direct comparison of the lattice parameters near the growth temperature $GT = 700^\circ\text{C}$ and at room temperature (RT) more reliable using data presented by Rawn and Chaudhuri [15] and Neumann et al. [13]. Here the resulting lattice mismatch near GT is subject only to small variations. The lattice parameters of GaN were

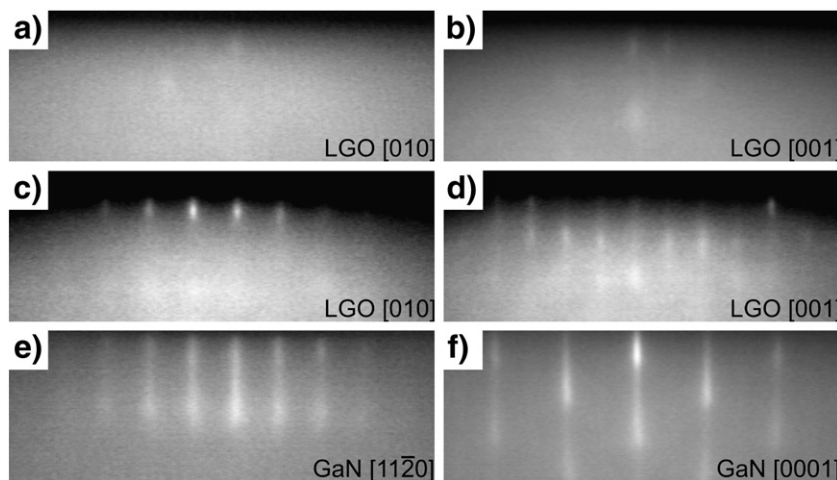


Fig. 2. a) and b): RHEED images of two LGO azimuths, separated by 90° before annealing the substrate. The same azimuths of LGO after annealing are shown in c) and d). The two corresponding M -plane GaN directions, namely $[1\bar{1}\bar{2}0]$ and $[0001]$, after growth can be seen in e) and f). The spacing of the streaks in $[1\bar{1}\bar{2}0]$ direction gives the c_{GaN} lattice constant whereas the a_{GaN} lattice constant is given by the separation of streaks in $[0001]$ direction.

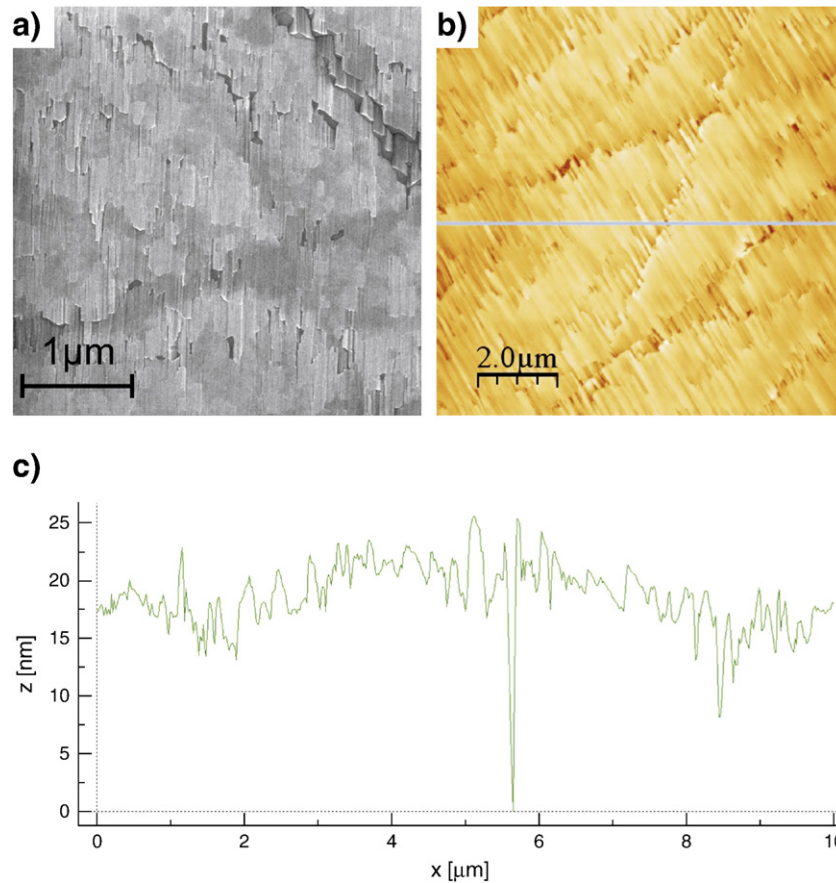


Fig. 4. An SEM image of the sample surface is seen in a). A $10 \times 10 \mu\text{m}^2$ AFM scan is shown in b), with a 10 μm long horizontal line depicting the profile given in c).

calculated by the CTE given in [16] for high temperatures. The difference in lattice mismatch between GT and RT for GaN_a on $\text{LGO}_{b/2}$ then lies at 0.93% to 1.18% and for GaN_c on LGO_c at 0.50% to 0.61%. In both the $[11\bar{2}0]$ GaN and the $[0001]$ GaN direction the stress induced from the LGO lattice onto the GaN lattice when cooling down is compressive. Since more stress is caused in the a -direction than in the c -direction of GaN, a cracking of the GaN film is expected along the c -direction. The cracks in c -direction are confirmed by SEM pictures where the orientation of the film is inferred from previous reports and experiences with M -plane GaN. From the relatively small change in lattice mismatch caused by thermal expansion it is unlikely that this mechanism is solely responsible for the peeling off of the epitaxial film from the substrate. However, a contribution of the anisotropic thermal expansion of GaN and LGO to this phenomenon can be expected.

A procedure for growth of M -plane GaN on LGO was found, however the growth conditions were not thoroughly optimized. The GaN film, when taken out of the growth chamber, had cracks at the edges probably caused by a too high temperature in the area of contact between the substrate and the Mo holder. However, the center of the film remained stable and did not lift-off or show cracks. Prior to GaN deposition the substrate was annealed at 800 °C for 60 min. Thereafter, growth of GaN commenced at slightly Ga rich conditions at a substrate temperature of 700 °C. The temperatures given correspond to the thermocouple readings.

The sample was characterized *ex-situ* by x-ray diffraction (XRD) in a Bruker AXS D8 Discover diffractometer. A ceramic x-ray tube of type KFL Cu 2 K was used to generate the characteristic $\text{Cu}_{K\alpha 1}$ line. Scanning electron microscopy (SEM) was performed on a LEO 1530 system at an operating voltage of 10 keV. Atomic force microscopy (AFM) images were taken with a SiN tip in contact mode with an Autoprobe CP head from Park Scientific Instruments calibrated with a commercial calibration sample.

3. Results and conclusion

Observation of the RHEED patterns of the LGO substrate before and after annealing showed a remarkable improvement of the surface. In Fig. 2 two azimuths serve to illustrate the development of the reflection patterns. While the top two pictures, a) and b), show the reflection patterns of the substrate in $[010]$ and $[001]$ direction before annealing, part c) and d) display the situation after 1 h annealing at 800 °C for the same directions respectively. Because of the weak reflection signal from the substrate before annealing it was impossible to find the exact $[010]$ and $[001]$ azimuths. The pictures given in a) and b) therefore only roughly correspond to these directions. The two lowest pictures, e) and f), in this figure show RHEED images of the sample after growth, taken at the same angles as c) and d) respectively. They show streaky images of M -plane GaN along the $[11\bar{2}0]$ and $[0001]$ directions, where the spacings of the streaks correspond to the c and a lattice constant respectively. Comparing the two RHEED images of LGO after annealing with the two lower pictures of GaN, the epitaxial relationship is demonstrated in accordance with Fig. 4. In other words, from the spacings of the RHEED streaks in Fig. 2 a high degree of lattice match of M -plane GaN on (100) LGO is evident for a_{GaN} on $b_{\text{LGO}}/2$ and c_{GaN} on c_{LGO} . From the streakiness of the RHEED images, the film is expected to be flat and smooth.

Surface scratches on the sample before and after growth are visible in optical microscope images seen in Fig. 3. These scratches most probably originate from mechanical polishing of the substrate. Fig. 4 shows the surface morphology of the GaN layer by means of SEM a) and AFM b). The epitaxial film has a thickness of 390 nm as measured by SEM. The slate-like surface modulation is typical for M -plane GaN. No indication of C -plane GaN could be observed at any point when performing microscopy on the film. The surface scratches from the substrate are visible as line discontinuities in the M -plane GaN film in both images. Despite these scratches, a small RMS roughness of

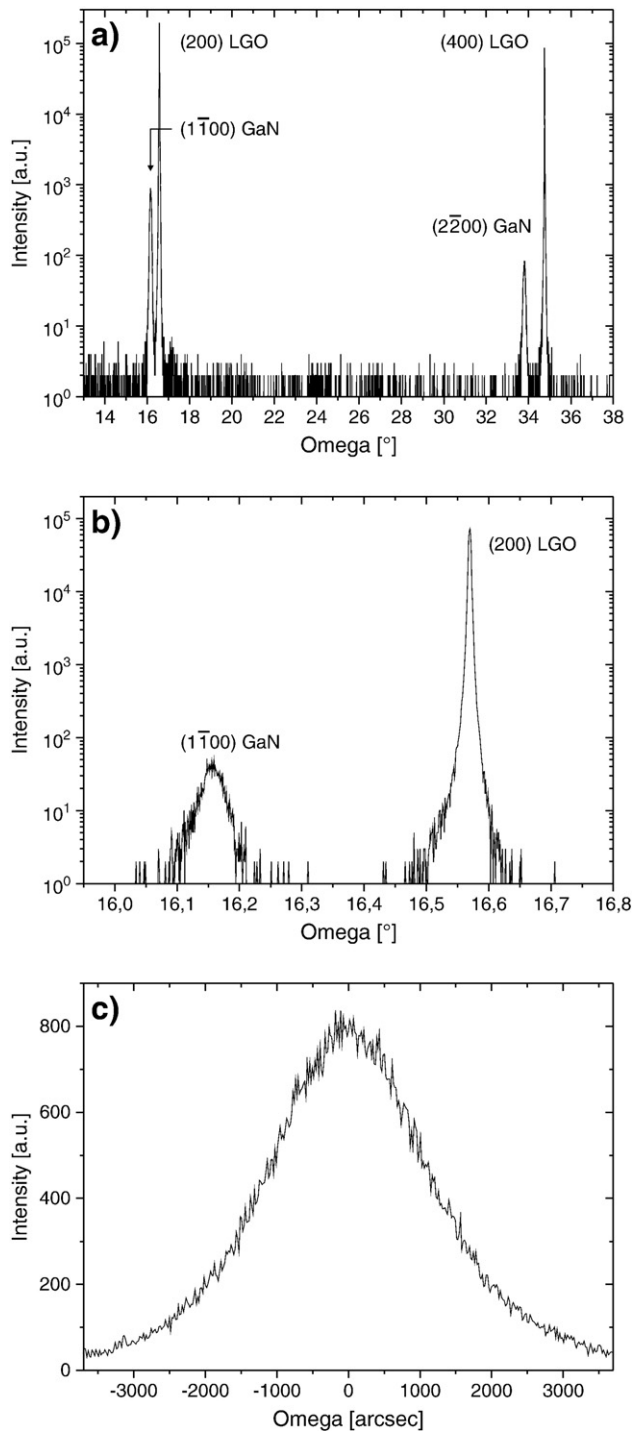


Fig. 5. Part a) shows a $\omega-2\theta$ x-ray scan in double crystal configuration of a 390 nm thick GaN layer grown on LGO. A higher resolution $\omega-2\theta$ scan with a triple crystal analyzer in the range $\omega = 16^\circ - 16.8^\circ$ is seen in b). c) presents the rocking curve of the $(1\bar{1}00)$ GaN reflection, the FWHM of which lies around 2500 arcsec.

2.9 nm is found in an area of $10 \times 10 \mu\text{m}^2$. Part c) of Fig. 4 shows the depth profile of the line indicated in b) over a range of $10 \mu\text{m}^2$. A peak to valley roughness below 5 nm in regions without scratches and surface height variations up to 25 nm at the location of scratches are displayed. It is expected that the surface roughness will improve when polishing procedures and growth conditions are optimized, thereby also increasing the GaN film quality tremendously.

To examine the crystal orientation, quality and strain state of the epitaxial GaN film, x-ray diffraction scans were performed. Fig. 5 a)

shows a $\omega-2\theta$ scan in the range $\omega = 13 - 38^\circ$ where the $(1\bar{1}00)$ GaN, (100) LGO, and $(2\bar{2}00)$ GaN, (200) LGO peaks can be seen. This scan was performed in a double crystal configuration with a resolution of 0.005° . No other major peak is observed in the spectrum. Only an extremely small hint of a peak around $\omega = 17.16^\circ$ with a maximum of 7 counts could be noticed, which may be attributed to a very small fraction of C-plane GaN. However, this signal is far too weak for further analysis and with respect to the $(1\bar{1}00)$ GaN peak with a maximum intensity of ~ 900 counts it is safe to state a very high phase purity of M-plane GaN. Part b) in Fig. 4 shows a more detailed measurement of the $(1\bar{1}00)$ GaN and (200) LGO peaks with a resolution of 0.001° using a triple crystal analyzer. The strain state can be estimated from this measurement using the relative shift of the $(1\bar{1}00)$ GaN peak with respect to the (200) LGO peak. Disregarding twist or tilt inside the GaN crystal, the GaN film is relaxed to roughly 80% compared to the maximal possible transverse deformation caused by the lattice misfit between LGO and GaN in the basal plane.

To determine the film quality, we measured the rocking curves of the $(1\bar{1}00)$ GaN peak position. The result is given in part c) of Fig. 5. A full width at half maximum (FWHM) with a large value of ~ 2500 arcsec is found. Although growth conditions were not optimized we expected a much lower value for the FWHM considering the quality of the sample surface from SEM and AFM data. The large FWHM value is probably mainly either due to irregularities propagated into the film from scratches on the substrate surface (see Fig. 4) or caused by contributions to the Bragg reflection from the cracked edges of the GaN film.

4. Summary

It has been shown that M-plane GaN can be grown epitaxially on (100) LiGaO₂ by plasma-assisted MBE. Thermal annealing of the substrate before growth is a procedure well suited to clean its surface. Streaky RHEED patterns after growth in addition to the SEM and AFM data show smooth M-plane GaN. The XRD results indicate a high degree of phase purity and a relaxation state close to 80%. The results obtained show the feasibility of high quality M-plane GaN growth on (100) LiGaO₂.

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References

- [1] P. Waltereit, O. Brandt, A. Trampert, H.T. Grahn, J. Menniger, M. Ramsteiner, M. Reiche, K.H. Ploog, *Nature* 406 (2000) 865.
- [2] L. Liu, J.H. Edgar, *Mater. Sci. Eng.*, R 37 (2002) 61.
- [3] M. Marezio, *Acta Cryst.* 18 (1965) 481.
- [4] M.A.L. Johnson, W.C. Hughes, W.H. Rowland, J.W. Cook, J.F. Schetzina, M. Leonard, H.S. Kong, J.A. Edmond, J. Zavada, *J. Cryst. Growth* 175 (1997) 72.
- [5] A.V. Andrianov, D.E. Lacklison, J.W. Orton, T.S. Cheng, C.T. Foxon, K.P. O'Donnell, J.F.H. Nicholls, *Semicond. Sci. Technol.* 12 (1997) 59.
- [6] R.J. Matyi, W.A. Doolittle, A.S. Brown, *J. Phys. D Appl. Phys.* 32 (1999) A61.
- [7] W.A. Doolittle, S. Kang, T.J. Kropewnicki, S. Stock, P.A. Kohl, A.S. Brown, *J. Electron. Mater.* 27 (1998) L58.
- [8] S.K. Duan, X.G. Teng, P.D. Han, D.C. Lu, *J. Cryst. Growth* 195 (1998) 304.
- [9] M. Losurdo, D. Giuva, G. Bruno, S. Huang, T.H. Kim, A.S. Brown, *J. Cryst. Growth* 264 (2004) 139.
- [10] H. Takahashi, H. Fujioka, J. Ohta, M. Oshima, M. Kimura, *J. Cryst. Growth* 259 (2003) 36.
- [11] K. Sakurada, A. Kobayashi, Y. Kawaguchi, J. Ohta, H. Fujioka, *Appl. Phys. Lett.* 90 (2007) 211913.
- [12] S. Nanamatsu, K. Doi, M. Takahashi, *Jpn. J. Appl. Phys.* 11 (1972) 816.
- [13] H. Neumann, E. Pirl, G. Kuhn, *J. Mater. Sci. Lett.* 6 (1987) 495.
- [14] T. Ishii, Y. Tazoh, S. Miyazawa, *J. Cryst. Growth* 189/190 (1998) 208.
- [15] C.J. Rawn, J. Chaudhuri, *J. Cryst. Growth* 225 (2001) 214.
- [16] C. Roder, S. Einfeldt, S. Figge, D. Hommel, *Phys. Rev. B* 72 (2005) 085218.
- [17] R. Schuber, M.M.C. Chou, P. Vincze, Th. Schimmel, D.M. Schaadt, *J. Cryst. Growth* 312 (2010) 1665.