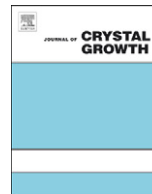




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Journal of Crystal Growth

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Molecular beam epitaxial growth of gallium nitride nanowires on atomic layer deposited aluminum oxide

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ARTICLE INFO

Article history:

Received 5 April 2011

Received in revised form

17 August 2011

Accepted 22 August 2011

Communicated by J.M. Redwing

Available online 26 August 2011

Keywords:

A1. Nanowires

A3. Molecular beam epitaxy

B1. Nitride

B1. Aluminum oxide

ABSTRACT

Semiconductor nanowires have received increasing focus from researchers due to their one dimensional characteristics, which offer new horizons for device designs. Nanowire growth has been shown to yield crystalline material on non-lattice matched substrates. Concerning gallium nitride nanowires, common growth substrates have been silicon (100) and (111) substrates. This manuscript discusses the successful molecular beam epitaxial growth of gallium nitride nanowires on amorphous aluminum oxide thin films, grown by atomic layer deposition. Results indicate that regardless of the amorphous nature of the oxide films, the gallium nitride nanowires grown are crystalline and free of defects even at the interface with the oxide. The results offer a method of realizing promising frontiers for device design in which a high quality crystalline material is desired on an amorphous substrate.

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1. Introduction

Semiconductor nanowires have been receiving a good deal of attention in the past few years from researchers around the globe [1–7]. Their one dimensional structure offers characteristics that hold high potential for filling niche applications over the use of two dimensional thin films. Of these, one of the most liberating characteristics is the ability to grow quality material on non-lattice-matched substrates. Concerning GaN nanowires, growth substrates commonly used were initially (111) silicon due to its hexagonal atomic pattern, which is similar to that of the *c*-plane in wurtzite nitride semiconductors. Soon discovered was the fact that (100) silicon could also be used for successful growth of nanowires [8]. Further, reports of a thin, amorphous, non-intentionally grown silicon nitride layer (~2 nm thick) appearing on silicon growth substrates indicated that the nanowire growth does not critically depend on the crystalline structure of the underlying substrate [9].

While the use of silicon substrates is a common method for nitride nanowire growth by MBE, as nanowires move forward into new paradigms, device design may warrant the need for nanowire growth on a systematically controlled oxide layer. Discussed in this manuscript is the successful growth of gallium nitride (GaN) nanowires by molecular beam epitaxy (MBE) on controlled aluminum oxide grown by atomic layer deposition (ALD).

2. Experiment

The same growth conditions that yield quality GaN nanowires on silicon substrates were used for nanowire growth on Al₂O₃. These conditions are described here. Silicon (111) substrates were dipped in buffered HF for 90 s to remove any native oxide, rinsed with DI water and dried with N₂. Aluminum oxide (Al₂O₃) was deposited by ALD in a Cambridge Savannah system using trimethyl aluminum and H₂O as precursors at a chamber temperature of 200 °C. Two targeted layer thicknesses for the Al₂O₃, 5 nm and 7 nm, were used and yielded similar nanowire growth results. To measure the true ALD aluminum oxide thickness, a Variable Angle Spectroscopic Ellipsometer (VASE) system was used. The results revealed that using 45 ALD cycles yielded ~5.5 nm Al₂O₃ and 64 cycles yielded ~7.2 nm of Al₂O₃. The sample discussed in this writing was grown on a target thickness of 7 nm of Al₂O₃, which was deposited by 64 cycles of ALD material deposition.

Following Al₂O₃ deposition, the substrate was cleaned by ultra-sonication in acetone, methanol and isopropyl alcohol for 20, 10 and 10 min, respectively, rinsed in DI water and blow dried with N₂. Upon loading into the MBE system, the samples were outgassed at 200 °C for 7 h followed by 400 °C for 2 h. Samples grown without Al₂O₃ layers were further outgassed in the growth chamber at 750 °C for 15 min and 850 °C for 10 min in efforts to remove any native oxides [10].

Nanowire growth occurred in a Veeco Gen 930 MBE system using a RF plasma source supplying a plasma power of 450 W. Gallium fluxes were measured using a nude ion gauge. As such, all flux measurements are beam equivalent pressures. Gallium fluxes

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that were used were between 2.21×10^{-8} and 1×10^{-7} Torr. Higher metal fluxes would result in a higher nanowire density [11]. The substrate temperature as measured by a thermocouple was 830°C throughout the growths. The nanowires were doped with silicon using a silicon cell temperature of 1120°C , which yielded a flux $\sim 1 \times 10^{-12}$ Torr. Growth occurred on raising the substrate to the growth temperature, leaking in nitrogen to a $2\text{--}3 \times 10^{-5}$ Torr back pressure, striking the plasma and then opening the gallium, silicon and nitrogen cells simultaneously. The growth conditions were held constant for 4–5 h, at which time the growth was terminated.

3. Results and discussion

Scanning electron microscope (SEM) images were obtained of as grown samples in a FEI Magellan SEM system. These samples were grown under identical conditions on identical 90 s HF cleaned silicon substrates. The differentiating trait is that one sample was grown directly on the silicon (111) substrate while the other was

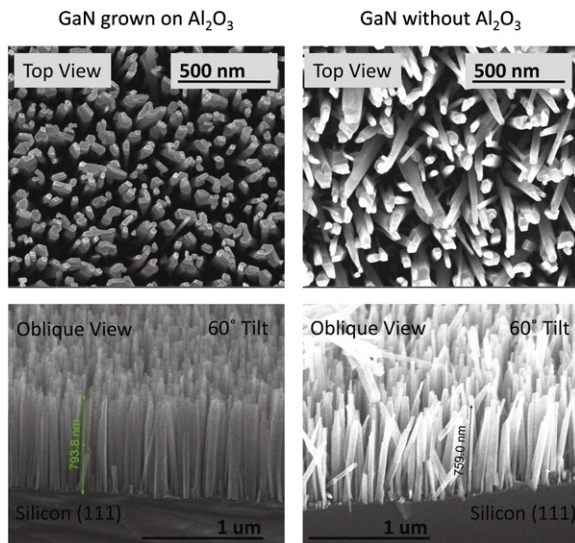


Fig. 1. Scanning electron microscope images of GaN nanowires grown on silicon substrates, with (left) and without (right) Al_2O_3 insulating layer. The top view shows the wires grown on the Al_2O_3 appear to be more aligned relative to each other. The bottom images show heights and diameters are comparable for the two growths.

grown after ~ 7 nm of ALD Al_2O_3 had been deposited on the silicon. Top view and oblique angle views of the nanowires are shown in Fig. 1. The nanowires have grown to heights ranging from 750 nm to 800 nm. Concerning the height of 800 nm, the maximum growth rates under these conditions equate to ~ 3.3 nm/min. Diameters of the nanowires range from 50 nm to a maximum of near 80 nm.

Comparing the two samples, the growth that occurred on the Al_2O_3 resulted in nanowires, which were more aligned with respect to each other. These wires appear to be growing vertical with respect to the substrate. In contrast, the nanowires grown on the silicon substrate show a more varied growth angle with respect to each other. The cause of the increase in variation of growth angle for the wires grown directly on silicon is not known for certain. One hypothesis for this observation is the SiN layer that is seen at the silicon surface after nanowire growth. The SiN layer has varying thicknesses across the sample, which could lead to an increased tilt in the growth. The SiN layer has been observed by other groups [9], and matching results are seen here when growing directly on silicon. Concerning diameters, overall shapes and heights, the two samples appear to be similar. The SEM images show that using the same growth conditions, it is possible to yield three dimensional nanowire structures on Al_2O_3 , just as has been reported on silicon substrates.

Photoluminescence (PL) emission spectra of GaN wires have been acquired using a home built setup consisting of a HeCd laser for excitation (325 nm), Janis cryostat ST-500 with a sample holder, and a Princeton Instruments/Acton 2500i spectrometer.

PL measurements were taken of ensembles of the as grown nanowires, which were grown on Al_2O_3 . A PL spectrum of the nanowires is shown in Fig. 2 along with the PL spectra of a commercial n-type free standing GaN thin film substrate obtained from Lumilog, batch 09-368. The nanowires have a slightly lower FWHM than the thin film both at 5 K and at 300 K. These values at 5 K are 5 meV for the nanowires compared to 6.5 meV for the thin film. At 300 K, the nanowires show a FWHM of 69 meV compared to the thin film at a value of 74 meV. Examining the intensity of the two specimens, at 5 K, the thin film gave a PL intensity 1.3 times that of the nanowires. At 300 K, the thin film once again showed a higher PL intensity—3 times higher than the nanowires. Considering the thin film, the intensity dropped 31 times from 5 K to 300 K, nearly half the change seen from the nanowires where the intensity dropped 67 times over the same temperature window. The significant difference in temperature dependent PL intensity seen between the nanowires and thin film is thought to stem from an increase of non-radiative recombination due to surface states occurring in the nanowires at room temperature [12].

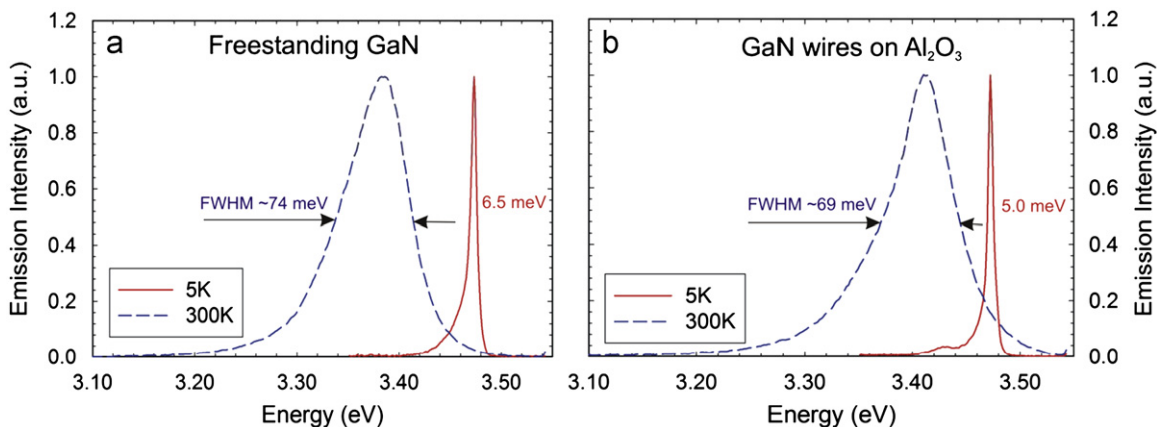


Fig. 2. (a) Photoluminescence spectrum of commercially grown (MOCVD) free standing GaN substrate. (b) PL spectrum of as grown ensemble GaN nanowires on Al_2O_3 layer. At 300 K: 5 K, the FWHM values are 74 meV: 6.5 meV for the commercially grown GaN and 69 meV: 5 meV for the nanowires grown on Al_2O_3 .

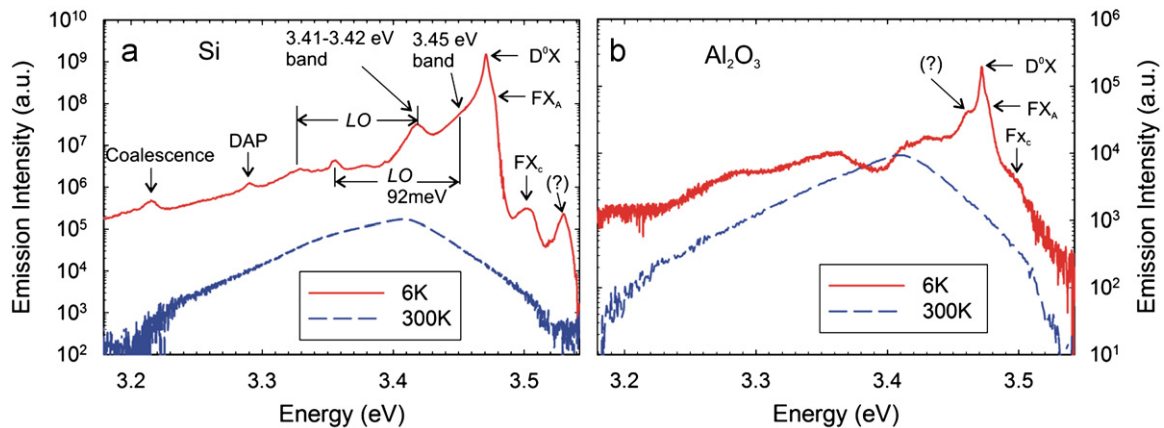


Fig. 3. Emission spectra of PA-MBE grown GaN wires on silicon (a) and Al_2O_3 (b) substrates. Red solid (blue dashed) line represents the spectra measured at 6 K (300 K). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To allow readers to quickly compare the FWHM data of the nanowires grown on Al_2O_3 with high quality GaN from current literature, PL data by Kornitzer et al. [13] reveals PL FWHM peaks of 100 ueV for both the donor and acceptor-bound excitons at 4.2 K.

Further investigation was carried out on the nanowire PL data (both on silicon and Al_2O_3) as shown in Fig. 3. All four spectra shown in Fig. 3 have been measured under the same excitation intensity of $\sim 300 \text{ W/cm}^2$. GaN wires grown on a silicon substrate are extremely bright and thus allowed for attenuation of the emission intensity accordingly for weak and intense parts of the spectra and “stitched” the whole spectra afterwards. The much lower intensity of GaN wires on the Al_2O_3 substrate did not allow for employing the same strategy of “stitching” spectra.

GaN wires grown on the silicon substrate exhibit a rich emission spectra at 6 K, where almost all known transitions can be identified. Free A-excitons, FX_A , have an emission peak at 3.4776 eV (full width at half maximum is $\sim 3.9 \text{ meV}$) and neutral donor-bound excitons (D^0X) are red-shifted by $\sim 6.6 \text{ meV}$ exciton-donor binding energy. The free B-excitons are not clearly resolved, but an emission peak of free C-excitons is clearly visible near 3.50 eV [13]. The 3.45 eV emission band is explained by recombination of excitons near Ga-vacancies favorably formed under nitrogen rich growth conditions. The 3.41–3.42 eV emission arises either from defects on wire/substrate interface or from excitons bound to stacking faults. Both bands have replica peaks shifted by 92 meV longitudinal optical phonon energy. Donor-acceptor pair (DAP) transitions near 3.29 eV and an emission peak arising from coalesced wires near 3.22 eV are also visible. More detailed information on undoped and Si-doped GaN wires can be found in [14]. GaN wires grown on silicon exhibit a mysterious peak near 3.530 eV while for GaN wires on the Al_2O_3 substrate, the peak at 3.4619 eV could not be identified, and corresponding research is ongoing.

GaN wires grown on a silicon substrate are 3–4 orders brighter than their counterparts grown on the amorphous Al_2O_3 layer and exhibit much richer spectra as evident from Fig. 3. It suggests the superior crystal quality of GaN wires grown on Si and it was confirmed later by the Raman spectroscopy carried out on a WiTec Alpha 500 AFM/Raman setup. The Raman signal from GaN wires on silicon is clearly visible and it is centered at $\sim 567 \text{ cm}^{-1}$ while the intensity of GaN wires on Al_2O_3 is within the apparatus noise.

Structural characterization data of the nanowires was obtained by transmission electron microscopy (TEM) imaging using an FEI

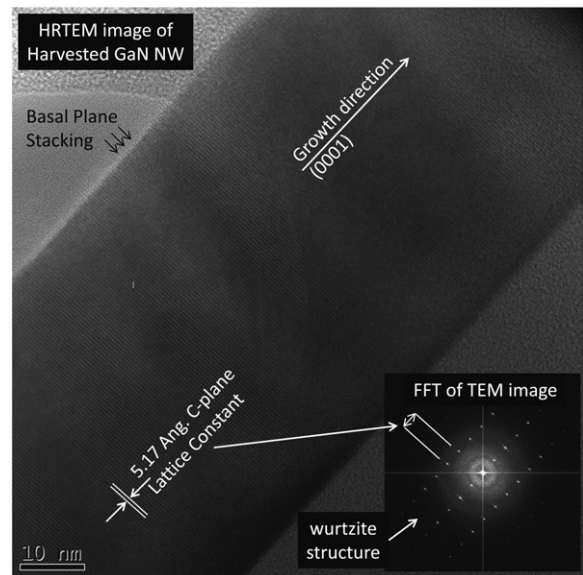


Fig. 4. High resolution transmission electron microscope image of a harvested GaN nanowire showing lattice fringes running perpendicular to the growth direction. Inset: fast Fourier Transform of the TEM image. The *c*-plane lattice spacing was extracted to be 5.17 Å, which compares well with wurtzite GaN.

Titan TEM with a beam accelerating voltage of 300 kV. Structural investigation of single wires was accomplished by harvesting wires from the substrate by ultra-sonication, for which the wires were suspended in an isopropyl alcohol solution. The solution was then dripped onto copper grids and allowed to dry, leaving behind the nanowires [10]. A high resolution TEM (HRTEM) image of a nanowire grown on Al_2O_3 is shown in Fig. 4. The image shows high quality material with lattice fringes running perpendicular to the nanowire growth direction. Investigation reveals that the nanowires grow along the (0001) direction. Fast Fourier Transform (FFT) capabilities on the TEM system allowed for direct measurement of the material in *k*-space. The results are shown in the inset of Fig. 4, revealing a wurtzite structure. The diffused ring patterns seen in the FFT image are suspected to be from the carbon film on the copper grid. The inverse of the reciprocal space measurements reveals a *c*-plane lattice constant of $\sim 5.17 \text{ \AA}$, which matches with values for relaxed GaN in literature [15]. The nanowires are free of threading dislocations, a common

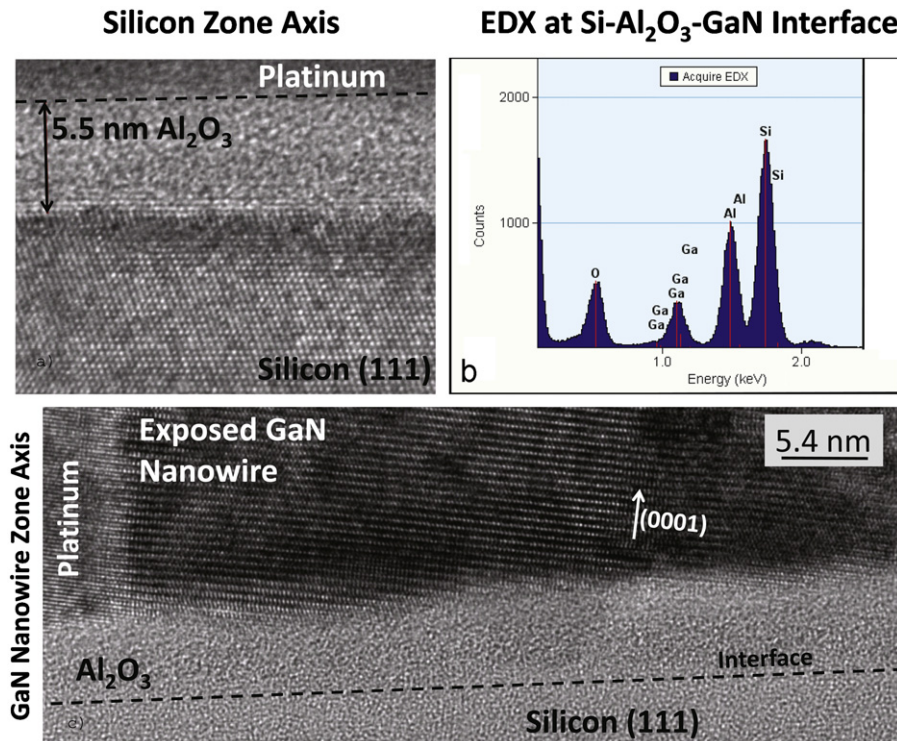


Fig. 5. Transmission electron microscope images of a cross sectioned sample after growth. (Top left) Sample is tilted to silicon zone axis, while (bottom) sample is tilted to NW zone axis. (Top right) EDX spectra of the silicon/ Al_2O_3 /nanowire interface.

defect seen when material is grown on a non-lattice-matched substrate.

To obtain an image of the silicon/ Al_2O_3 /GaN interface, a TEM specimen was prepared by cross sectioning the growth substrate using a focused ion beam (FIB). Prior to cross sectioning, the sample was coated with a protective electron beam platinum layer followed by an ion beam platinum layer, which encased the nanowires. Thinning of the lamella was accomplished by ion milling with gallium atoms. The TEM images of Fig. 5 show an aluminum oxide thickness of roughly 5.5 nm. This is relative to, but slightly off from a variable angle spectroscopic ellipsometry (VASE) measurement performed on ALD oxides deposited under similar conditions, which revealed a thickness of 7.2 nm. The discrepancies in the oxide thickness values obtained from TEM images and VASE measurements are attributed to a slight inaccuracy of the oxide refractive index used in the VASE calculations.

While a diffused diffraction pattern could indicate the structure of the aluminum oxide layer, due to the thin width of the layer, ~ 6 nm, an alternate method must be used. To confirm the structure of the aluminum oxide the sample was tilted to the zone axis of the silicon. While the lattice fringes of the silicon are visible in Fig. 5(a), the Al_2O_3 layer is indeed amorphous. Also shown in Fig. 5(c) a segment of a nanowire at the oxide/nanowire interface in which the overcoating protective platinum has been etched away, revealing the base of the nanowire. The image shows lattice fringes in the nanowire indicating crystalline material. Once again the aluminum oxide is shown to be amorphous in contrast to the crystalline nanowire. A major point to take away from this manuscript is that while the Al_2O_3 is amorphous, the nanowires are growing with a crystalline structure even at the region directly in contact with the amorphous aluminum oxide. Fig. 5(b) also displays EDX spectra taken at the interface of the silicon/ Al_2O_3 /nanowire revealing high counts of silicon, oxygen and aluminum as expected. The peak near 2.1 keV is from the protective platinum overcoat. The high

aluminum and oxygen peaks further document that the nanowires are indeed growing on the ALD deposited aluminum oxide as opposed to silicon.

4. Conclusions

The data has shown that it is possible to grow high quality GaN nanowires on a controlled Al_2O_3 ALD oxide by MBE. Not only does this result in a crystalline material of high quality away from the growth interface, but also the structural investigation indicates that the initial nanowire growth occurs as crystalline and free of threading defects. This result could prove useful to the nanowire community by indicating that growth on a controlled oxide is possible, and that the oxide need not be crystalline to obtain crystalline growth material. However, one drawback that has been observed in examining the data, as seen in the PL peaks, is that while the NWs are free of threading dislocations, there is a high probability of mid-gap states at the NW–oxide interface due to the mismatch of the atomic structure. The information discussed herein could offer new possibilities into the design of future devices utilizing nanowire technology by suggesting the possibility of using non-crystalline growth substrates.

The authors would like to thank NSF award #s 0645698 and 0907583 monitored by Dr. LaVerne Hess for financial support along with Wangquing Yuan and Christopher Seibert for VASE measurements.

References

- [1] K.A. Bertness, A. Roshko, N.A. Sanford, J.M. Barker, A.V. Davydov, *Journal of Crystal Growth* 287 (2006) 522.
- [2] R. Calarco, R.J. Meijers, R.K. Debnath, T. Stoica, E. Sutter, H. Luth., *Nano Letters* 7 (2007) 2248.
- [3] A. Kikuchi, M. Kawai, M. Tada, K. Kishino, *Japanese Journal of Applied Physics* 43 (2004) L1524.

- [4] R. Meijers, T. Richter, R. Calarco, T. Stoica, H.P. Bochem, M. Marso, H. Luth, *Journal of Crystal Growth* 289 (2006) 381.
- [5] Y.S. Park, S.H. Lee, J.E. Oh, C.M. Park, T.W. Kang, *Journal of Crystal Growth* 282 (2005) 313.
- [6] R.K. Debnath, R. Meijers, T. Richter, T. Stoica, R. Calarco, H. Luth, *Applied Physics Letters* 90 (2007) 123117.
- [7] S. Ishizawa, H. Sekiguchi, A. Kikuchi, K. Kishino., *Phys. Stat. Sol (b)* 244 (2007) 1815.
- [8] W. Guo, M. Zhang, A. Banerjee, P. Bhattacharya., *Nano Letters* 10 (2010) 3355.
- [9] E. Calleja, J. Ristic, S. Fernandez-Garrido, L. Cerutti, M.A. Sanchez-Garcia, J. Grandal, A. Trampert, U. Jahn, G. Sanchez, A. Griol, B. Sanchez, *Physica Status Solidi (b)* 244 (2007) 2816.
- [10] K.A. Bertness, N.A. Sanford, J.M. Barker, J.B. Schlager, A. Roshko, A.V. Davydov, I. Levin, *Journal of Electronic Materials* 35 (2006) 576.
- [11] K. Goodman, *Molecular beam epitaxial growth and characterization of nitride nanowires*, Dissertation, University of Notre Dame, , 2011.
- [12] J.B. Schlager, N.A. Sanford, K.A. Bertness, A. Roshko, *Journal of Applied Physics* 109 (2011) 044312.
- [13] K. Kornitzer, T. Ebner, K. Thonke, R. Sauer, C. Kirchner, V. Schwegler, M. Kamp, M. Leszczynski, I. Grzegory, S. Porowski, *Physical Review B* 60 (1999) 1471.
- [14] F. Furtmayr, M. Vilemeyer, M. Stutzmann, A. Laufer, B.K. Meyer, M. Eickhoff, *Journal of Applied Physics* 104 (2008) 074309.
- [15] K. Pakula, J.M. Baranowski, C.T. Foxon, T.S. Cheng, *Applied Physics Letters* 69 (1996) 73.