Hindawi
Advances in Condensed Matter Physics
Volume 2018, Article ID 1040689, 5 pages
https://doi.org/10.1155/2018/1040689

Research Article

MBE Growth and Optical Properties of GaN, InN, and A^3B^5 Nanowires on SiC/Si(111) Hybrid Substrate

R. R. Reznik,[1,2,3,4] K. P. Kotlyar,[1] I. V. Ilkiv,[1] A. I. Khrebtov,[4] I. P. Soshnikov,[1,3,5] S. A. Kukushkin,[6] A. V. Osipov,[6] E. V. Nikitina,[1] and G. E. Cirlin[1,2,3]

[1] *St. Petersburg Academic University-Nanotechnology Research and Education Centre RAS, Khlopina 8/3, St. Petersburg, Russia*
[2] *Peter the Great St. Petersburg Polytechnic University, Polytechnicheskaya 29, St. Petersburg, Russia*
[3] *Institute for Analytical Instrumentation RAS, Rizhsky 26, St. Petersburg, Russia*
[4] *ITMO University, Kronverkskiy Pr. 49, St. Petersburg, Russia*
[5] *Ioffe Physical Technical Institute RAS, Politekhnicheskaya 26, St. Petersburg, Russia*
[6] *Institute of Problems of Mechanical Engineering Russian Academy of Science, Bolshoj 6, St. Petersburg, Russia*

Correspondence should be addressed to G. E. Cirlin; cirlin@beam.ioffe.ru

Received 5 January 2018; Revised 27 April 2018; Accepted 20 May 2018; Published 11 June 2018

Academic Editor: Joseph S. Poon

The possibility of GaN, InN, and A^3B^5 nanowires MBE growth on a silicon substrate with a nanoscale SiC buffer layer has been demonstrated. Optical studies indicated a higher structural quality GaN NWs compared with the best structures of GaN NWs without silicon carbide buffer layer. The diameter of A^3B^5 NWs is smaller than diameter of similar NWs which were grown on a silicon substrate, because of higher lattice mismatch. In particular, InAs NWs diameter was evaluated as little as 10 nm, one of the smallest ever demonstrated for this NWs system.

1. Introduction

One of the crucial aims to nanotechnology is the creation of nanoscale building blocks of various sizes and shapes [1]. Nanostructures of wideband gap gallium nitride are of particular interest because of their applications in short-wavelength optoelectronic devices and high-power/high-temperature electronics. GaN nanowires (NWs) represent unique nanostructures that can be used for high mobility field effect transistors, photodetectors, and miniaturized UV-blue nanolasers [2, 3]. Moreover, due to their high surface to volume ratio, nanowires are potential candidates for sensor applications and they are also under intensive study in a view of the next generation of solar cells. Besides, InN exhibits the narrowest band gap (for nitrides) which can be down to 0.67 eV at low temperatures, the lowest effective electron mass, and the highest peak drift velocity and electron mobility [4–7]. Thereby, InN is an attractive material for applications in transistors, terahertz emitters, and detectors [6].

The synthesis of GaN and InN nanowires via the vapor-liquid-solid (VLS) process [1, 8] commonly uses metal clusters such as Ni, Fe, and Co, which inevitably results in undesired contamination within the single-crystalline grown nanowires. Plasma-assisted molecular beam epitaxy (PA-MBE) was also successfully applied to produce GaN, InN nanocolumns [9–11]. The growth parameters have to be adjusted to the nitrogen-rich conditions to obtain columnar structures with separated and uniform-in-diameter rods which exhibit relatively good crystalline quality [11].

However, lack of gallium and indium nitride's substrates encourages researchers to seek suitable wafers to grow such structures. The use of sapphire substrates leads to the generation of high dislocation density due to the significant (13%) lattice mismatch. Substrates of silicon carbide, the most suitable in terms of matching the lattice parameters, cannot be widely used because of their small size and high cost. On the other hand, the successful attempts to grow GaN layers on silicon [12] are very promising, as silicon is a rather cheap material and additionally exhibits acceptable thermal conductivity. Moreover, Si substrates can be much bigger in size and enable the integration of optoelectronic devices based on gallium nitride with the silicon micro- and nanoelectronics platform. However, lattice mismatch of Si (111) and GaN is 17%, and the difference in thermal expansion coefficients reaches 33% resulting in a high density of different growth defects suffer to use these structures in the devices. For example, threading dislocations are nonradiative recombination centers, Coulomb scattering centers, leading to the decrease of the electron mobility. Dislocations increase the reverse current in p-n-junctions and the dark current of the photodetectors (e.g., in [13]). Hence, to extend the lifetime of nitride based optoelectronic devices an increase of their perfection is highly desirable.

In this work, we introduce PA-MBE NWs growth on Si (111) substrate with nanometer (about 50–100 nm) silicon carbide buffer layer, which was formed on the Si substrate using chemical substitution atoms method [14]. The difference in lattice parameters between, e.g., GaN and SiC(111) is only 3% [14] incompatible with that for Si(111). In addition to nitrides, A3B5 nanowires such as GaAs, AlGaAs, and InAs can be successfully grown on such hybrid substrates. In the latter case, it was assumed that a very high lattice mismatch between SiC and A^3B^5 materials would lead to significant reduction in a NWs diameter [15]. Due to this fact, the quantum-dimensional effects for these nanostructured materials might be manifested more clearly.

2. Experiments

The formation of the buffer layer of silicon carbide on Si (111) substrate was performed by the method described early in [14, 16, 17]. This method differs significantly from all currently existing methods and technologies for growing single crystals, films, and nanostructures. Briefly, the method is based on the substitution of silicon atoms on carbon ones on a surface of the silicon substrate at elevated temperatures.

Growth experiments for GaN and InN NWs were carried out using Riber Compact 12 MBE setup equipped with the effusion Ga and In effusion cells and the plasma activated nitrogen source. For the growth of GaN NWs, firstly, the substrate was transferred into the growth chamber, and the substrate temperature was set at 950°C for cleaning. Then, the substrate temperature was lowered to 600°C and gallium source was opened for 20 seconds to form nanoscale islands on surface for further NWs growth. Finally, and the substrate temperature was raised up to the growth temperature 800°C. Then nitrogen source plasma was ignited; nitrogen flow and the gallium source were opened simultaneously. The growth rate for Ga was set at 0.01 ML/s (according to the previous calibrations). Total growth time of each GaN NWs sample was equal to 16 hours. In contrast, InN NWs growth was carried out without formation of indium droplets, and growth temperature was 350°C. A^3B^5 nanowires were grown by MBE using Riber 21 setup equipped with a separate vacuum chamber to deposit gold. After HF treatment in water solution (1:10), SiC/Si(111) hybrid substrates were loaded into the vacuum chamber and outgassed at 850°C before the gold deposition at 550°C. The substrates were kept at 550°C for 1 min after the gold deposition to improve the droplet size homogeneity and subsequently cooled down to room temperature. After that, the substrates were transferred to the main growth chamber with no vacuum brake. For AlGaAs NW growth runs, the substrate temperature was set at 510°C, the equivalent AlGaAs growth rate was fixed at 0.3 nm/s, and the total V/III flux ratio was 3. Nominal Al composition z = 0.3 was chosen, as calibrated using reflection high-energy electron diffraction oscillation technique on standard GaAs(001) substrates. For the growth of GaAs and InAs NWs, growth temperatures were chosen at 530°C and 300°C; equivalent growth rates were fixed at 0.3 and 0.1 nm/s, respectively. The appearance of pronounced wurtzite-type RHEED patterns was documented after 20 seconds of the growth for all samples.

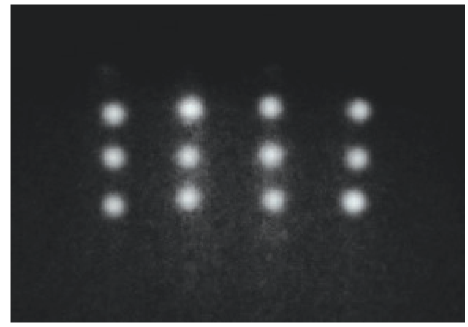


Figure 1: RHEED pattern of the GaN NWs on the SiC buffer layer after 120 minutes of growth.

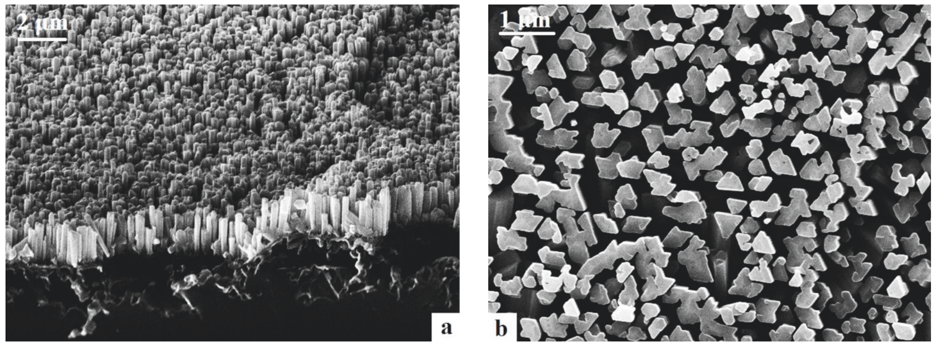
The nanowire growth was monitored *in situ* using reflection high-energy electron diffraction (RHEED) showing GaN and InN NWs wurtzite phase (Figure 1) after an incubation period (typically, 5 min).

After the growth, the morphology of all grown samples was studied by scanning electron microscopy (SEM). Optical properties of GaN and InN nanowires were investigated by room temperature photoluminescence (PL) and Raman techniques.

3. Results and Discussion

Figure 2 shows typical SEM images of GaN nanowires grown on SiC/Si hydrid substrate. It is seen that GaN NWs on SiC/Si(111) substrate formed mainly in [111] direction and their average height is about 1.6 μm. It should be noted that grown structures have high surface density ~ $2 \cdot 10^{10} cm^{-2}$ and some of the nanowires tend to merge. From SEM image (Figure 2(a)) it is clear that some NWs are inhomogeneous in their diameter which increases to the top of NWs, possibly due to lateral growth. Moreover, relatively low N/Ga fluxes ratio can play an important role in the density and the shape of nanowires.

Most often, an increase of the diameter to the top of NWs is observed at high temperature and relatively small V/III ratio. In our case, smaller in length InN NWs exhibit constant diameters (Figure 3) whereas longer NW are less uniform in diameter from the base to the top. InN NWs are formed in [111] direction and their average height is about 250 nm for the short NWs and 1 μm for the longer ones. Like in the case of GaN NWs, the surface density of the InN NWs arrays is pretty high.



(a) (b)

Figure 2: SEM images of GaN NWs grown on SiC/Si(111) substrate: (a) tilted by 20^0 cross section view; (b) top-view.

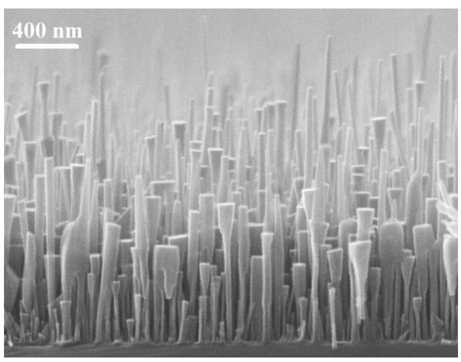


Figure 3: SEM images of InN NWs grown on SiC/Si(111) substrate.

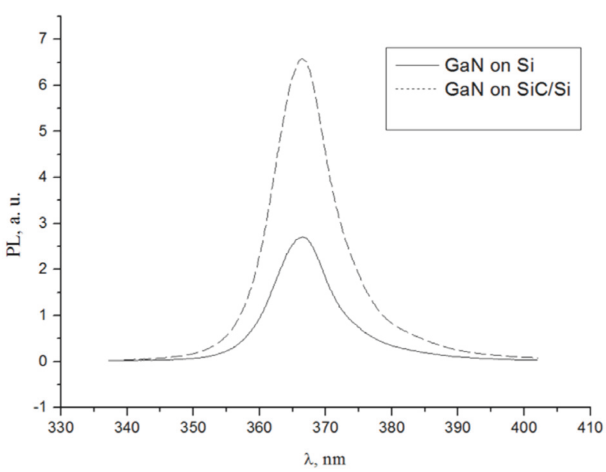


Figure 4: Typical RT PL spectra of GaN NWs grown on SiC/Si substrate and the most successful GaN structure grown on silicon.

Figure 4 shows a comparison of room temperature room temperature (RT) PL spectra of the grown sample and the most successful of GaN NWs sample grown directly on silicon. Maxima of both spectra coincide in wavelength and conform to experimentally measured emission value for the bulk GaN [18]. At the same time, the integral PL intensity of GaN NWs grown on SiC buffer layer is more than 2 times higher than that grown on silicon at the same growth conditions.

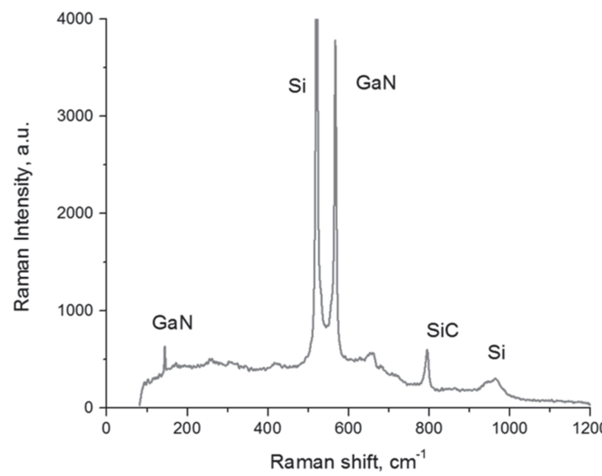
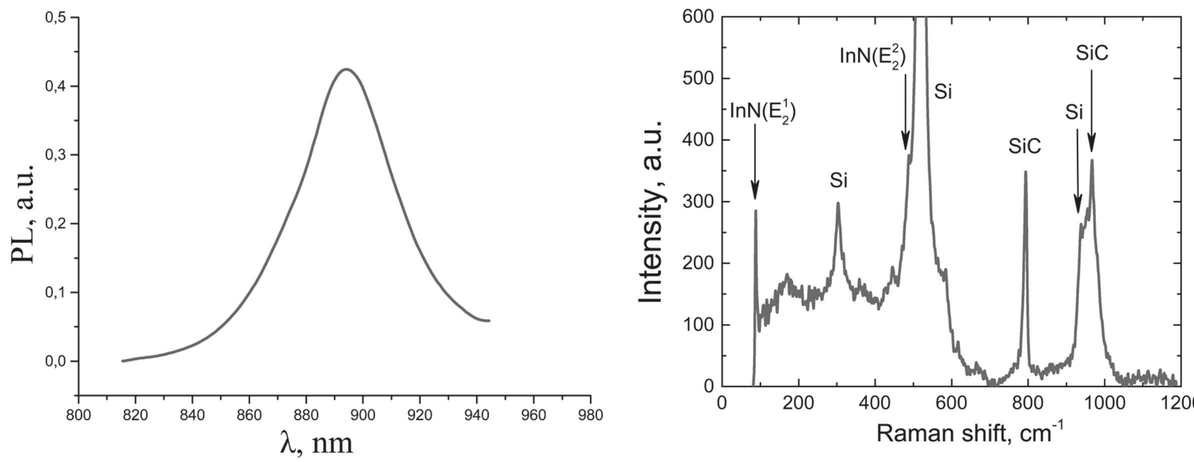


Figure 5: Typical Raman spectrum of GaN NWs grown on SiC/Si hybrid substrate.

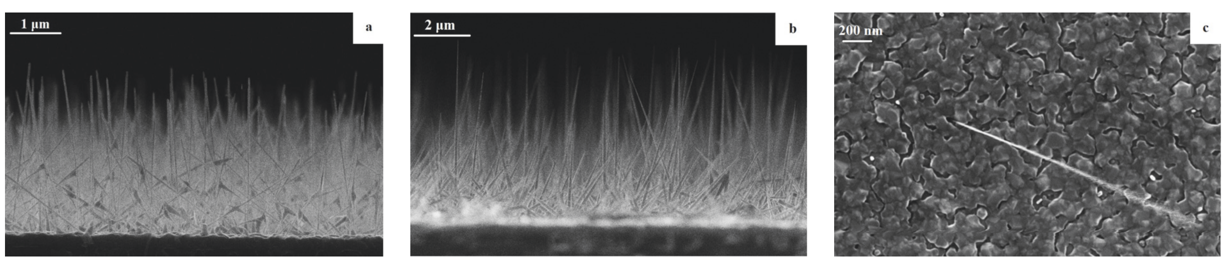
Figure 5 shows a typical Raman spectrum of GaN NWs sample grown on SiC/Si. Despite the small thickness of the SiC, cubic SiC related peak is clearly visible, along with the peaks of the hexagonal GaN and Si. We note here the extremely small width of GaN peaks (1.5 cm^{-1}), indicating a high structural perfection of GaN NWs.

The optical study results for InN NWs arrays grown on SiC/Si hybrid substrate are presented in Figure 6. We note two interesting features of PL spectrum: (i) full width on half maxima (FWHM) of PL band is rather small (55 meV), which is not typical for nonordered nanowire arrays and (ii) the PL band position. According to the experimental data [19] the observed position of PL peak corresponds to rather big amount impurities/structural defects in InN. At the same time, the bigger the blue shift of the PL peak from high quality InN is (~0.7 eV at RT) the bigger that value of FWHM was well documented [15]. In our case, the position of PL band together with the small FWHM value cannot be simply attributed to high defective InN. This



(a) (b)

Figure 6: Typical RT PL (a) and Raman spectra (b) of InN NWs grown on SiC/Si hybrid substrate.



(a) (b) (c)

Figure 7: SEM images of A^3B^5 NWs grown on SiC/Si(111) substrate: (a) GaAs NWs (cross-sectional); (b) AlGaAs NWs (cross-sectional); (c) InAs NWs (top view).

in accordance with extremely narrow Raman InN related peaks shown in Figure 6(b). We believe that the phenomenon observed is attributed to the formation of specific band gap alignment at InN/SiC/Si heterointerface. Detailed study of this observation will be presented elsewhere.

Typical scanning electron microscopy images of GaAs, AlGaAs, and InAs NWs grown on Si(111) substrate with SiC buffer layer are shown in Figure 7. It is seen that GaAs NWs are oriented in main (111) and other orientations and their diameter is constant over the entire length of the NWs with average value 35 nm, which is about three times less than for the GaAs NWs grown on a silicon substrate (110 nm) [20]. The array of GaAs NWs on a hybrid substrate has a surface density of $2{\cdot}10^8$ cm^{-2}, whereas their average height is 2 μm.

The results of morphological properties studies of the grown AlGaAs NWs arrays showed that, as in the case of GaAs NWs, AlGaAs NWs grow in different directions, and their average height is the same 2 μm. However, the arrays of such NWs have a smaller surface density, about $6{\cdot}10^7$ cm^{-2}. In addition, AlGaAs NWs have a cone-like shape, their average diameter at the bottom is 80 nm and at the top is 15 nm. This shape is explained by the difference in Ga and Al adatoms migration coefficients over the sidewalls surface; thus, lateral growth occurs eventually [21]. Nevertheless, the diameter of AlGaAs NWs grown on a SiC/Si(111) substrate is much smaller than the diameter of such NWs grown on Si(111) (typically, 100-120 nm [21]).

Because of the considerable mismatch between InAs and SiC, the critical Au droplet diameter is very small [22], so InAs NWs density turned out to be extremely low. The diameter of such InAs NWs cannot be precisely determined by means of a scanning electron microscope since NWs oscillate under the electron beam influence. With certainty their diameter as little as 10 nm can be evaluated, which is less than the de Broglie wavelength for InAs.

4. Conclusion

The possibility of GaN, InN, GaAs, AlGaAs, and InAs nanowires growth on a silicon substrate with a nanoscale buffer layer of silicon carbide has been demonstrated. It was found that the intensity of the photoluminescence signal of the GaN NWs on SiC/Si(111) substrate integrally more than 2 times higher than that of the best structures of GaN NWs grown on Si(111). The extremely small width of GaN lines in Raman spectrum indicates perfect crystallographic quality of GaN NWs grown on SiC/Si which opens a new route of the use of these structures in future optoelectronic devices. The diameter of A^3B^5 NWs is smaller than diameter of similar NWs which were grown on a silicon substrate, because of higher lattice mismatch. In particular, InAs NWs diameter was evaluated to be as little as 10 nm, one of the smallest ever demonstrated for this NWs system.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

An earlier version of this work was presented as a poster at AIP Conference Proceedings 2016.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The authors are grateful to the support of the Ministry of Education and Science of Russian Federation (state task, Project no. 16.2483.2017/4.6). I. P. Soshnikov acknowledges the support of FASO Russia (state task, Project no. AAAA-A16-116041110123-5).

References

[1] Y. Wu and R. Fan, "Inorganic semiconductor nanowires," *International Journal of Nanoscience*, vol. 1, no. 1, 2002.

[2] Y. Huang, X. Duan, Y. Cui, and C. M. Lieber, "Gallium Nitride Nanowire Nanodevices," *Nano Letters*, vol. 2, no. 2, pp. 101–104, 2002.

[3] J. Johnson, H. Choi, P. Yang, and R. Saykally, "Single gallium nitride nanowire lasers," *Nature Materials*, vol. 1, pp. 106–110, 2002.

[4] W. Walukiewicz, J. W. Ager, K. M. Yu et al., "Structure and electronic properties of InN and In-rich group III-nitride alloys," *Journal of Physics D: Applied Physics*, vol. 39, no. 5, pp. R83–R99, 2006.

[5] A. A. Klochikhin, V. Y. Davydov, V. V. Emtsev et al., " Acceptor states in the photoluminescence spectra of ," *Physical Review B: Condensed Matter and Materials Physics*, vol. 71, no. 19, 2005.

[6] A. G. Bhuiyan, A. Hashimoto, and A. Yamamoto, "Indium nitride (InN): A review on growth, characterization, and properties," *Journal of Applied Physics*, vol. 94, no. 5, pp. 2779–2808, 2003.

[7] E. Bellotti, B. K. Doshi, K. F. Brennan, J. D. Albrecht, and P. P. Ruden, "Ensemble Monte Carlo study of electron transport in wurtzite InN," *Journal of Applied Physics*, vol. 85, no. 2, pp. 916–923, 1999.

[8] X. Duan, C. M. Lieber, and J. Am. Chem, "Laser-Assisted Catalytic Growth of Single Crystal GaN Nanowires," *Journal of the American Chemical Society*, vol. 122, no. 1, pp. 188-189, 2000.

[9] E. Dimakis, G. Konstantinidis, K. Tsagaraki, A. Adikimenakis, E. Iliopoulos, and A. Georgakilas, "The role of nucleation temperature in In-face InN-on-GaN(0001) growth by plasma-assisted molecular beam epitaxy," *Superlattices and Microstructures*, vol. 36, no. 4-6, pp. 497–504, 2004.

[10] J. Grandal, M. A. Sanchez-Garci, F. Calle, and E. Calleja, "Morphology and optical properties of InN layers grown by molecular beam epitaxy on silicon substrates," *physica status solidi c*, vol. 2, 2005.

[11] T. Stoica, R. Meijers, R. Calarco, T. Richter, H. J. Luth, and J. Cryst, "MBE growth optimization of InN nanowires," *Journal of Crystal Growth*, vol. 290, no. 1, pp. 241–247, 2006.

[12] I. G. Aksyanov, V. N. Bessolov, Y. V. Zhilyaev et al., "Chloride vapor-phase epitaxy of gallium nitride on silicon: Effect of a silicon carbide interlayer," *Technical Physics Letters*, vol. 34, no. 6, pp. 479–482, 2008.

[13] R. A. Oliver, M. J. Kappers, C. McAleese, and J. Mater, "The origin and reduction of dislocations in Gallium Nitride," *Journal of Materials Science: Materials in Electronics*, vol. 19, 1, pp. 208–214, 2008.

[14] S. A. Kukushkin and A. V. Osipov, "New method for growing silicon carbide on silicon by solid-phase epitaxy: Model and experiment," *Physics of the Solid State*, vol. 50, Article ID S1063783408070081, 2008.

[15] S. Zhao, Z. Mi, M. G. Kibria, Q. Li, and G. T. Wang, "Understanding the role of Si doping on surface charge and optical properties: Photoluminescence study of intrinsic and Si-doped InN nanowires," *PHYSICAL REVIEW B*, vol. 85, Article ID 245313, 2012.

[16] S. A. Kukushkin, A. V. Osipov, and N. A. Feoktistov, "Synthesis of epitaxial silicon carbide films through the substitution of atoms in the silicon crystal lattice: A review," *Physics of the Solid State*, vol. 56, no. 8, pp. 1507–1535, 2014.

[17] S. A. Kukushkin and A. V. Osipov, "heory and practice of SiC growth on Si and its applications to wide-gap semiconductor films," *Journal of Physics D: Applied Physics*, vol. 47, Article ID 313001, 2014.

[18] M. Tchernycheva, C. Sartel, G. Cirlin et al., "Growth of GaN free-standing nanowires by plasma-assisted molecular beam epitaxy: structural and optical characterization," *Nanotechnology*, vol. 18, no. 38, p. 385306, 2007.

[19] T. Stoica, R. J. Meijers, R. Calarco, T. Richter, E. Sutter, and H. Lüth, "Photoluminescence and Intrinsic Properties of MBE-Grown InN Nanowires," *Nano Letters*, vol. 6, no. 7, pp. 1541–1547, 2006.

[20] G. E. Cirlin, V. G. Dubrovskii, I. P. Soshnikov et al., "Critical diameters and temperature domains for MBE growth of III-V nanowires on lattice mismatched substrates," *physica status solidi (RRL) - Rapid Research Letters*, vol. 3, no. 4, pp. 112–114, 2009.

[21] V. G. Dubrovskii, I. V. Shtrom, R. R. Reznik et al., "Origin of Spontaneous Core–Shell AlGaAs Nanowires Grown by Molecular Beam Epitaxy," *Crystal Growth & Design*, vol. 16, no. 12, pp. 7251–7255, 2016.

[22] G. E. Cirlin, I. V. Shtrom, R. R. Reznik et al., "Hybrid AlGaAs/GaAs/AlGaAs nanowires with a quantum dot grown by molecular beam epitaxy on silicon," *Semiconductors*, vol. 50, no. 11, pp. 1421–1424, 2016, Semiconductors.