Virginia Commonwealth University
VCU Scholars Compass

Electrical and Computer Engineering Publications

Dept. of Electrical and Computer Engineering

2007

Nanostructuring induced enhancement of radiation hardness in GaN epilayers

V. V. Ursaki
Technical Institute of Moldova

I. M. Tiginyanu
Technical Institute of Moldova, tiginyanu@asm.md

O. Volcuic
Technical Institute of Moldova

See next page for additional authors

Follow this and additional works at: http://scholarscompass.vcu.edu/egre_pubs

Part of the Electrical and Computer Engineering Commons

Authors

V. V. Ursaki, I. M. Tiginyanu, O. Volcuic, V. Popa, V. A. Skuratov, and Hadis Morkoç

Nanostructuring induced enhancement of radiation hardness in GaN epilayers

V. V. Ursaki, I. M. Tiginyanu,[a] O. Volciuc, and V. Popa
Laboratory of Low-Dimensional Semiconductor Structures, Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau 2028, Republic of Moldova and National Center for Materials Study and Testing, Technical University of Moldova, Chisinau 2004, Republic of Moldova

V. A. Skuratov
Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, 141980 Dubna, Moscow region, Russia

H. Morkoç
Department of Electrical and Computer Engineering, Virginia Commonwealth University, Richmond, Virginia 23284 and Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284

The radiation hardness of as-grown and electrochemically nanostructured GaN epilayers against heavy ion irradiation was studied by means of photoluminescence (PL) and resonant Raman scattering (RRS) spectroscopy. A nanostructuring induced enhancement of the GaN radiation hardness by more than one order of magnitude was derived from the PL and RRS analyses. These findings show that electrochemical nanostructuring of GaN layers is a potentially attractive technology for the development of radiation hard devices. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2723076]

Gallium nitride (GaN) is a promising radiation hard semiconductor material for the development of optical and high-power high-frequency electronic devices. From the point of view of optical properties, the material is some two orders of magnitude less sensitive to the proton irradiation than gallium arsenide (GaAs).[1,2] In order to attain many advantages of GaN, controllable doping and formation of semi-insulating regions, among others, must be achieved. Ion implantation is widely used for planar selective area doping of GaN.[3] In order to minimize the ion bombardment induced damage, it is important to characterize the features of lattice disorder caused by ion damage and ion implanted material provides a good opportunity for this purpose. While photoluminescence (PL) can be used for characterization of the materials at low implantation doses, Raman scattering (RS) is a powerful, nondestructive tool to assess the lattice disorder at high implantation doses.[4–9] The purpose of this work is to compare the damage introduced by high energy heavy ion implantation in as-grown and electrochemically nanostructured GaN epilayers and to evaluate a possible contribution of electronic stopping power in damage production. To date, only a few information about structural response of GaN to swift heavy ion irradiation is known.[10,11]

It was previously demonstrated[12,13] that electrochemical etching produces fully relaxed from strain columnar nanostructures in GaN which are suitable for the development of selective methane gas sensors in environments containing ethanol vapor. In this letter, we show that these nanostructures also exhibit radiation hardness more than one order higher in magnitude than that inherent to as-grown layers.

The GaN layers used in our experiments were grown by low-pressure metalorganic chemical-vapor deposition on (0001) *c*-plane sapphire using a modified EMCORE GS-3200 system and trimethylgallium and ammonia as source materials. A buffer layer of about 25 nm thick GaN was first grown at 510 °C followed by a 2.0 μm thick *n*-GaN layer grown at 1100 °C. The concentration of free electrons in the *n*-GaN layer was 1.7×10^{17} cm^{-3}. Anodic etching of samples was carried out at a current density of 5 mA/cm^{-2} in 0.1 mol aqueous solution of KOH under *in situ* UV illumination provided by focused radiation from a 250 W Hg lamp on the GaN surface which was also in contact with the electrolyte. The duration of anodization was 6 min, leading to the formation of pyramidal GaN nanostructures illustrated by the scanning electron microscope (SEM) image in the inset of Fig. 1. The as-grown and electrochemically treated samples were irradiated at room temperature by 85 MeV Kr^{+15} ions (10^{12} and 10^{13} cm^{-2}) or by 130 MeV Xe^{+23} ions (5×10^{11} and 5×10^{12} cm^{-2}). The irradiation was carried out on the IC-100 cyclotron at FLNR, JINR, Dubna.

PL was excited by the 351.1 nm line of an Ar$^+$ Spectra Physics laser and analyzed through a double spectrometer. The resolution was better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 optical cryogenic system.

The energy of the 351.1 nm laser radiation (3.530 eV) is in resonance with the GaN band gap (3.503) at 10 K. Under these excitation conditions, the emission consists of two components: PL and RRS. The emission from the sample is dominated by strong near band gap luminescence in the case of high quality samples, while RRS becomes observable in the emission spectra of samples with low PL intensity. Note that RRS from solids can be observed if the energy of the incoming or scattered photons matches the real electronic states in the material. One refers to incoming and outgoing resonances, respectively (see, e.g., Ref. 14). The resonance of the 351.1 nm laser radiation with the GaN band gap at 10 K ensures good conditions for incoming resonant Raman scattering.
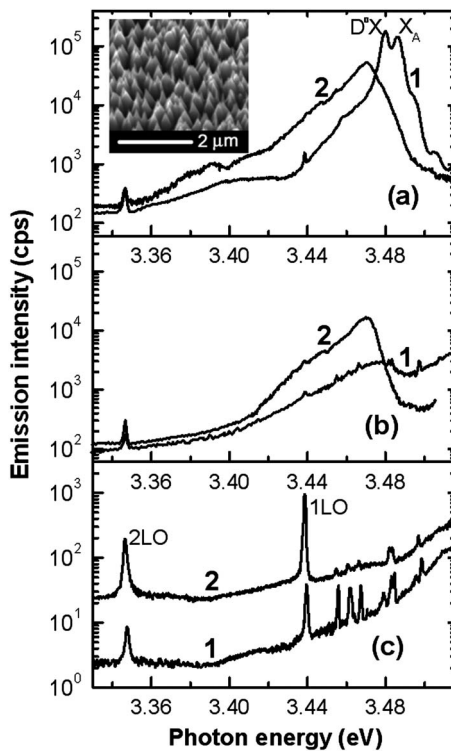
a)Electronic mail: tiginyanu@asm.md

FIG. 1. Emission spectra of as-grown (curve 1) and nanostructured (curve 2) GaN samples before (a) and after Kr^{+15} ion irradiation at the doses of 10^{12} cm^{-2} (b) and 10^{13} cm^{-2} (c). The intensity scale of curve 1 in section (c) has been divided by a factor of 10 for clarity. Inset is SEM image taken from a GaN sample subjected to anodic etching.

Figure 1 compares the emission spectra of the as-grown (curve 1) and electrochemically treated (curve 2) samples before ion irradiation (a) and after irradiation with Kr^{+15} ions at doses of 10^{12} cm^{-2} (b) and 10^{13} cm^{-2} (c), respectively.

The emission spectrum of the as-grown layer is dominated by the D^0X bound exciton and X_A free exciton luminescence.[12,15] The position of the D^0X (1.480 eV) and $X_A^{n=1}$ (1.486 eV) luminescence peaks are shifted by $\sim$10 meV toward high energies in comparison with the position of corresponding excitons in relaxed GaN layers due to compressive biaxial stress in our as-grown samples. The position of the PL line in the electrochemically treated sample is redshifted by $\sim$10 meV in comparison with the as-grown layer due to nanostructuring induced strain relaxation.[12] The integrated PL intensity in the nanostructured sample is comparable with that of the as-grown layer. Irradiation of Kr$^+$ ions at the dose of 10^{12} cm^{-2} leads to a decrease of the PL intensity by almost two orders of magnitude, while the corresponding decrease is only a factor of 3 in the nanostructured sample. This is indicative of considerable nanostructuring induced increase in the radiation hardness. In both samples irradiated at the dose of 10^{13} cm^{-2} the luminescence background is completely quenched and the emission spectrum is dominated by the RRS signal. Similar trends are observed in samples irradiated with Xe ions, but the damage introduced by the irradiation at the dose of 5×10^{11} cm^{-2} is more severe than the damage caused by the Kr ions at the dose of 10^{12} cm^{-2}.

It has been suggested that the intensity of the 1LO and 2LO RRS modes cannot be used to characterize the damage introduced in the sample, since the intensity of the 1LO peak is more intense in samples with poorer crystallinity, while the

intensity of the 2LO mode is insensitive to the lattice disorder.[6,9] This is indeed true, but only for the specific excitation with the 325 nm laser line. In this case the analysis of high-order peaks is necessary in order to assess the crystal quality of the implanted samples. The frequency of the 4LO RRS multiphonon peak is the closest to the outgoing resonance conditions with the 325 nm excitation line, this peak being the most sensitive to lattice disorder under those experimental conditions.

In the case of the 351.1 nm excitation wavelength, the energy of photons scattered by the first-order LO phonons and second-order LO phonons is in resonance with the exciton energy at low (10 K) and room temperatures, respectively, leading to a resonant increase in the intensity of these phonon lines in the outgoing RRS spectrum. Therefore, these lines become suitable to assess the damage introduced by ion implantation in GaN. Two opposite mechanisms influence the change in the intensity of the 1LO line with introducing damage in GaN. The first one is the increase in the intensity of the 1LO line with the increase of the implantation dose due to the enhancement of Raman scattering efficiency of the impurity induced Fröhlich mechanism and the disorder-induced broadening of the resonance profile of the scattering mechanisms, as described in Refs. 7 and 9. The second one is the decrease in intensity of this phonon line due to the transition from the outgoing to the incoming regime of RRS. It is known that the strength of the exciton resonance sharply decreases with introducing damage in any crystal. The decrease of the exciton strength leads to the decrease in the intensity of phonon lines in outgoing RRS mediated by excitons. As a result, at high irradiation doses the incoming mechanism predominates the RRS process when the energy of the incoming photons is in resonance with electronic states in the material.

The sharp decrease of the intensity of 1LO line under the 351.1 nm line excitation with the increasing irradiation dose due to the second mechanism overcomes the increase caused by the first mechanism. This results in an overall decrease of the intensity of this line with the increasing dose. Nearly the same decrease of the intensity is observed for the 2LO line. Note that with quenching of the PL and the decrease of RRS lines intensity a series of narrow lines of unidentified nature emerges in the near band gap region of the emission spectrum at high irradiation doses [see Figs. 1(c) and 2].

In spite of the transition from the outgoing to the incoming regime of RRS with increasing irradiation dose, the contribution from the outgoing mechanism remains essential for the nanostructured samples irradiated with Kr ions at 10^{13} cm^{-2} dose or with Xe ions at 5×10^{12} cm^{-2} dose. This assumption is supported by the analysis of the temperature dependence of emission illustrated in Fig. 2 for a nanostructured sample irradiated with Xe$^+$ ions at 5×10^{12} cm^{-2}. An increase in the lattice temperature leads to the redistribution in the intensity of lines in RRS in favor of the line whose energy better matches the exciton energy at the particular temperature. At low temperatures, the exciton energy is closer to the energy of photons scattered by first-order LO phonons when excited by the 351.1 nm laser line. In accord with the previous statement, the 1LO RRS line is more intense at low temperatures. With increasing temperature, the exciton energy shifts towards the position of the 2LO RRS line which leads to the redistribution of the RRS intensity in favor of this RRS line. There is a clear correlation between
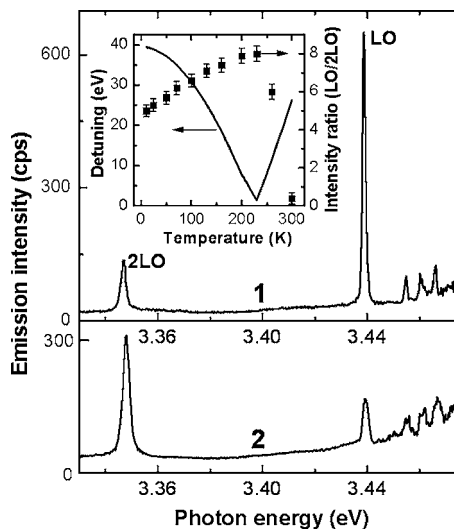
FIG. 2. Emission spectra of nanostructured GaN sample irradiated by Xe^{+23} ions at the dose of 5×10^{12} cm^{-2} measured at 10 K (curve 1) and at room temperature (curve 2). Inset is the temperature dependence of the 1LO/2LO phonon intensity ratio (square symbols, right-hand axis) and the detuning between the 1LO line energy and the exciton energy (solid line, left-hand axis).

the detuning of the energy of the 1LO line from the exciton energy and the ratio of the 1LO/2LO intensities as illustrated in the inset of Fig. 2.

In contrast to the RRS behavior in the nanostructured samples, the analysis shows no contribution from the outgoing mechanism in the RRS emission from the as-grown layers irradiated at the same ion dose. For instance, the 1LO/2LO intensity ratio practically does not depend on temperature in the sample irradiated with Xe^{+23} ions at 5×10^{12} cm^{-2} dose. This is indicative of a pure incoming mechanism of RRS in this sample.

Figure 3 summarizes the intensity of the 2LO line as a function of the damage dose defined as $\Phi \times S_n$, where Φ is the ion fluence and S_n is the energy loss per unit length,
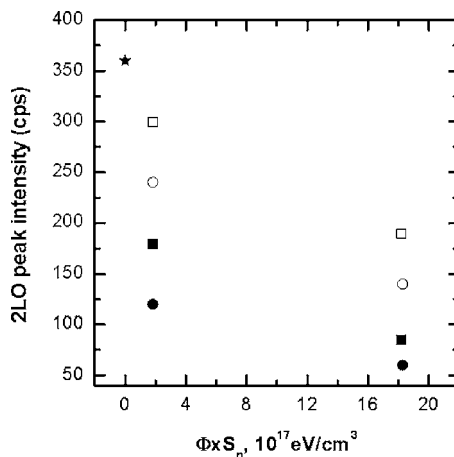

FIG. 3. Intensity of the 2LO phonon line as a function of damage dose in GaN samples. The full and open symbols are for as-grown and nanostructured samples, respectively. Circles and squares stand for Xe^{+23} and Kr^{+15} ions, respectively. The intensity of the 2LO line in the as-grown and nanostructured samples (which is identical in both samples) is also presented as star symbol.

deposited in elastic collisions. The S_n values were calculated by using SRIM2006 code. A fascinating result is that the electrochemical nanostructuring leads to one order of magnitude enhancement of radiation hardness against high energy heavy ion irradiation in GaN layers. We suggest that this enhancement is due to the increase of the specific surface of the nanostructured sample which we believe allows the migration of the defects formed during the ion bombardment process towards the surface, and due to the enhanced dynamic annealing of these defects. Another important result consists in the quite large difference between Xe and Kr ion irradiation effects observed at the same damage dose that was achieved by proper choosing of corresponding ion fluences. This may indicate on the contribution of the high level ionizing energy loss in damage formation.

In conclusion, we demonstrate the utility of electrochemical technologies of nanostructuring GaN for the purpose of enhancing its radiation hardness. The enhanced radiation hardness of the nanopyramidal GaN structures against the high energy heavy ion irradiation is demonstrated by both the PL and RRS analyses. The near band gap excitonic PL dominates the emission spectra of nanostructured GaN layers up to dose of 10^{12} cm^{-2} for high energy Kr and Xe ions, while the luminescence is totally quenched in the as-grown layers at this irradiation dose. At higher doses, the intensity of the RRS lines is much higher in the nanostructured samples and the mechanism of RRS is different in comparison with that inherent to as-grown layers.

[1] S. M. Khanna, J. Webb, H. Tang, A. J. Houdayer, and C. Calone, IEEE Trans. Nucl. Sci. **47**, 2322 (2000).

[2] F. Gaudreau, C. Carlone, Alain Houdayer, and S. M. Khanna, IEEE Trans. Nucl. Sci. **48**, 1778 (2001).

[3] N. Papanicolau, M. V. Rao, B. Molnar, J. Tucker, A. Edwards, O. W. Holland, and M. C. Ridgway, Nucl. Instrum. Methods Phys. Res. B **148**, 416 (1999).

[4] S. C. Rao, S. Sundaram, R. L. Schidt, and J. Comas, J. Appl. Phys. **54**, 1808 (1983).

[5] E. Bedel, G. Landa, J. B. Renucci, J. M. Roquais, and P. N. Favennec, J. Appl. Phys. **60**, 1980 (1986).

[6] R. Cusco, G. Talamas, L. Artus, J. M. Martin, and G. Gonzalez-Diaz, J. Appl. Phys. **79**, 3927 (1996).

[7] W. H. Sun, S. J. Chua, L. S. Wang, and X. H. Zhang, J. Appl. Phys. **91**, 4917 (2002).

[8] B. Boudart, Y. Guhel, J. C. Pesant, P. Dhamelincourt, and M. Poisson, J. Phys.: Condens. Matter **16**, S49 (2004).

[9] D. Pastor, J. Ibanez, R. Cusco, L. Artus, G. Gonzalez-Diaz, and E. Calleja, Semicond. Sci. Technol. **22**, 70 (2007).

[10] S. O. Kucheyev, H. Timmers, J. Zou, J. S. Williams, C. Jagadish, and G. Li, J. Appl. Phys. **95**, 5360 (2004).

[11] V. Suresh Kumar, P. Puviarasu, K. Thangaraju, R. Thangavel, V. Baranwal, F. Singh, T. Mohanty, D. Kanjilal, K. Asokan, and J. Kumar, Nucl. Instrum. Methods Phys. Res. B **244**, 145 (2006).

[12] I. M. Tiginyanu, V. V. Ursaki, V. V. Zalomai, S. Langa, S. Hubbard, D. Pavlidis, and H. Föll, Appl. Phys. Lett. **83**, 1551 (2003).

[13] V. Popa, I. M. Tiginyanu, V. V. Ursaki, O. Volciuc, H. Morkoç, Semicond. Sci. Technol. **21**, 1518 (2006).

[14] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors* (Springer, New York, 1996), p. 401.

[15] V. V. Ursaki, I. M. Tiginyanu, V. V. Zalamai, S. Hubbard, and D. Pavlidis, J. Appl. Phys. **94**, 4813 (2003).