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GaN optical degradation during high energy Sn^{5+} ion irradiation

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Abstract GaN(0001) epilayers grown on sapphire substrates by metal organic chemical vapor deposition (MOCVD) have been irradiated with 75 MeV Sn^{5+} ions at the fluences of 10^{11}, 10^{12}, and 10^{13} ions/cm^2. Structural and optical studies reveal that GaN epilayer withstands 75 MeV Sn^{5+} ion irradiations up to 10^{11} ions/cm^2 ion fluences. High resolution X-ray diffraction results showed that the FWHM corresponding to (0002) plane increased from 227 to 279 arc-seconds after Sn-ions irradiation. Red shift was observed in the yellow luminescence (YL) emission by photoluminescence (PL), corresponds to the concentration of ion fluences. Donor-bound exciton (DBE) and free exciton (FE^A, FE^B and FE^C) emissions were observed for as-grown and irradiated GaN samples up to 10^{12} ions/cm^2 at 2K PL measurements. Free excitons are dominated by low-temperature PL measurements for as-grown and irradiated GaN samples at 10^{11} and 10^{12} ion fluences. Atomic force microscopy images show the RMS roughness increases with increasing Sn-ion fluences by removing as-grown GaN surface defects.

Introduction

Gallium nitride is one of the most suitable materials for blue and ultra-violet laser diodes [1, 2]. The recent research interest in III-Nitride semiconductors is due to their unique optical and electronic properties compared to conventional compound semiconductors. The presence of high-energy charged particles in the outer space requires radiation resistant materials for opto-electronic device applications. High-energy irradiation introduces defects or damages in the material and it degrades their device performance. Extensive research has been carried out for understanding the phenomena of various defects present in nitrides and the role of these defects in optical and electrical properties of semiconductors [3–13].

III-Nitrides such as GaN and AlN are well-known materials in wide band gap semiconductors. Swift heavy ions (SHI) creates defects along its trajectory in a solid, leading to tracks propagation because the energy of point defect creation is significantly less than the average binding energy of target electrons. These defects are responsible for modification of physical properties in the materials. The origin of defects has been widely studied by artificial irradiation experiments but the defects presence in GaN epilayer/sapphire substrate is still unresolved. In the GaN epilayer, the dislocation or stacking faults cause radiative recombination between the deep donors and the shallow acceptors vice versa and results in yellow luminescence (YL) in addition to the near band edge emission (NBE) [14–16]. Some of the GaN results suggested that there was a blue shift in YL band with increasing ion fluences due to ion-beam implantation [17]. Most of the high-energy irradiation results were proved with some explanations about planar defects, de-lamination, and tracks propagation, which are parallel to the basal plane of the GaN epilayer [18–20]. There has been a strong interest of radiation-induced defects on GaN epilayer and related materials, which have been shown to affect the optical and structural properties of semiconductors [21–27]. In the present investigation, the effects of high-energy (75 MeV) Sn^{5+}

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ion irradiation on GaN epilayer at various ion fluences (10^{11}, 10^{12}, and 10^{13}) have been studied.

Experimental

The samples were unintentionally doped n-type GaN grown by metal organic chemical vapor deposition (MOCVD) on sapphire substrate of (0001) orientation at growth temperature of 1050 °C after depositing a thin GaN buffer layer at 600 °C. The thickness of n-type GaN layer was about 3 µm. The intrinsic carrier concentration of as-grown GaN sample was measured at 4×10^{16} cm^{-3} by Hall measurements. The samples were degreased with organic solvents and etched with $HCl:H_2O$ (1:1) for 10 s to remove the native oxide. The samples were irradiated at room temperature with Sn^{5+} ions at 75 MeV. Pelletron tandem accelerator has been used to irradiate the GaN samples at 1×10^{11}, 10^{12} and 10^{13} ion fluences. SHI irradiation on GaN samples was carried out at a background pressure of 10^{-6} Torr. In order to reduce the sample heating during ion-beam irradiation, the samples were mounted on a 'Cu' block with conductive silver paste. The surface of GaN epitaxial sample was focused perpendicularly to the ion-beam incident axis. The ion beam current was maintained around 3 µA during the ion beam irradiation of GaN samples. The irradiation has been carried out over the entire area (0.7×0.6 cm^2) of the sample by scanning the ion beam. The fluences on the sample kept in cylindrical secondary electron suppressed geometry was estimated by investigating the total charge accumulated on the sample, using a current integrator and then counting by a scalar counter. Stopping Range of Ions in Matter (SRIM) software was used to calculate the depth profile distributions of the irradiated ions. For 75 MeV-Sn^{5+} irradiated GaN thin film, the projected ion range in GaN/Sapphire was 14.55 µm and the lateral straggling was 1.04 µm.

Philips X'pert X-ray diffractometer (HRXRD) measurement has been used for analyzing the structural qualities of as-grown and irradiated GaN epilayers. X-ray rocking curves of (0002) diffracted plane on as-grown GaN and Sn^{5+} ion irradiated GaN layer were recorded and the results of full width at half maximum (FWHM) were analyzed.

The transient pulsed PL spectrum was recorded for all GaN samples. The 266 nm laser excitation was used to pump optically on GaN samples in a low-temperature photoluminescence measurement setup for GaN epilayer. The emission was detected by a nitrogen-cooled charge coupled detector. The excitation intensity was kept at about 5 W/cm^2. The spectral resolution was about 0.2 meV in the wavelength region of around 355 nm. A digital instrument Nanoscope 3000 atomic force microscope (AFM) with standard silicon tips was used to study the surface topography of the as-grown and irradiated GaN samples. The average RMS roughness values were calculated for all the samples.

Results and discussion

High resolution X-ray diffraction

Surface damage due to SHI-irradiation at larger ion fluences is interesting to understand the mechanical properties of GaN epilayer [18]. Figure 1 shows the FWHM value of as-grown and irradiated GaN (0002) samples reflection measured by high resolution X-ray diffraction (HRXRD) measurement. The FWHM values of GaN samples are 227, 230, 244, and 279 arc-secs for as-grown and irradiated samples with the Sn-ion fluences of 10^{11}, 10^{12}, and 10^{13} ions, respectively. Figure 1 shows the crystalline quality of GaN epitaxial layer decreases with the increase of ion fluences from 10^{11} to 10^{13} ions. There are no appreciable structural changes in FWHM rocking curve values between as-grown and irradiated GaN samples while increasing the ion fluences up to 10^{11} ions/cm^2. Radiation-induced structural damage with ion fluences results few tens of arc-secs from 227 to 279 by FWHM analysis along the (0002) plane direction to GaN epilayer by X-ray rocking curve measurement.

The changes in the FWHM values indicate the ion-induced lattice disorders and decrease in the crystalline quality of GaN epilayers. As evident from Fig. 1, the variation of FWHM values for as-grown and the irradiated samples with lowest ion fluences are almost negligible.

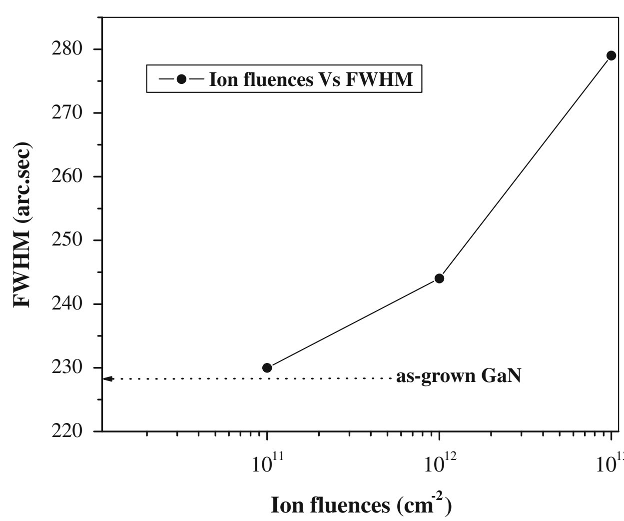

Fig. 1 FWHM value of (0002) reflection corresponding to as-grown and irradiated GaN-samples at various ion fluences obtained by HRXRD rocking curve measurement

When the ion fluences increased from 10^{11} to 10^{13}, the FWHM values are also increased appreciably. This tendency confirms that there is a structural damage in GaN epilayer due to heavy ions at higher ion fluences only. It shows the level of radiation tolerance of GaN epilayer at 75 MeV Sn^{5+} ions. The broadening of FWHM may be because of the presence of additional defects, dislocations and strain in the material. Therefore, the results suggest the minimum strain effects present in GaN epilayer due to the high-energy SHI irradiation process up to 10^{11} ion fluences. The increase of Sn^{5+} ion fluences above 10^{11} ions/cm^2 creates mechanical stress in both sapphire substrate and GaN film which could be attributed to ion-beam-induced rearrangement and weakening of atomic bonds at the film substrate interface [18, 28, 29].

Photoluminescence studies

Figures 2 and 3 show low-temperature photoluminescence (PL) spectra of as-grown and irradiated GaN samples. The PL spectral line position of excitons depends on the strain-state of GaN epitaxial layer. The intrinsic exciton features (A, B, and C) are observed at low temperature PL measurement with an accuracy of about 2 meV by α-polarization selection method for GaN thin films. The low temperature PL measurement at 2K of as-grown GaN sample shows similar results to the previously published reports [30, 31]. Donor bound exciton (DBE) states of as-grown, irradiated GaN samples at 10^{11} and 10^{12} ion fluences observed at 3.478, 3.478, and 3.4709 eV, respectively. In Figs. 2 and 3, the PL spectral lines are dominated by free excitonic (FE^A, FE^B, and FE^C) emissions for as-grown and irradiated GaN samples at 10^{11} and 10^{12} ion fluences. The spectral line values of DBE and FE of as-grown and irradiated GaN samples are shown in Table 1.

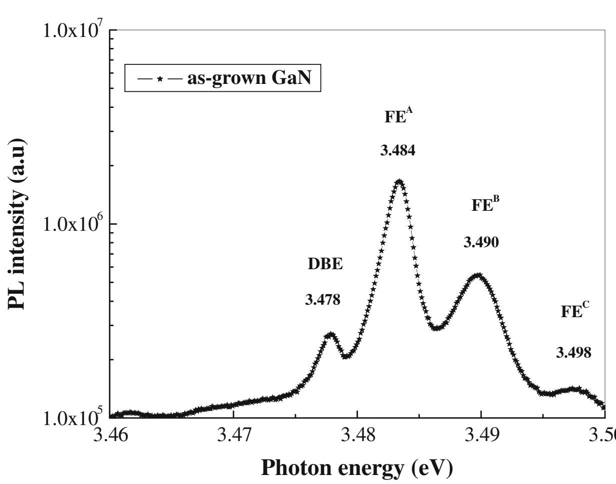

Fig. 2 The photoluminescence spectrum at 2K of as-grown GaN epilayer shows donor-bound exciton (DBE) and two dominant free excitons (FEs)

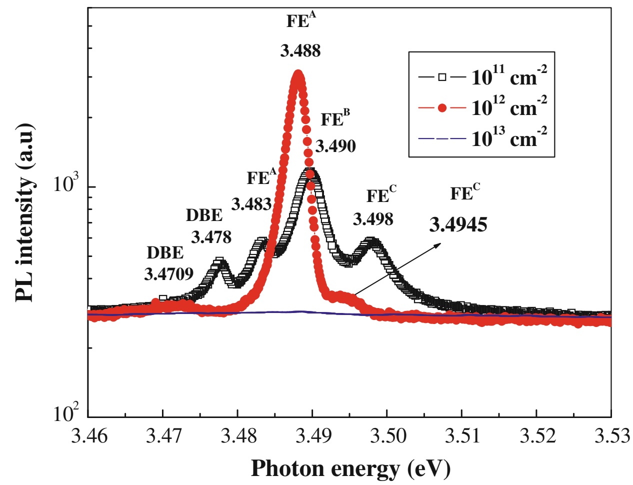

Fig. 3 Photoluminescence spectrum at 2K of GaN epilayer irradiated at 10^{11}, 10^{12}, and 10^{13} ion fluences showing donor-bound excitons (DBEs) and free excitons (FEs)

Table 1 The experimental PL data at 2K measurement of donor-bound exciton (DBE) and free exciton (FE) values of as-grown and irradiated GaN samples

Sample specifications	DBE (eV)	FE^A (eV)	FE^B (eV)	FE^C (eV)
As-grown	3.478	3.484	3.490	3.498
1×10^{11} ions/cm^2	3.478	3.483	3.490	3.498
1×10^{12} ions/cm^2	3.4709	3.488	No values	3.494
1×10^{13} ions/cm^2	No values	No values	No values	No values

Low temperature PL spectral positions of the excitons for an epitaxial layer depend on the strain state of epilayers. The intrinsic optical properties of GaN epilayer are dominated by excitons. In the α-polarization method, three transitions of exciton states with crystalline symmetries were observed [29]. According to these three transition of free exciton states (A, B, and C) with crystalline symmetries; PL line dominates at as-grown GaN epilayer. The photon energy region for DBE spectra for strain-free GaN semiconductors is about 3.470 to 3.472 eV [32]. It is believed that different shallow donors contribute to the spectra observed in this region in different samples to determine the characteristic of DBE line for a particular shallow donor. In homoepitaxial GaN samples grown by MOCVD technique, dominant line was observed at 3.4709 eV and several additional lines are possible nearer to this spectral emission background region [33]. This broad background lines could be due to additional donor species present as residual impurities [34]. In Fig. 2, the intrinsic exciton features A, B, and C is identified for as-grown GaN samples measured at 2K PL setup. The spectral positions of the exciton emissions in as-grown GaN sample results similar to the results reported earlier in Refs. [35] and [36]. Here, the PL line of as-grown and irradiated GaN sample at 1 × 10^{11} ion fluences shows almost similar excitonic signatures; these are associated with extended defects, such as dislocations or stacking faults.

Figure 3 shows PL spectrum of irradiated GaN with ion fluences at 10^{11}, 10^{12}, and 10^{13} ions/cm^2. The additional free exciton of FE^A, FE^B, and FE^C are present at 3.483–3.488, 3.490, and 3.494–3.498 eV, respectively. The low temperature PL line spectrum of as-grown and irradiated GaN sample at 1 × 10^{11} ion fluences remains almost same. The DBE and free excitons (FE^A and FE^C) emission peaks appear at 3.4709, 3.488, and 3.494 eV for 10^{12} ion fluences, respectively. DBE and FE emissions are disappeared at the fluences of 10^{13} ions. The absence of DBE and FE emissions show the excitons of GaN epitaxial layer depend upon the strain-state of heteroepitaxial layers under the influence of SHI high-energy irradiation. There was no significant change in DBE and FE energy levels in as-grown and irradiated GaN samples at 10^{11} ion fluences. DBE and FE emissions were disappeared completely at higher ion fluences. The strain-induced or defects related as-grown and irradiated GaN sample at 10^{11} ion fluences showed no spectral position shifts in the DBE and FE (FE^A, FE^B, and FE^C) emission but there was a blue and red shift observed by 5 and 4 meV at 10^{12} ions on FE^A and FE^C, respectively. DBE energy level of GaN epilayer irradiated at 10^{12} ion fluences results similar to the strain-free pure GaN crystalline symmetries as reported earlier [29, 32]. GaN epilayer irradiated at 10^{13} ion fluences results low PL intensity due to the creation of highly resistive region on GaN epilayer by inducing high-energy SHI, which was measured by Hall measurements in the order of 10^{10} Ω cm.

Figure 4 shows room-temperature PL measurement spectrum due to SHI irradiation at 75 MeV. There was a red shift in the YL peak from 2.21 to 2.18 eV for 10^{11} ions/cm^2 irradiated samples compared to the as-grown and irradiated GaN samples. The intensity of NBE is much stronger than the other samples at 10^{11} ion fluences, which clearly indicates that the red shift in YL region during 10^{11} enhances at near band-edge luminescence properties [28, 35]. The as-grown GaN sample contains some defects due to the unresolved growth issues during the MOCVD epitaxial growth techniques. 75 MeV high-energy ion-fluences (10^{11}, 10^{12}, and 10^{13} ions/cm^2) may passivate these defects in the energy band-gap region and enhance the radiative recombination of NBE of GaN epilayer by reducing PL intensity in YL region. Normally, good qualities of pure and strain-free GaN epilayers show no luminescence in YL region. The luminescence is supposed to be related to oxygen in the as-grown GaN sample [37].

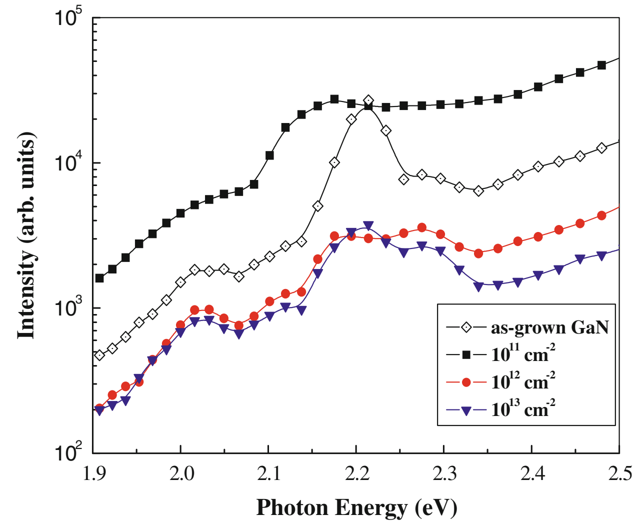

Fig. 4 YL spectrum of as-grown and radiated GaN epilayer measured at room temperature PL. Red shift appears at 10^{11} ion fluences

At higher ion fluences, the rate of non-radiative recombination may be higher due to heavy ion damage in the lattice of GaN epilayer. It suggests that the YL band involves electronic states associated with defects, which result the recombination process present in between shallow-donor and deep-acceptor related to N vacancies (V_N) and Ga vacancies (V_{Ga}), respectively due to donor–acceptor pair model [17]. During the irradiation of tin ions with moderate ion fluences the heavy ions may interact strongly with the heavy 'Ga' atoms and may result in Ga vacancies by point-defect clusters [37]. Formation of 'Ga' vacancies and the passivation of point defects by SHI-high-energy irradiation may be the probable reasons for the red shift in YL band. However, at higher fluences the lattice damage in GaN may enhance the non-radiative recombination and decreases the optical luminescence of both NBE and YL.

Atomic force microscopy

The surface morphology features of as-grown and irradiated GaN samples were studied at (4 × 4) μm^2 scanned area by atomic force microscopy (AFM) measurement. It is difficult to observe the ion damages during the time of high-energy irradiation measurement. The average RMS roughness measured at (1 × 1) μm^2 surface areas of as-grown and irradiated GaN epilayer with Sn-ion fluences 10^{11}, 10^{12}, and 10^{13} are 0.346, 0.358, 0.449, and 0.424 nm, respectively. Figure 5 shows the average RMS roughness values of as-grown and irradiated GaN epilayer. The average RMS roughness of GaN epilayer increases with increasing ion fluences from 10^{11} to 10^{12} and decreases

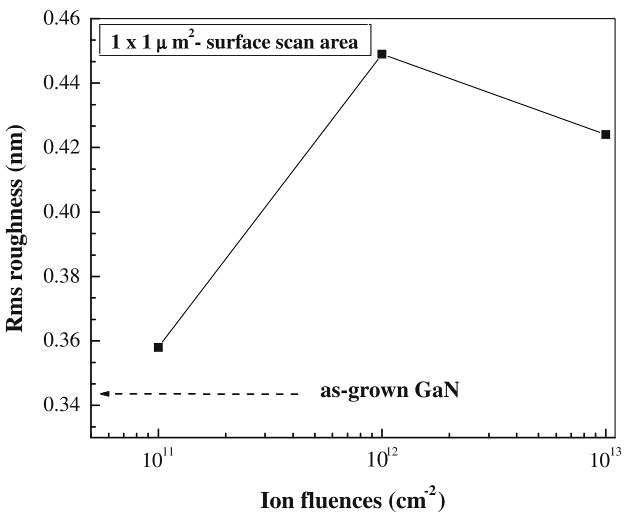

Fig. 5 Average RMS roughness value of as-grown and irradiated GaN epilayer scan at (1 × 1) μm^2. GaN epilayer roughness increases with increasing ion fluences up to 10^{12} ions

thereafter at 10^{13} ion fluences due to minimum irradiation damage on the surface. Figure 6 shows the AFM images of as-grown and GaN irradiated samples measured at larger scan area of (4 × 4) μm^2. All GaN samples except the sample-irradiated at 10^{11} ion fluences show dark spots in the larger surface scan area measured at (4 × 4) μm^2. The track information or step bunching was observed for all GaN samples. The amount of dark spots and defects have been decreased significantly when the ion fluences increased up to 10^{11} and the dark spots re-appeared when the ion fluences were further increased. The average RMS roughness on the GaN epilayer surfaces increases with the higher ion fluences except 10^{13} ions/cm^2. Interestingly, 10^{13} ion fluences remove as-grown GaN dark-pits ambiguities formation. These images are clearly evidenced that the higher-energy irradiation at higher ion fluences deteriorates the sample surface up to 10^{12} ion fluences. The average RMS surface roughness decreases slightly at 10^{13} ion fluences when compared to 10^{12} ion fluences, the

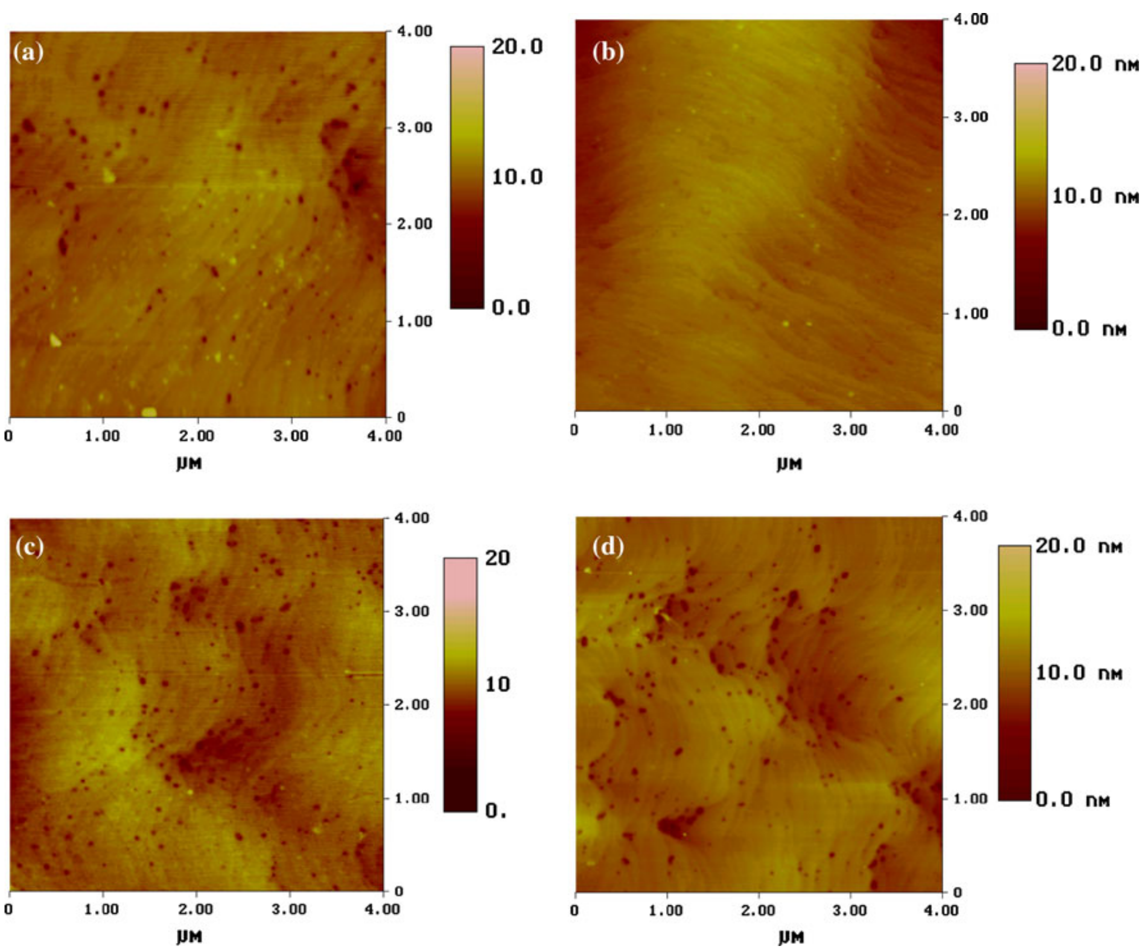

Fig. 6 AFM images of surfaces scan at (4 × 4) μm^2 of **a** as-grown and **b–d** irradiated GaN epilayers of different fluences: **b** 10^{11}, **c** 10^{12}, and **d** 10^{13} ions/cm^2. Irradiation induced surface damages and pits appear as *dark spots*

HRXRD and PL results show poor surface quality and optical property as discussed earlier.

Conclusion

The optical properties of the GaN epilayers were studied after various levels of high energy SHI radiations. It was shown that the GaN epilayer does not deteriorate much and the minimum damage occurs up to ion fluences of 10^{11} ion/cm^2. It was found that the HRXRD rocking curve values of GaN epilayer increases with increasing ion fluences. The absence of DBE and FE emissions at a very high ion-fluence (10^{13}) shows the strain-state of GaN epitaxial layer. Red shift in the yellow luminescence region depends up on the concentration of ion fluences at room temperature. The higher ion fluences deteriorate the surface of GaN epilayer by removing as-grown GaN surface defects. The HRXRD and PL results showed the poor surface morphology and optical property during higher ion fluences (at 10^{13} ions/cm^2). This reveals that the existing as-grown surface defects could be removed by the selection of radiation fluences appropriately.

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