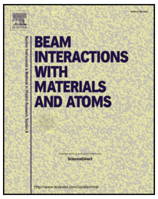
Nuclear Inst. and Methods in Physics Research B 431 (2018) 12–18

Contents lists available at ScienceDirect

Nuclear Inst. and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



Optical bandgap and stress variations induced by the formation of latent tracks in GaN under swift heavy ion irradiation

F. Moisy*, M. Sall, C. Grygiel, A. Ribet, E. Balanzat, I. Monnet

CIMAP Normandie Universite/ENSICAEN/CEA/CNRS, 6 Bd Maréchal Juin, 14050 Caen, France

ARTICLE INFO

Keywords:
GaN
Irradiation
Bandgap
Stress
Transmission Electron Microscopy
Ion tracks

ABSTRACT

In this work, GaN epilayers, grown on (0001) sapphire substrate, were studied under swift heavy ion irradiation with a broad variety of projectiles at different energies. Several characterization techniques including transmission electron microscopy, optical absorption spectroscopy and Raman scattering spectroscopy, employed for different irradiation conditions, allowed the identification and the attribution of the origin of the observed modifications. It has been established that for projectiles presenting an electronic stopping power higher than a threshold of 17 keV.nm^{-1}, there was the formation of disordered latent tracks on the ion paths. We have shown that these tracks become more continuous and are visible until a higher depth with the increase of the projectile electronic stopping power. We have also highlighted that the latent tracks induce the appearance of a biaxial stress of the order of some GPa and strongly modify the optical bandgap values. Contrary to this effect of electronic energy loss, the atomic displacements generated by nuclear energy loss process did not imply significant biaxial stress and optical bandgap closing.

1. Introduction

GaN is a common wide bandgap semiconductor material for applications in high power electronic and optoelectronic devices [1–3]. Physical properties of this material are very sensitive to the nature and the level of point and/or extended defects. Thus, it is important to understand the mechanisms responsible of their appearance since they control the reliability of the GaN-based devices. Indeed, in the real world conditions, GaN can be subjected to radiation and sometimes to swift heavy ion irradiation in a large range of energy. For example, such extreme radiative environments can be found during a doping process by ionic implantation (low energy irradiation around some keV.u^{-1}), during their use in space where ions can reach many GeV.u^{-1} or also in power devices where high density of energy is transported in a short interval of time [4–8].

In the low energy irradiation regime (some keV.u^{-1}), material modifications mainly come from energy deposition by ballistic collisions, quantified by the nuclear stopping power (S_n). This damaging process induces for example the formation of point defects in GaN [9]. For the high energy irradiation regime (some MeV.u^{-1} up to GeV.u^{-1}), the energy deposition by electronic excitations (electronic stopping power S_e) is dominant in comparison to ballistic collisions which are nevertheless not completely negligible. Thus, the high energy irradiation regime is interesting to study the respective contributions of nuclear and electronic energy losses on the material modifications and damaging. It also allows us to investigate coupled effects between these electronic and nuclear processes; such studies were, for example, performed concerning the point defects formation in AlN and $Al_xGa_{1-x}N$ nitrides [10,11]. Generally, in most of the insulating and semiconducting materials, ion track formation under swift heavy ion irradiation is often controlled by a threshold of electronic stopping power above which they appear [12–14]. Indeed, according to the thermal spike model [14], the energy deposited by electronic excitations is transferred, by an electron-phonon coupling, to the lattice and subsequently induces the melting or even the vaporization of matter along the ion path. After a quench, tracks are formed and the steady state of disturbed matter can be disordered or even amorphous. A discussion dedicated to nitride semiconductors and the formation of tracks is found in the literature [15]. In another study, Kucheyev et al. [16] showed by Transmission Electron Microscopy (TEM) and Rutherford Backscattering/channeling Spectrometry (RBS/c) that after irradiation with 200 MeV Au, ion tracks in GaN are disordered rather than amorphous. In addition, they observed by TEM that the tracks exhibit smaller diameter for $g = 0002$ than for $g = 1-100$, indicating differences in damaging according to different crystallographic directions. Moreover, many studies relate the appearance of residual stress and optical bandgap (E_g) closing after swift heavy ion irradiation [17–21]. However, the energy deposition process inducing these modifications is

---

* Corresponding author.
E-mail addresses: florent.moisy@ensicaen.fr (F. Moisy), grygiel@ganil.fr (C. Grygiel), ribet@ganil.fr (A. Ribet), balanzat@ganil.fr (E. Balanzat), monnet@ganil.fr (I. Monnet).

https://doi.org/10.1016/j.nimb.2018.06.014
Received 26 March 2018; Received in revised form 14 June 2018; Accepted 14 June 2018
0168-583X/

not well explained, especially, the respective contributions of the electronic and nuclear energy losses are not detailed.

In the current work, GaN films are irradiated by swift heavy ions and thereafter analyzed by Transmission Electron Microscopy (TEM), Raman scattering and optical absorption spectroscopies in order to investigate the formation of ion tracks and its correlation with the stress and the optical bandgap evolution. An original experimental approach by using a wide range of ions and energies (i.e. variations of electronic and nuclear stopping powers) is used to accurately determine the deposition processes at the origin of these bandgap and stress variations.

2. Materials and methods

The samples studied are 3.5 µm thick wurtzite GaN epilayers, grown by Metal-Organic Chemical Vapor Deposition (MOCVD) on (0001)-Al_2O_3 sapphire substrate. The GaN layers are n-doped with Si dopant with a carrier concentration of around 2×10^{18} cm^{-3}. The samples have been irradiated with Swift Heavy Ions (SHI) at a normal incidence with different beamlines (IRRSUD and Medium Energy, ME) of the GANIL facility (Caen, France). The flux used during all the irradiation experiments, is kept low enough (around 2×10^9 ions.cm^{-2}.s^{-1} on IRRSUD and 2×10^8 ions.cm^{-2}.s^{-1} on ME) to avoid macroscopic temperature of the sample exceeding room temperature (RT) and subsequent annealing of defects. Irrespective of the ion species used, its projected range (R_p) is larger than the thickness of the GaN layer and are implanted deeply (some tens of microns) in the sapphire substrate.

To quantify and to compare for each ion the damage induced by elastic collisions, the number of displacements per atom (dpa) created by ballistic collisions is used instead of S_n. This dpa value is obtained by multiplying the mean elastic displacement cross section (σ_d) by the fluence (ϕ). By using SRIM code [22], values of electronic stopping power (S_e) and σ_d, are calculated and presented in Table 1. Note that σ_d values are obtained via full cascade calculations and are averaged over the entire GaN layer. Threshold displacement energies of 25 eV and 28 eV for Ga and N atoms respectively and a material density of 6.15 g.cm^{-3} are used for the calculations. Only the S_e at the entrance of the projectile (the higher value) has been considered here, since, from the threshold value established for ion track formation (see part III.A), it is the best way to know if there is the presence of ion track or not. Indeed, an averaged value of S_e (averaged over the entire GaN layer) less than the threshold does not mean that there is no presence of ion track on the surface of the GaN layer.

In the current study, three characterization techniques were used, one is *in situ,* UV–Visible absorption spectroscopy, and the two others are *ex situ,* TEM and the Raman scattering spectroscopy.

The UV–visible spectroscopy experiments were performed by using a homemade device called "CASIMIR" which is directly mounted on the irradiation beamlines and coupled with a UV–visible spectrometer. The setup consists of a cryogenic rotating head required for the cooling down of the sample until 15 K. The rotation allows the sample to switch between the irradiation position and the acquisition one. The *in situ* analysis (i.e. irradiation and analysis performed at different times) is performed successively. *In situ* analysis allows time-saving and avoids reproducibility problems as only one sample is used. Standard irradiations on plates at RT were also performed. Indeed, no change in the absorption spectra irrespective to the temperature used during irradiation (between 15 and 300 K). However, absorption spectra acquisitions (both *in situ* and *ex situ*) were always performed at 15 K in order to be coherent for the analysis as the spectrum shape is slightly sensitive to the temperature. The spectrometer is a Varian Cary 300 operating in transmission mode in the UV–Visible region (200–900 nm). Consequently, the technique probes the total sample thickness (film plus substrate), meaning that the information is representative of the entire thickness of the GaN layer. This is the main reason why we took averaged σ_d values. For the *ex situ* characterizations, we systematically used samples irradiated in a standard mode, namely irradiations on plates at RT, along the [0001] direction.

For the transmission electron microscopy analysis, cross section (XTEM) samples were prepared either by conventional ion milling method using a Gatan ion polishing system, or by focused ion beams (FIB) with a dual beam FEI HELIOS Nanolab 660. In each case, the final step was performed at low voltage and low current in order to limit damage during the milling. The characterizations were carried out with a JEOL 2010 microscope operating at 200 kV. Bright and dark field images, selecting different diffraction vectors: $g = 2-1-10$, $g = 01-10$ and $g = 0002$, were acquired to improve the contrast between the ion tracks and the rest of the GaN layer according to different crystallographic directions. Indeed, to observe the deformation field (D) induced by a given defect on a TEM image, it is necessary to satisfy the criterion $D.g \neq 0$. In practice, defects and damages that induce deformation field in the basal (0001) plane of GaN, for example along the directions $[2-1-10]$ or $[01-10]$, will not be observable under $g = 0002$, because $g.D = 0$.

The Raman scattering spectroscopy is performed *ex situ* at room temperature (RT) with a Horiba Jobin-Yvon LabRam Raman spectrometer working in the 50–1000 cm^{-1} range, coupled with a confocal microscope. Backscattering geometry has been used. By this configuration, the incident and scattered polarizations are parallel to the [0001] direction of the GaN layer and of the sapphire substrate. The red 633 nm line of a He-Ne laser was used as excitation source and the objective of the microscope was 100×. The diameter of the spot focused on the surface of the sample is around 1 µm. With a such Raman spectrometer, the thickness probed by the laser (depth resolution) is also around 1 µm. However, it is difficult to evaluate more precisely this value in our case, since it depends on the absorption properties of the GaN, which are modified under irradiation.

Table 1
Summary of the irradiation conditions: ion, beam energy, σ_d the mean elastic displacement cross-section (averaged over all the GaN layer) and S_e the electronic stopping power (at the material entrance).

Ion	Energy (MeV)	σ_d (10^{-16} cm^2.ion^{-1})	S_e (keV.nm^{-1})
^{238}U	1119	1.1	56.4
^{208}Pb	850	1.1	46
^{129}Xe	330	0.9	31.9
^{208}Pb	116	7.5	26.1
^{238}U	109	10.1	24.3
^{238}U	106	10.2	23.8
^{129}Xe	92	3.4	23
^{86}Kr	74	1.5	17
^{129}Xe	58	5.4	18
^{39}Ar	35	0.5	9.0
^{20}Ne	20	0.1	4.3

3. Results

3.1. Latent track formation

First, the conditions associated to latent track formation, by using XTEM as a direct observation method, have been evidenced. Fig. 1a and b show cross-section TEM pictures of GaN layers after irradiation with 58 MeV and 92 MeV Xe ions, respectively (same fluence of 5×10^{13} ions.cm^{-2}).

Samples irradiated at high fluences of 5×10^{13} ions.cm^{-2} are shown here. Considering a track radius between 1 and 2 nm for ion irradiation at these S_e values in GaN [15], ion impacts overlap so many times at 5×10^{13} ions.cm^{-2} that the maximum damaged thickness is easily visible. Native dislocations, originating from the lattice mismatch between the substrate and the GaN layer are also visible in these figures (Fig. 1a and b). From bright field image for the case of 58 MeV Xe ion irradiation (Fig. 1a), a damaged zone (contrast with many black "pockets"), corresponding to the overlap of discontinuous ion tracks is