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Effects of electronic and nuclear stopping power on disorder induced in GaN under swift heavy ion irradiation

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ABSTRACT

Wurtzite GaN epilayers, grown on the c-plane of sapphire substrate, have been irradiated with swift heavy ions at different energies and fluences, and thereafter studied by Raman scattering spectroscopy, UV–visible spectroscopy and transmission electron microscopy. Raman spectra show strong structural modifications in the GaN layer. Indeed, in addition to the broadening of the allowed modes, a large continuum and three new modes at approximately 200 cm^{-1}, 300 cm^{-1} and 670 cm^{-1} appear after irradiation attributed to disorder-activated Raman scattering. In this case, spectra are driven by the phonon density of states of the material due to the loss of translation symmetry of the lattice induced by defects. It was shown qualitatively that both electronic excitations and elastic collisions play an important role in the disorder induced by irradiation. UV–visible spectra reveal an absorption band at 2.8 eV which is linked to the new mode at 300 cm^{-1} observed in irradiated Raman spectra and comes from Ga-vacancies. These color centers are produced by elastic collisions (without any visible effect of electronic excitations).

1. Introduction

III–N semiconductors (AlN, GaN, InN and their corresponding alloys) are interesting materials for the development of electronic and optoelectronic devices due to their excellent properties such as large direct bandgap and high thermal conductivity. Thus, they have lots of applications in high efficiency Light Emitting Diodes (LED), transistors and so on. Particularly, GaN received strong attention for applications in the blue and UV spectral domains [1–5].

In order to improve functional properties of these semiconductors, ion implantation is a well-used technique for n- or p-doping or rare-earth incorporation [6–11]. In this case, projectiles have energies of some keV/u, thus radiation induced damages occur and are mainly induced by elastic collisions. Many papers have been published on III–V semiconductors (GaAs, InP, InAs, GaP) in this range of energy projectile [12]. Concerning ion implantation in GaN, a number of studies are published in the literature for example with Mg, Si, O, N, Ce, Ar, C, P and Ca ions [13–16].

Moreover, in order to integrate these materials in devices working on the outer space, where they can be subjected to cosmic rays and/or solar winds, their behavior under Swift Heavy Ions (SHI) has to be understood. In this case, projectiles have energies of some MeV/u. Thus, an effect of electronic excitations can take place even if direct formation of defects by pure radiolysis is not expected in semiconductors. Many works have already been reported about SHI irradiations in GaN [17–20].

In addition, an effect of both the elastic collisions and electronic excitations has already been studied in other semiconductors. Indeed, in AlN, we have demonstrated that color center creation comes from a synergy between these two processes [21]. On the contrary, in many other semiconductors, like SiC, recovery of elastic damages can take place by the effect of electronic excitations [22].

In this work, irradiation conditions cover a span of electronic (S_e) and nuclear (S_n) stopping powers. This allows studying the contribution of electronic excitations and nuclear collisions on disorder induced in GaN.

2. Experimental details

Samples used for these experiments are 3.5 μm thick single crystal wurtzite GaN epilayers grown by Metal–Organic Chemical

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Vapor Deposition (MOCVD) on c-plane sapphire substrate. They are n-doped with Si at a carrier concentration of $\approx 2 \times 10^{18}$ cm^{-3}. SHI irradiations were performed at the GANIL accelerator (Caen, France) whereas the C and He ones were done at JANNUS facility (Saclay, France). Eu ion implantation experiments were also carried out at LATR (Instituto Superior Técnico, Portugal). The energy loss values of ion beams on the GaN target, obtained with TRIM 2008 calculations [23], are indicated in Table 1 and cover a large range of S_e and σ_d (mean elastic displacement cross section). The σ_d has been calculated after dividing the total number of vacancies per ion and unit of length (obtained after full cascade calculation), by the atomic density of the material. This value has been averaged over all the irradiated part of the layer, which is the thickness of the layer for all irradiation conditions, except for Eu 300 keV. Indeed, except for this latter, where the damaged thickness is around 140 nm, the range of the particles widely exceeds the thickness of the GaN layer and are implanted deeply (at some µm) in the sapphire substrate, so it has been considered that all the GaN layer is homogeneously irradiated. The number of displacement per atom (dpa) produced in the layer is obtained by multiplying the σ_d by the fluence (ϕ in ion/cm^2). Threshold displacement energies used for calculations are 25 eV and 28 eV for Ga and N atoms respectively. The value taken for the density of the material was 6.15 g cm^{-3}. During irradiation, the ion-beam flux was kept low enough to avoid any ion-beam heating.

Raman scattering spectra were obtained in the 50–1000 cm^{-1} range at Room Temperature (RT) using Horiba Jobin-Yvon LabRam Raman spectrometer on backscattering geometry where incident and scattered polarizations are parallel to the [0001] direction. The red 633 nm line of a He–Ne laser was used as excitation source. UV–vis spectra were done at 15 K inside the irradiation device, composed of a cryogenic head coupled with Varian Cary 300 UV–Visible spectrometer operating in the 190–900 nm spectral range. Irradiations and spectra were performed under vacuum conditions ($\approx 10^{-8}$ mbar) at normal incidence, so a 90° rotation allows switching from these two positions without removing the sample from the vacuum chamber. Ex-situ spectra from samples irradiated at RT were also performed since no annealing of the defects was observed between 15 K and 300 K. However, absorption measurements were always carried out at 15 K in order to compare the spectra under identical recording conditions. Absorption band areas observed after irradiation are normalized by the irradiated thickness, i.e. the thickness of the layer (except for Eu implanted layers, where the damaged thickness is around 140 nm). Cross-sectional Transmission Electron Microscopy (TEM) characterizations were done with a JEOL 2010 microscope operating at 200 kV.

Table 1
Experimental conditions: σ_d is the mean elastic displacement cross-section over all the irradiated part of the layer. S_e is the electronic stopping power at the entrance in the material.

Ion	Energy (MeV)	σ_d (10^{-16} cm^2/ion)	S_e (keV/nm)
^{238}U	1119	1.1	56.4
^{208}Pb	116	7.5	26.1
^{238}U	106	10.2	23.8
^{129}Xe	92	3.4	23.0
^{86}Kr	74	1.5	17.2
^{129}Xe	58	5.4	18.0
^{84}Kr	46	2.6	14.7
^{39}Ar	35	0.5	9.0
^{129}Xe	30	10.8	10.7
^{39}Ar	25	0.8	8.6
^{20}Ne	20	0.1	4.3
^{12}C	8	0.1	2.3
^{4}He	4.5	4×10^{-3}	0.3
^{152}Eu	0.3	22	0.7

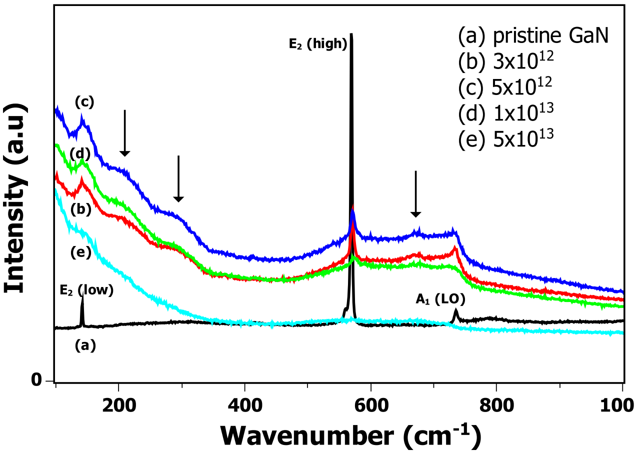

Fig. 1. Raman spectra of non irradiated GaN and after 106 MeV U ion irradiation at different fluences indicated in ions/cm^2.

3. Results and discussion

3.1. Point defects and disorder

Raman scattering spectroscopy is commonly used on GaN to probe information about disorder, stress and doping rate as it is reported in the review [24]. Fig. 1 shows Raman spectra of virgin GaN and after irradiation with 106 MeV U ions irradiation at different fluences until 5×10^{13} ions/cm^2 (where many overlaps of the ion tracks take place). For the virgin sample, all the allowed modes (E_2 (low) (142.3 cm^{-1}), E_2 (high) (568.9 cm^{-1}) and A_1 (LO) (735.9 cm^{-1})) predicted by group theory analysis for wurtzite structure in the standard backscattering configuration along *c*-axis ($Z(XX)\bar{Z}$) are present. The high frequency shift of the E_2 (high) mode relative to the corresponding one in bulk GaN (566.8 cm^{-1}) is attributed to compressive stress in the c-plane coming from a lattice parameter mismatch between the GaN layer and the sapphire substrate [25,26]. The broad shoulder at 800 cm^{-1} is attributed to the L$^+$ branch of the A_1 (LO) phonon–plasmon coupled mode due to the strong n-type doping with Si [27]. After irradiation with SHI at relatively low fluences (Fig. 1b and c), three broad vibration modes at approximately 200 cm^{-1}, 300 cm^{-1} and 670 cm^{-1} appear (indicated by arrows on Fig. 1) while the other modes tend to be broadened. The background increases after irradiation, especially at low frequency and in the region between the E_2 (high) and the A_1 (LO) peaks. This clearly indicates disorder induced in the material by irradiation. The increase of background is due to disorder and cannot come from a luminescence phenomenon since no difference is observed on the spectra by changing the wavelength of the laser source; it is rather linked to the increase of the elastic or quasielastic scattering on defects (point defects, clusters or small pockets of amorphous or highly disordered crystal in the tracks). Broad peaks at 200 cm^{-1}, 300 cm^{-1} and 670 cm^{-1} were already reported in implanted GaN, for example in Refs. [13,16,28]. They are attributed to Disorder-Activated Raman Scattering (DARS) where spectra are driven by the phonon Density Of States (DOS) of the material. It can be explained by the fact that damages created by irradiation produce long range disorder which induces a loss of translation symmetry of the lattice, so wave vector conservation in the Raman scattering process breaks down and the phonons from the entire Brillouin zone are observed. In such a case, the Raman spectrum results from a convolution of the phonon DOS and the Raman scattering cross-section of each vibration mode. In our irradiations, the implantation of ions occurs