Irradiation-induced improvement in crystalline quality of epitaxially grown InGaN thin films: A preliminary study

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Abstract. Irradiating materials with energetic particles is commonly thought to introduce undesirable phenomena, but recent experiments on ion irradiation of various nanostructures have shown that it can be beneficial and that ion beams may be harnessed to tailor the structure, mechanical, electronic, and even magnetic properties of nano-systems with high precision. However, the structural transformation and physical property changes in III-nitride thin films under ion irradiation have not yet been fully investigated. In this work, we focused on InGaN material for investigation of the effects of Phosphorus (P^+) ion irradiation on its structure, optical and electronic properties. Presently, there are a limited number of reports on InGaN:P in the literature. Hence, it was necessary to investigate the effects of P^+ incorporation into InGaN thin films. Preliminary results from Rutherford backscattering spectrometry and channeling (RBS/C) indicate that the crystalline quality of the InGaN thin films is improved by ion beam irradiation. Irradiating with 0.7 MeV P^+ ions to 1 x 10^{14} ions/cm^2 at room temperature reduces the channeling minimum yield (X_{min}) from about 60% to about 30%, but X_{min} increases considerably above this dose. Detailed experimental investigations will be carried out to obtain more information on the observed irradiation-induced-improvement in crystalline quality of InGaN thin films.

1. Introduction

The preparation and characterization of advanced optoelectronic material thin films has attracted tremendous scientific attention in recent years. It is well known that the structural, electrical, and optical properties of thin films are strongly correlated with their composition, microstructure, film thickness and impurities [1]. Irradiation of materials with energetic particles, such as ions or electrons, usually spoils their chemical or physical properties as a result of nuclear collisions and electronic excitation. However, ion irradiation may, on the whole, have beneficial effects on the target [2]. Two important examples of positive effects of ion beam irradiation are ion implantation onto semiconductors and the radiation-assisted treatment of cancer [3]. Some of the recent studies on the effects of ion irradiation on properties of materials can be found in Kumar *et al.*, 2014 [4] and Som *et al.*, 2014 [5]. Ion beam irradiation provides an active research field for the low-temperature processing, especially in semiconductor technology. The generation and migration of vacancies induced by ion irradiation make it possible to synthesize and modify materials at temperatures well below those required for thermally activated processes [6]. The evolvement of the structure of thin films by ion irradiation is interesting both from theoretical and experimental points of view. In this preliminary study, we investigate the effects of Phosphorus (P^+) ion irradiation on the crystalline quality of epitaxial InGaN/GaN thin films grown on sapphire substrates. Rutherford backscattering combined with channeling(RBS/C) was utilized to characterize the as-grown and the ion-irradiated InGaN/GaN samples. Future studies will look into structural, electrical and optical property changes after P^+ ion irradiation using additional and/or complementary techniques like transmission electron microscopy (TEM), X-ray diffraction (XRD), four-probe electrical method, and spectroscopic ellipsometry (SE).

2. Background

2.1. Group-III Nitride Materials

Group III-nitride semiconductors, aluminium nitride (AlN), gallium nitride (GaN), indium nitride (InN) and related alloys are obtained by combining group III elements (Ga, Al, In) with the group V element, N [7]. The III-nitrides are an unparalleled material system with many prominent features such as wide bandgap (0.7 eV for InN, 3.4 eV for GaN, and 6.2 eV for AlN), high mechanical and thermal stability, large piezoelectric constants, and excellent electro-optical properties [8]. The bandgap energy of a semiconductor is an essential parameter which influences its transport and optical properties including many other phenomena [9]. The energy gap of ternary III-nitride alloys like indium gallium nitride (InGaN), aluminum gallium nitride (AlGaN), or indium aluminum nitride (InAlN), can be adjusted to conform to light emission in the whole visible spectrum and into the deep ultraviolet (UV) region. In principle, the bandgap energy of the alloys can be varied continuously from 0.7 eV (pure InN) to 6.2 eV (pure AlN).

In contrast to conventional semiconductors like silicon (Si) or gallium arsenide (GaAs) which have a diamond or zinc-blende (zb) structure with cubic symmetry, the group III-nitrides can crystallize in a hexagonal wurtzite (wz) or in a cubic zb crystal structure [8]. The thermodynamically stable crystalline structure of the III-nitrides is the hexagonal wz crystal structure [10], which are partially ionic solids due to large differences in the electronegativity of the group-III metal cations (Al = 1.18, Ga = 1.13, In = 0.99) and nitrogen anions (N = 3.0) [8,11,12].

The III-nitrides have been studied intensively due to the great number of potential applications, and have recently attained an important position in the science and technology of compound semiconductors [13]. GaN and its alloy InGaN have become dominant materials for producing high brightness LEDs and LDs that emit light in the green/blue region of the visible spectrum. InGaN based light emitting diodes are already in use in full colour liquid crystal diode (LCD) displays and traffic lights. All these applications demonstrate the technological relevance of the III-nitride compounds and the reason for these materials to be the subject of an active research field (see, for example, [8,14-17]).

2.2. Ion implantation into InGaN alloys

$In_xGa_{1-x}N$ has the widest direct bandgap range of any compound semiconductor, varying from 0.7 eV (for x = 1) to 3.4 eV (for x = 0), which can be utilised in optoelectronic device applications from ultraviolet to infrared. This makes InGaN ideal for a wide range of applications, from high-density optical data storage, medical photonics, to communication devices. Recently, there has been a lot of interest in using InGaN in solar photovoltaic (PV) technology [18-21].

Ion implantation is an adaptable technique for introducing an array of doping or compensating impurities into semiconductors. Implantation can also be used to introduce a controlled level of impurities into the lattice for defect studies. It is the technique of choice to dope selective areas of a layer to desired carrier concentrations (for example, to create contact or channel regions) and to form semi-insulating regions for device isolation in such applications as field effect transistors (FETs). As the crystal quality of the group III-nitride materials continues to improve, ion implantation is playing an enabling role in exploring new dopant species and device structures [22]. Presently, some of the ion implantation doping and doping during film growth studies for InGaN that can be found in the literature are for the following impurities: N and F [23], Er [24], and Si and Zn [25]. There are no or limited studies on phosphorus (P)-doped InGaN available in the literature at the moment. However, P ion doping has been investigated for other wide bandgap materials like ZnS [26,27], ZnSe [28,29], ZnO [30-32], diamond [33-35], and SiC [36,37]. Moreover, phosphorus is a common dopant for n-type Si. Therefore, it was necessary to investigate the effects of P^+ incorporation into InGaN thin films.

3. Experimental techniques

Ion beam analysis (IBA) methods have been used in materials analysis for several decades [38]. With these methods, information about composition, uniformity, impurities, and elemental depth profiles of major, minor, and trace elements of materials is obtained through detection of products from the interactions between energetic ions (typically MeV) and electrons and atoms in the target material. For example, in the particle induced X-ray emission (PIXE) technique [39] the characteristic X-rays of target atoms are detected, and in Rutherford backscattering spectrometry (RBS) [40] and elastic recoil detection (ERDA) [41,42], back scattered and recoiled ions, respectively, are detected.

Four InGaN thin films grown, with a GaN buffer layer, on sapphire by metal organic chemical vapour deposition (MOCVD) were used in this work. Rutherford backscattering spectrometry and channeling (RBS/C) measurements were performed using a collimated beam of He^{++} ions of energy 2.084 MeV delivered by a 5UDH-2 Pelletron Tandem Accelerator at National Centre for Physics (NCP) in Islamabad, Pakistan. The samples were mounted on a high-precision goniometer in a vacuum chamber, so that the orientation of the samples relative to the He^{++} beam could be precisely controlled. A silicon particle detector, with an energy resolution of 25 keV, was placed at a scattering angle of 170°. First, three InGaN samples were irradiated, at room temperature, with P^+ ions of energy 700 keV at ion fluences of 1×10^{14}, 1×10^{15} and 7.75×10^{15} ions cm^{-2}. The fourth sample was not irradiated and taken as a reference/control sample. Then the defects in the crystalline structure produced by P^+ ion irradiation on the InGaN thin films were explored using RBS/C and compared with the as-grown sample.

4. Results and Discussion

Rutherford backscattering and channeling (RBS/C) is a nondestructive quantitative technique used to characterize composition, thickness, interface and crystalline quality of an epilayer as a function of depth [43]. Ion channeling has proved to be successful for strain measurement for a wide range of semiconductor thin films including III-nitrides [44]. When the ion beam is directed along a high-symmetry crystal direction, a phenomenon called "channeling" occurs. The incident ion beam will undergo a series of correlated small angle scatterings, and as a result the backscattering events significantly reduce compared with the backscattering events when the ion beam is randomly directed. X_{min}, which is the ratio of the backscattered yield when the ion beam is aligned with a crystallographic axis (Y_A) to that with the random direction (Y_R), is a measure of the crystalline quality of the film [45].

The RBS/C data was acquired using model RC43 analytical software supplied by the National Electrostatics Corp. (NEC) [46]. First, an RBS random spectrum of the as-grown sample was taken and then fitted with the Rutherford Universal Manipulation Program (RUMP) [47] in-order to determine the thickness and amounts of In, Ga, and N (figure 1). The InGaN thin film and GaN buffer were found to be 950 and 1830 nm thick, respectively. The composition of the epilayer was calculated to be $In_{0.05}Ga_{0.47}N$. The ratio of the backscattered events from the aligned spectrum to that from the random spectrum in the same region close to the surface had minimum yield X_{min} = 58.43 %, indicating that the $In_{0.05}Ga_{0.47}N$ layer had a poor crystalline quality. A X_{min} value of 1 – 2 % indicates perfect crystalline quality of the thin film [48]. Figure 2(a) shows a comparison of the RBS channeling and random spectra and figure 2(b) shows the channeling crystal image of the as-grown InGaN thin film. It is clear from figure 2(a) that the InGaN thin films were of poor crystalline quality because the aligned spectrum is very close to the random spectrum, indicating that the dechanneling rate was high.

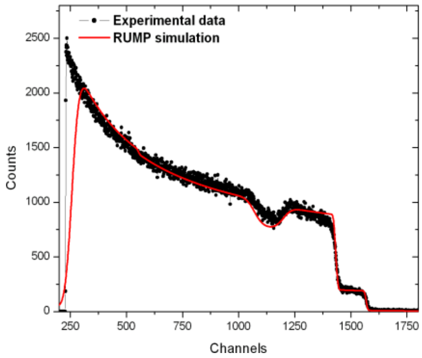


Figure 1. RBS random spectrum of as-grown InGaN sample simulated with RUMP program.

Next, the aligned and random spectra of the three P^+ ion-irradiated samples were acquired and $X_{\min}$ calculated. Figures 3, 4 and 5 below show the aligned and random spectra for each of the three P^+ ion-irradiated InGaN thin film samples with the corresponding channeling crystal image.

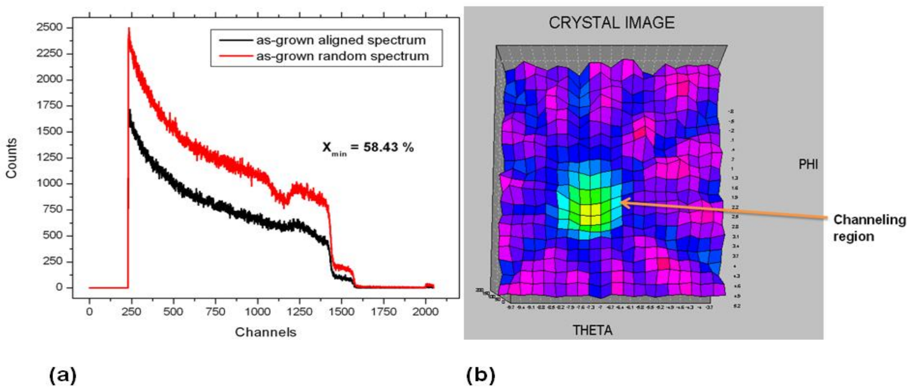


Figure 2. (a) RBS random and channeling spectra, and (b) Channeling crystal image of the as-grown InGaN thin film sample

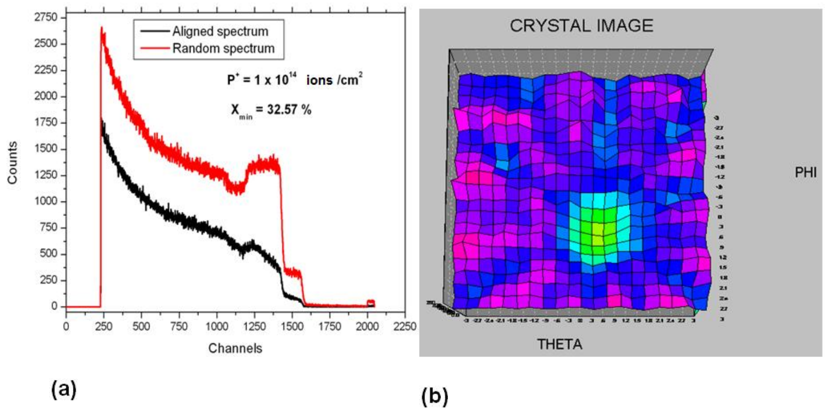
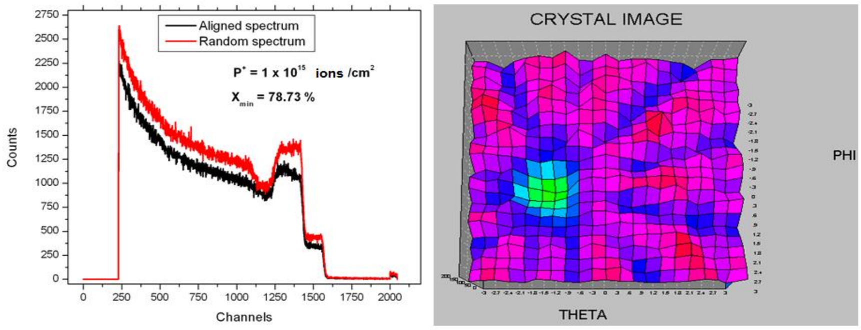


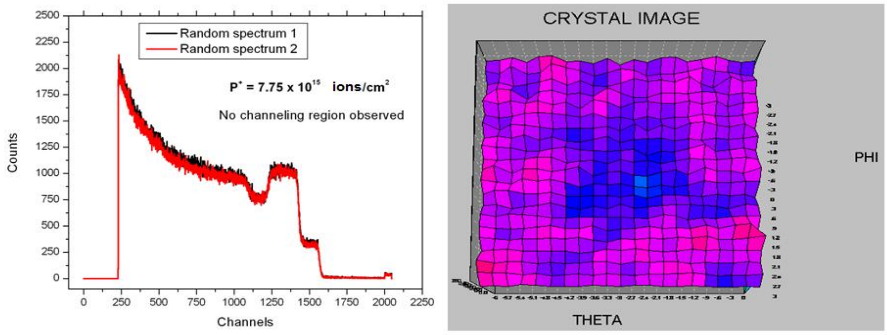
Figure 3. (a) RBS random and aligned spectra, and (b) Channeling crystal image of the InGaN thin film sample at P^+ ion fluence of 1 x 10^{14} ions/cm^2



(a) (b)

Figure 4. (a) RBS random and aligned spectra, and (b) Channeling crystal image of the InGaN thin film sample at P^+ ion fluence of 1 x 10^{15} ions/cm^2

It is clear from figure 4 and figure 5 that the dechanneling rate increases with the increase in ion irradiation for P^+ fluences of the order of 10^{15} ions/cm^2. No channeling region was observed at P^+ = 7.75 x 10^{15} ions/cm^2 (see figure 5(b)), which was the highest ion fluence reached in this study. However, at P^+ = 1 x 10^{14} ions/cm^2 the channeling minimum yield, $X_{\min}$, is lower than that of the as-grown sample (see figures 2 and 3). This observation suggests that the crystalline quality of the InGaN thin films is improved by low doses of ion irradiation. The same phenomenon has been observed by Takahiro and co-workers on epitaxially grown Ag thin films and Cu films on Si substrates [6,49,50]. Follow up experiments and additional techniques like transmission electron microscopy (TEM) may provide further information on the improvement of crystalline quality induced by ion irradiation.



(a) (b)

Figure 5. (a) RBS random spectra, and (b) Channeling crystal image of the InGaN thin film sample at P^+ ion fluence of 7.75 x 10^{14} ions/cm^2.

Figure 6 shows the variation of the calculated channeling minimum yield, $X_{\min}$, with P^+ ion fluence for all the four InGaN samples used in this study. As can be seen in figure 6, the channeling minimum yield of the as-grown sample fell from about 60% to about 30% at a P^+ ion dose of 1 x 10^{14} ions/cm^2.

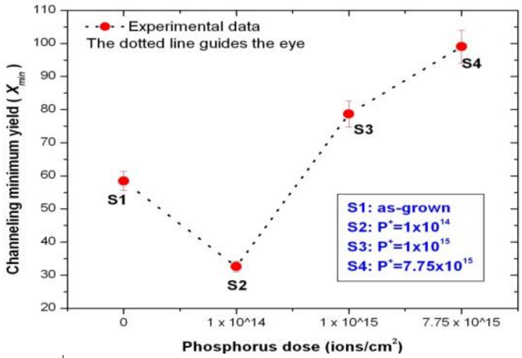


Figure 6. Variation of X_{min} with P^+ ion fluence. Note the decrease in X_{min} at $P^+ = 1 \times 10^{14}$

5. Conclusion

In this study, Rutherford backscattering spectrometry and channeling (RBS/C) structural analysis of P^+ ion-irradiated InGaN/GaN thin films grown by MOCVD on sapphire has been presented. We performed RBS/C experiments to find the composition, thickness, crystalline quality and channeling minimum yield, X_{min}, dependency on ion fluence. Irradiations with 0.7 MeV P^+ ions were carried out to fluences ranging from 1×10^{14} to 7.75×10^{15} ions/cm^2 at room temperature. The InGaN thin film and GaN buffer were found to be 950 and 1830 nm thick, respectively. The composition of the epilayer was calculated to be $In_{0.05}Ga_{0.47}N$. The crystalline quality of the InGaN thin films was analysed before and after irradiation. Results from RBS/C indicate that the quality of the InGaN thin films is improved by ion irradiation. Irradiation with 0.7 MeV P^+ ions to 1×10^{14} ions/cm^2 at room temperature reduced X_{min} from 58.4% to 32.6% at the InGaN surface but X_{min} increased considerably above this dose. We suggest that the improvement in the crystalline quality of the InGaN thin films could have been brought about by collision-induced atomic re-arrangements at low ion doses.

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