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Effect of In implantation and annealing on the lattice disorder and nano-mechanical properties of GaN

K. Filintoglou [a], P. Kavouras [b], M. Katsikini [a,*], J. Arvanitidis [a,b], D. Christofilos [c], S. Ves [a], E. Wendler [d], W. Wesch [d]

[a] School of Physics, Section of Solid State Physics, Aristotle University of Thessaloniki, 54124, Thessaloniki, Greece
[b] Department of Applied Sciences, Technological Educational Institute of Thessaloniki, 57400 Sindos, Greece
[c] Physics Division, School of Technology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[d] Institut für Festkörperphysik, Friedrich Schiller Universität Jena, Max Wien Platz 1, 07743 Jena, Germany

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ABSTRACT

The effect of 700 keV In implantation and subsequent annealing on GaN was studied by Rutherford Backscattering spectroscopy, Raman spectroscopy and nano-indentation as a function of the ion fluence (F) ranging from 5×10^{13} to 1×10^{16} cm^{-2}. Symmetry allowed and disorder activated Raman scattering peaks were analyzed using the spatial correlation model, allowing their assignment to phonon branches of crystalline GaN or defects and the estimation of the corresponding phonon coherence length (L). The L values decrease abruptly at a critical fluence of approximately 2×10^{14} cm^{-2}. After a slight increase in the nano-hardness (H) and reduced elastic modulus (E_r) values at low implantation fluences, they exhibit a steep reduction. These variations are accompanied by changes in the shape of the load–displacement curves, which are indicative of elasto-plastic behavior up to a critical F, whereas they approach the ideal plastic behavior at higher fluences. Annealing at 1000 °C of the sample implanted with 1×10^{15} ions/cm^2 results in efficient recovery of its structural and nano-mechanical properties. However, annealing of specimens implanted at higher fluences causes partial recovery that starts mainly from the transition region between the heavily damaged and the underlying undamaged GaN. The highly correlated behavior of L, H and E_r on the implantation fluence implies a common origin of the studied effects.

1. Introduction

GaN is a direct wide band-gap semiconductor characterized by high photoluminescence quantum efficiency, large electron saturation drift velocity, high breakdown voltage, low dielectric constant and high thermal conductivity. It is used for the fabrication of lasers and light emitting diodes operating in the blue–UV range of the spectrum, for high performance UV detectors and for high temperature, high frequency devices, mostly in combination with InGaN and/or AlGaN layers [1,2]. Furthermore, $In_xGa_{1-x}N$ with graded x concentration is suggested for the fabrication of efficient photovoltaic devices that cover the entire solar spectrum [3]. Ion implantation is an attractive synthesis technique of nano-crystals and buried layers as it offers the advantage of precise dose and profile control of the implants [4–7]. Its main disadvantage is the resulting lattice damage, which, however, can be reduced after annealing. Ion implantation and subsequent annealing were utilized for the synthesis of $In_xGa_{1-x}As$ in GaAs [8,9], $In_xGa_{1-x}P$ in InP [10] and for the isoelectronic element incorporation in InP [11]. Implantation at relatively high fluences, results in amorphization of the sample [12]. However, it has been suggested that amorphous GaN might be useful for optoelectronic applications since the strong ionic character of the Ga – N bonds inhibits the formation of Ga – Ga and N – N homopolar bonds, which might introduce states in the gap [13–15]. GaN has high amorphization threshold fluence, reaching the value of 2.4×10^{16} ions/cm^2 in the case of implantation with Si ions. Damage accumulation in GaN has been investigated using various implants [16–24]. The effective application of implanted GaN depends also on the mechanical response of the system [25,26]. Indeed, studies on the processes controlling hardness, contact damage and cracking at the small contact scales of epitaxially grown GaN films have been proved to be of major technological importance [27,28]. This is because mechanical properties of thin films are involved in many wear processes that cannot be extracted from simple bulk hardness data.

In this work, we apply Rutherford Backscattering Spectroscopy (RBS), Raman spectroscopy and nano-indentation for the study of wurtzite n-type GaN implanted with In at fluences (F) ranging about three orders of magnitude. The heavily implanted samples were subjected to rapid thermal annealing (RTA) in order to reduce the implantation-induced lattice damage and to enhance the promotion of In atoms into host lattice sites towards the formation of $In_xGa_{1-x}N$

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[*] Corresponding author. Tel.: +30 2310 998500; fax: +30 2310 998028.
E-mail address: katsiki@auth.gr (M. Katsikini).

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phases in the GaN epilayer. RBS is a well-established technique for the determination of the concentration and depth distribution of both the implanted ions and the host atoms as well as for the assessment of the lattice damage [29]. Raman spectroscopy has been applied for the study of GaN implanted mainly with dopants [30–33]. The mechanical properties, namely nano-hardness and reduced elastic modulus were studied by the quasi-static nano-indentation technique. Our work contributes towards the elucidation of the role of In implantation in the technologically important compound GaN, by revealing the existence of a critical implantation fluence beyond which a dramatic change in the mechanical properties as well as in the lattice order occurs.

2. Sample preparation and experimental details

The 450 nm-thick GaN (0001) layer was grown on Al_2O_3 by plasma assisted Molecular Beam Epitaxy using an AlN buffer layer. The sample was Si doped with carrier concentration $n = 3\times10^{18}$ cm^{-3}. Different pieces of the same wafer were implanted at 77 K with 700 keV In ions at F ranging from 5×10^{13} to 1×10^{16} cm^{-2}. In order to minimize channeling effects, the ion implantation was performed at 7° to the c-axis. The samples implanted with $F = 1\times10^{15}$, 5×10^{15} and 1×10^{16} cm^{-2} were subjected to RTA at 800, 900 and 1000 °C for 15 s using separate pieces for each temperature. In order to prevent nitrogen loss during annealing, the samples were sandwiched with unimplanted ones and the annealing was performed in N_2 atmosphere under a pressure of 26.7 kPa. The damage accumulation was measured by RBS performed at room temperature with 1.4 MeV He ions backscattered at 170°. The Raman spectra were recorded in the backscattering geometry using a triple monochromator (DILOR XY) equipped with a liquid nitrogen cooled charge coupled detector. The spectral resolution of the system was ~2.5 cm^{-1} and the beam size was ~1 μm. The Raman spectra were excited using the 514.5 nm line of an Ar^+ laser and a Ne lamp was used for spectra calibration.

The nano-hardness (H) and the reduced elastic modulus (E_r) were assessed by means of a Hysitron Ubi-1 TriboLab modular nano-indentation instrument. A pyramidal diamond Berkovich tip with a total included angle of 142.3° and a curvature radius of approximately 120 nm was used for indentation. The instrument stability was checked by measuring a fused-quartz reference sample. In all cases, a trapezoidal loading–unloading profile was recorded, with 5 s loading and unloading segments, enveloping a 2 s holding segment. The H and E_r were determined from the unload–displacement curves using the Oliver and Pharr model [34]. The influence of contact depth on the H and E_r values was estimated for each sample by a series of indentations with loads varying from 1 to 9 mN, with an increment of 1 mN and 10 indents per load. This indentation scheme was adopted since, according to RBS, the implanted layer extends to a depth of 200–300 nm from the sample surface depending on F [31,35]. In all indentation tests Bückle's rule is not satisfied, implying that the H and E_r values were influenced by the unimplanted portion of the GaN film and the substrate.

The H values were obtained by the simple extrapolation technique [36]. The E_r values were determined by means of a simple method by Bec et al. that allows the determination of elastic properties of films from nano-indentation experiments minimizing the contribution of the substrate [37]. According to this model, the reduced elastic modulus of the film (E_r^f) can be determined if the film's thickness (t), the reduced elastic modulus of the substrate (E_r^s) and the combined reduced elastic modulus of the film and substrate (E_r^c) are known, by means of the equation:

$$\frac{1}{E_r^c} = \frac{2\rho}{1 + 2t/(\pi\rho)}\left(\frac{t}{\pi\rho^2 E_r^f} + \frac{1}{2\rho E_r^s}\right) \tag{1}$$

where ρ is the contact radius. The implanted layer thickness was estimated from the RBS data and corresponds to the depth where the relative defect concentration falls to the half of the maximum value in each sample [31]. The E_r^s value was obtained from corresponding measurements on the as-grown GaN film. Other models, based on rather complex analytical formulations, for example those developed by Gao et al. [38] and Rar et al. [39], also called as the Song–Pharr model, bear the significant difficulty that they assume prior knowledge of the Poisson's Ratio of both the substrate and the film. Similarly, the sophisticated models by Jönsson and Hogmark [40], Chicot and Lesage [41], or Korsunsky et al. [42], assume a prior knowledge of the elastic constant or require normal indentation size effect for both the coating and the substrate, which is a highly arbitrary assumption [43]. Finally, quantitative results concerning the elasto-plastic response, namely the indentation energy dissipated in the form of plastic (W_p) and elastic energy (W_e), were assessed by the profile of the load–displacement curves.

3. Results and discussion

3.1. Rutherford backscattering

The defect depth-profiles for the as-implanted samples as a function of F have been published elsewhere [31,44]. They show a characteristic bimodal depth distribution, revealing that the lattice damage proceeds from the surface and the bulk with the two regions coalescing as F increases. The damage concentration ($n_{d.a.}^{\max}$) in the maximum of the measured distribution exhibits a characteristic three-step sigmoidal dependence on log$F$ which is similar to the behavior found for other species implanted into GaN [29]. An abrupt increase in $n_{d.a.}^{\max}$ from 6% to 80% is caused around $F = 3\times10^{14}$ cm^{-2} and a plateau in $n_{d.a.}^{\max}$ is observed from $F = 7\times10^{14}$ to 2×10^{15} cm^{-2}. The implantation fluence $F = 5\times10^{15}$ cm^{-2} can be considered as the amorphization threshold with the amorphized region extending up to ~200 nm from the surface followed by a partially damaged transition layer towards the substrate [44].

Fig. 1 displays the energy spectra of backscattered He ions on heavily implanted samples prior to annealing. The Ga signal initiates at channel 250 and extends up to channel 400 whereas the In signal is visible at channels 375 to 440. The onsets of the N and Al signals – the latter stems from the sapphire substrate and the buffer layer – are found approximately at channels 80 and 130, respectively. The as-grown sample spectrum included in Fig. 1 clearly reflects the high quality of the pristine GaN sample and the interface. The damage saturation in the heavily implanted samples is also evident. The effect of annealing on the random and aligned RBS spectra of the heavily implanted samples is clearly evident in Fig. 2(a,b). The small deviations

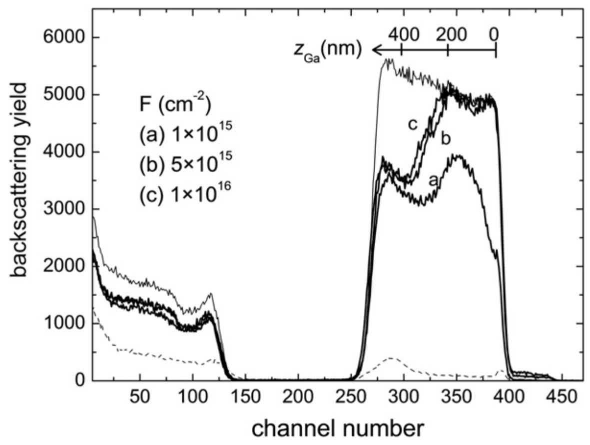

Fig. 1. Typical backscattering yield of the as-implanted samples. The thick (thin) solid lines correspond to aligned (random) spectra, respectively. The spectrum of the as-grown sample is denoted by the dashed line. The z_{Ga} scale corresponds to the depth distribution of the Ga atoms.