Thermal Behavior of the Mechanical Properties of GaN throughout Hydrogen-Induced Thin Layer Transfer

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We report on the thermoevolution of the mechanical properties of hydrogen-implanted bulk GaN under the conditions of thin layer transfer based on wafer bonding and ion-cut process. The mechanical properties were measured using a nanoindenter equipped with a continuous stiffness measurement attachment. The data were taken in depth control mode. Based on nanoindentation analysis, we obtained a modulus of 374±7.3GPa and a hardness of 18±1GPa for the virgin bulk GaN sample. After H-implantation, the hardness values were found to increase to 29.6±3GPa rendering the GaN in the implant zone more brittle. The modulus, however, decreased to 321±25GPa as a result of H-implantation. The influence of thermal treatment on the elasto-mechanical properties of H-implanted bulk GaN is investigated and its role in ultrathin layer splitting is discussed.

Introduction

Wafer bonding in combination with sub-surface defect engineering provides a wealth of opportunities to fabricate a variety of compound semiconductor-based hetero-devices (1). A compound semiconductor thin layer transfer – a crucial step in the fabrication process – is achieved via sub-surface microcracking upon thermal annealing at intermediate temperatures. This process is commonly known as the ion-cut or Smart-Cut™. The control and the application of this process to cleave thin layers from bulk or freestanding GaN (fs-GaN) wafers are technologically relevant. Indeed, fs-GaN is currently mostly used in the fabrication of blue laser diodes providing a wide spectrum of applications in optoelectronic data storage, visual information, medical devices, and biophotonics. Several industries (e.g., power devices, ultra-high brightness LEDs, etc) can also benefit from the availability of fs-GaN. The current cost of fs-GaN wafers is, however, very high. Therefore, large scale production of these new devices would require an important decline in fs-GaN price to compete with the alternative technologies (e.g., SiC). One of the possible strategies to reduce the cost would be to cleave several thin layers from a single fs-GaN wafer (donor wafer) and transfer them onto different handle wafers. In principle, this can be achieved using the ion-cut process. This work elucidates some subtle changes in the mechanical properties of fs-GaN leading to sub-surface
microcracking and ultimately to thin layer transfer. Understanding these fundamental scientific aspects is vital for a better control of the ion-cut technology.

Here the effect of H implantation-induced exfoliation was investigated by nanoindentation analysis. During nanoindentation testing, the elastic modulus and hardness are the most frequently measured properties. The modulus and hardness of a material can be extracted from the load-depth curve. The hardness is defined as the ratio of the maximum load (from the load-depth curve) to the projected area. The relationship is shown as followed:

\[ H = \frac{P_{\text{max}}}{A_c} \]  

where \( P_{\text{max}} \) = the maximum indentation load, \( A_c \) = contact area

The contact area for a perfect indenter shape is given by

\[ A_c = 24.5h_c^2 \]  

The contact depth can be calculated from

\[ h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S} \]  

where \( h_{\text{max}} \) = maximum penetration depth, \( S \) = unloading stiffness, \( \varepsilon \) = constant dependant on the indenter geometry. \( \varepsilon = 0.75 \) for Berkovich indenter tip (2)

The modulus is defined as the ratio of the slope of the unloading curve measured at the tangent to the data point at the maximum load and the projected area. The relationship is described by

\[ E_{\text{eff}} = \frac{1}{2} \frac{\sqrt{\pi}}{A} \frac{dP}{dh} \]  

where \( E_{\text{eff}} \) is the effective modulus, \( dP/dh \) = slope of the unloading curve from the load-depth curve, \( A \) = contact area.

In this work, the change in the micro-structural properties of LED quality GaN has been investigated as a function of different H-fluences and thermal evolution by nanoindentation, and by atomic force microscope (AFM).

**Experimental Set-up**

In case of GaN, the optimal splitting H-fluence was found to be \( 2.6\times10^{17} \) H ions cm\(^{-2} \) at 50 keV (3). In this experiment, LED quality 300μm thick GaN samples were implanted with hydrogen ions at 50 keV with a hydrogen dose of \( 2.6\times10^{17} \)cm\(^{-2} \). The samples were then annealed in air at temperatures ranging from 300°C to 600°C for 5 min to study the thermo-evolution of the mechanical properties throughout H ion-induced ultrathin layer splitting. The mechanical properties were measured using a Nanoindenteter XP by Agilent equipped with a continuous stiffness measurement (CSM) attachment. The data were taken in depth control mode. Prior to the measurements, the nanoindentation equipment was calibrated, where a triangular pyramidal diamond Berkovich tip was used as the indenter on fused silica standards. The surface morphology was investigated using a Nanoscope Dimension™ 3100 AFM by Veeco.

**Results**

Figure 1 displays the cross-sectional TEM image of a GaN sample immediately following H-implantation. Hydrogen ion implantation induced lattice damage starts \( \sim200 \)
nm below the surface as shown in Fig.1. The Gaussian peak of the implanted hydrogen dose in the GaN sample was located at approximately ~320 nm underneath the surface (4).

![Figure 1. Cross-sectional TEM micrograph of H-implanted GaN sample at a fluence of 2.6 × 10¹⁷ H⁺/cm² at 50 keV immediately after implantation. H and displacement profiles as measured by elastic recoil detection and ion channeling are superposed onto the as-implanted image.](image)

The surface morphology was first investigated by AFM. Figure 2 displays the AFM plot of a 2.6×10¹⁷ cm⁻² H-fluence GaN sample. The AFM analysis revealed an RMS roughness value of 4 nm of the virgin GaN sample. The RMS roughness increased slightly to a value of 6 nm after implantation. We performed a series of 20 indents with penetration depths of 1μm and 2μm in the as-implanted GaN samples that did not receive yet any thermal treatments. Figure 3 shows the load-depth curve of the H-fluence of 2.6×10¹⁷ cm⁻² samples. Neither pop-in, nor sink-in nor phase induced transformation can be detected in the load-depth plot of Fig.3, which indicates that the H implantation did not cause any phase change in the implant damage zone.
Figure 2. Surface morphology of GaN samples. a) AFM scan of an H-implanted GaN sample at an energy of 50 keV and fluence of $2.6 \times 10^{17}$ H ions cm$^{-2}$. b) AFM scan of a virgin non implanted bulk GaN sample.
Figure 3. Load-depth curve of a 1000 nm deep indent (dash line) compared to a 2000 nm deep indent (solid line).

The nanoindentation data evaluation revealed a modulus of 374±7.3GPa and a hardness of 18±1GPa for the virgin bulk GaN sample comparable to the literature values of 18-20GPa for bulk hardness and 295±3GPa for bulk modulus (5). The bulk values were measured by performing nanoindentation on the backside of the GaN samples, which did not receive H-implantation. The effect of the initial hydrogen implantation was a measurable increase in hardness values to 29.6±3GPa at a 200nm depth, while the modulus was found to be reduced to 321±25GPa measured at the same depth of 200nm. Figure 4 a) shows the hardness and Fig. 4b) shows the modulus as a function of indentation depths and the comparison with the virgin bulk GaN sample versus the hydrogen implanted GaN samples. One can see a clear change in both hardness and modulus of GaN after H-implantation. The hardness increased in the H-implanted region, which means the GaN material was rendered more brittle exclusively in that zone. As the indenter Berkovich tip penetrates far beyond the hydrogen implantation range into the GaN the measured hardness values slowly converge towards the bulk hardness of GaN. The effect of thermal evolution of the implanted hydrogen on the elasto-mechanical properties of the GaN films was also investigated. After annealing in a rapid thermal anneal (RTA) furnace for 5 min, there was no significant change in the hardness and modulus values for annealing temperatures in the range of 300°C to 500°C. The H-implanted sample annealed at 300°C exhibited a modulus value of 340±14GPa and a hardness value of 29.4±2GPa. After a thermal budget of 500°C, the modulus value of 362±25GPa and a hardness value of 29.6±2GPa. The chosen temperature range for the annealing experiments is relevant for the ion cut technology in order to precipitate the ultimate layer splitting.
Figure 4. a) Depth profile of the hardness in: virgin GaN (squares); as-implanted GaN (circles); H-implanted and annealed at 300 °C (up triangles) or at 500 °C (down triangles). b) Depth profile of the modulus in: virgin GaN (squares); as-implanted GaN (circles); H-implanted and annealed at 300 °C (up triangles) or at 500 °C (down triangles).
Following the thermal annealing cycles the nanoindentation load-displacement curves provide no indication for the expected development of microcracks as a precursor for layer splitting. It is well established that extensive microcracks constitute an early stage that precedes the complete layer splitting for the ion-cut or Smart-Cut\textsuperscript{TM} technology (3,6). In a previous work (3), microcracks and blisters were observed on H-implanted GaN annealed at higher temperature of 700 °C for 10 min. However in this study, the analysis was performed in subcritical temperature regime, where the samples have been annealed at temperature range from 300 °C until a maximum of 500 °C for 5 min. This accounts for the morphological difference between the two systems and explains the absence of microcracks and H blisters in the present study.

This is an ongoing research project and at this stage we can only hypothesize that maybe hydrogen was lost due to outdiffusion when the GaN samples were RTA annealed without a capping layer, leading to a subcritical hydrogen dose. In a regular ion-cut or Smart-Cut\textsuperscript{TM} process the H-implanted GaN sample is bonded to a handle wafer, which acts as a stiffener and a capping layer during the last thermal annealing cycle that initiates the layer splitting. Such a bonded handle wafer prevents any loss of implanted hydrogen due to outdiffusion during annealing. In our experimental set-up the wafer bonding process was omitted, because the nanoindentation system required free access to the GaN surface. A bonded handle wafer would have precluded indentation from the top surface. For a GaN sample bonded to a handle wafer, the hydrogen implanted region would only be accessible via a polished cleavage side or an angle lapped site. Another possibility would be that the anticipated formation of micro-cracks during thermal annealing leads to an effect in the GaN that is too small to be detected by the nanoindentation equipment.

**Conclusions**

This nanoindentation study provides us with unprecedented insights in the mechanical behavior of H-implanted GaN throughout sub-surface microcracking leading to thin layer transfer. Thick 300μm bulk GaN samples were implanted with hydrogen ions at 50 keV with a hydrogen dose of 2.6×10\textsuperscript{17} cm\textsuperscript{-2}. The modulus and hardness were measured before and after hydrogen implantation and the effect of thermal evolution of the implanted hydrogen on the elasto-mechanical properties of the GaN films was investigated. The hardness was found to increase after implantation leading to higher brittleness in the hydrogen implantation zone but no significant change in hardness was observed after the annealing experiments. In contrast with development of the hardness values, the modulus decreased after implantation. After thermal annealing, the modulus started to increase to converge to the bulk GaN virgin value.

**References**