Investigation of hydrogen implantation induced blistering in GaN

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A systematic investigation of surface blister formation on GaN epitaxial layers implanted with 100 keV H_2^{+1} ions with a dose of 1.3×10^{17} cm⁻² and annealed at various temperatures in the range of 350–700 °C was carried out. Two different activation energies were found for the formation of surface blisters: 1.79 eV in the lower temperature regime of 350–400 °C and 0.48 eV in the higher temperature regime of 400–700 °C. The depth and width of the blisters were determined using a stylus profilometer. The hydrogen implantation-induced damage was assessed using cross-sectional transmission microscopy revealing a band of defects extending from 230–500 nm from the surface of GaN.

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1 Introduction GaN and related nitrides have a wide range of applications in the area of optoelectronics as well as high frequency, high power electronic devices. These nitrides are mostly grown epitaxially on lattice and thermal mismatched substrates like sapphire, SiC or even on Si due to the fact that free-standing bulk GaN substrates are very expensive and are mostly available in small sizes [1, 2]. The heteroepitaxial growth of GaN on foreign substrates leads to the formation of growth-related defects like dislocations, stacking faults, twins etc. that occur to relax the strain. The high density of dislocations in the epitaxial layers of GaN grown on hetero-substrates has deleterious effects on the performance and reliability of the devices fabricated utilising these layers. One of the methods to fabricate low-cost and high structural quality substrates, comparable to free-standing GaN substrates, for the epitaxial growth of group-III nitrides would be direct wafer bonding and layer transfer of thin GaN films via a high dose hydrogen implantation and layer splitting upon annealing [3, 4]. The free-standing GaN substrate can be utilised to transfer multiple layers on other substrates. This process is based upon the agglomeration of hydrogen implantation-induced platelets upon annealing and the subsequent formation of overpressurized microcracks. For the case of the implanted wafer bonded to a handle wafer, splitting of a thin slice of material parallel to the bonding interface occurs [3, 5–7]. For this process to occur a narrow parameter window of implantation dose, annealing temperature and time has to be defined since the layer splitting is a strongly material dependent process. The physical mechanisms leading to the process of layer splitting can be conveniently investigated by studying the development of surface blisters in hydrogen implanted and annealed but unbonded wafers [7, 8]. In the present investigation we have performed a systematic study of the formation of surface blisters on hydrogen implanted and annealed GaN layers grown epitaxially on sapphire.

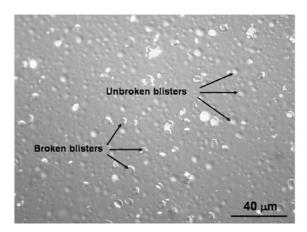
2 Experimental GaN epitaxial layers 4 μ m in thickness were grown on 2-inch (0001) c-plane sapphire substrates using metallorganic vapour phase epitaxy (MOVPE). The GaN epitaxial layers were

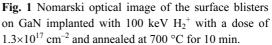
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implanted at room temperature with 100 keV H_2^+ ions with a dose of 1.3×10^{17} cm⁻². During implantation the sample surface normal was inclined at ~7° relative to the incident ion beam in order to avoid channelling effects. After implantation the wafers were cut into small pieces (~3×3 mm²) and annealed at different temperatures ranging from 300–700 °C. The formation of optically detectable surface blisters on GaN was observed using an optical microscope in the Nomarski contrast mode. The annealing time required to form optically detectable blisters at a particular temperature is defined as the blistering time at that temperature. In this way the blistering times were determined at different temperatures ranging from 300–700 °C. The width and depth of the broken blisters on the surface of GaN were determined using a Tencor stylus profilometer. The microstructural characterization of the implantation-induced damage in GaN was performed using cross-sectional transmission electron microscopy (XTEM). The XTEM measurements were carried out using a Philips CM200 FEG machine operated at 200 kV.

3 Results and discussion Figure 1 shows the Nomarski optical image of the GaN surface implanted with H_2^+ ions and annealed at 700 °C for 10 min. As can be seen in the image, most of the surface blisters are unbroken but some broken blisters are also visible. As the annealing time increases the proportion of the broken blisters will also increase. It is to be noted that the minimum dose required for observing the blistering phenomenon in GaN is much higher than that required for the other well-studied semiconductors like Si, Ge, GaAs, InP, SiC etc. [9]. The typical value of the H_2^+ ions dose required for observing the blistering phenomenon in these semiconductors is about 5.0×10^{16} cm⁻² [3, 6, 7]. The relatively higher value of hydrogen dose required in the case of GaN is due to the efficient dynamic annealing of the ion-induced defects during implantation in this material, as observed in some earlier studies also [9, 10].





An Arrhenius plot of the blistering time as a function of reciprocal temperature is shown in Fig. 2. There are two activation energies for the formation of surface blisters: in the lower temperature range of 350-400 °C the activation energy is found to be 1.79 eV while in the higher temperature range of 400-700 °C its value is 0.48 eV. In analogy to the case of hydrogen implanted and annealed Si [3, 11], the lower activation energy in the higher temperature regime can be related to the free atomic diffusion of hydrogen in the ion-induced damage region in GaN. In the higher temperature regime the atomic hydrogen is not trapped by the defects inside GaN and hence it diffuses in free atomic form. In contrast, in the lower temperature regime hydrogen is trapped by the defects in GaN and its diffusion is limited by a trapping-detrapping phenomenon that is important in this temperature range [3, 11, 12]. Hence activation energy for diffusion in the lower temperature range is composed of the activation energy for free atomic diffusion of hydrogen with traps in GaN. This leads to a higher value of activation energy for the diffusion of hydrogen in GaN in the lower temperature regime [11].

As shown in Fig. 1 there are some broken blisters on the surface of GaN and line scans using a Tencor stylus profilometer were taken along some of these broken blisters. Figure 3 displays one such line scan.

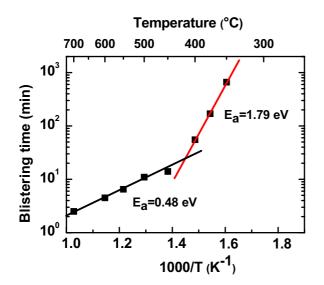


Fig. 2 Arrhenius plot of the blistering time as a function of reciprocal temperature for GaN implanted with 100 keV H_2^+ with a dose of 1.3×10^{17} cm⁻².

The width of the blisters lies between $2-6 \mu m$ and the depth of the blisters is $350\pm30 nm$. This depth would correspond to the thickness of the transferred GaN layer on the handle wafer in case the implanted GaN wafer was bonded to the handle wafer before the annealing. This depth is quite close to the peak of hydrogen concentration inside GaN in the case of 100 keV H_2^+ implantation, as calculated using SRIM2003 simulation code [13]. The hydrogen implantation-induced damage was characterized using XTEM measurements. Figure 4 shows the XTEM image of the hydrogen as-implanted GaN layer. It can be seen from the figure that there exists a damage band which extends between 230-500 nm from the surface. It is to be noted that the H_2^+ dose used here is 1.3×10^{17} cm⁻² which is sufficient to cause amorphization of most of the semiconductors like Si, GaAs, InP etc. But GaN is not amorphized due to the efficient dynamic annealing of the implantation-induced defects [9, 10]. The damage band consists of vacanices and interstitials and their complexes with hydrogen. It has been shown in some earlier studies that hydrogen forms complexes with Ga vacancies caused by the high dose hydrogen implantation [14, 15]. The hydrogen attaches with the dangling bonds of neighbouring nitrogen atoms and passivates them. Thus the agglomeration of vacancies and hydrogen leads to the formation of nanocavities in GaN filled with molecular hydrogen [13], which serve as precursors to the formation of microcracks and ultimately surface blisters in GaN after annealing.

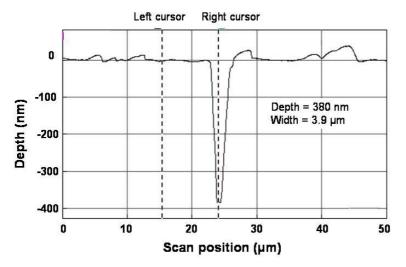


Fig. 3 The line scan taken using the stylus profilometer along a broken blister on the surface of hydrogen implanted and annealed GaN layer.

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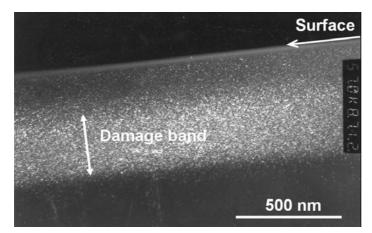


Fig. 4 XTEM image of the GaN layer implanted with 100 keV H_2^+ ions with a dose of 1.3×10^{17} cm⁻².

4 Conclusions MOVPE grown GaN/sapphire epilayers were implanted with 100 keV H_2^+ ions with a dose of 1.3×10^{17} cm⁻². A systematic and detailed investigation of the blistering kinetics was carried out after annealing the implanted samples in the temperature range of 350–700 °C. We found two different activation energies for the blister formation: 1.79 eV in the lower temperature range of 350–400 °C and 0.48 eV in the higher temperature range of 400–700 °C. The linear profile of the broken blisters was measured using a stylus profilometer which reveals that the depth of the blisters is about 350±30 nm. The XTEM charaterization of the implanted GaN shows a damage band extending between 230–500 nm from the surface. The hydrogen implantation-induced vacancies and their complexes with hydrogen lead to the formation of nanocavities filled with molecular hydrogen, which ultimately forms micro-cracks and then surface blisters after annealing the GaN samples.

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