Study of implantation-induced blistering/exfoliation in wide bandgap semiconductors for layer transfer applications

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We present an overview of the implantation-induced blistering/exfoliation process in wide bandgap semiconductors such as GaN, AlN and ZnO. These semiconductors were implanted with 50 keV hydrogen ions at various fluences and subsequently annealed at higher temperatures up to 800 °C in order to trigger surface blistering. In the case of GaN and AlN, a detailed blistering kinetics investigation was also performed. Various techniques such as optical microscopy, atomic force microscopy, cross-sectional transmission electron microscopy and stylus profilometry were used for the characterization of the implanted samples. In the case of room temperature implanted samples, it was observed that the damage band formed inside the samples was decorated with hydrogen filled nanovoids. These nanovoids served as precursors for the formation of two-dimensional extended defects called nanocorrels and microcracks upon annealing and eventually led to surface blistering or exfoliation.

1 Introduction

Wide bandgap semiconductors such as GaN, AlN and ZnO are of great importance due to their applications in electronic and optoelectronic devices [1–4]. The growth of epitaxial layers for device fabrication is mostly carried out on foreign substrates such as sapphire, SiC and Si due to the fact that high structural quality single crystal substrates of these wide bandgap semiconductors are very expensive and mostly available in small sizes [5–7]. Hydrogen implantation-induced layer splitting of semiconductors in combination with direct wafer bonding can potentially be used to provide inexpensive templates of high structural quality [8–10]. Using this method the free-standing wafers of these semiconductors can be utilized to transfer multiple layers on to other foreign substrates, which in turn serve as template layer for the growth of epitaxial device layers [8–10]. For this process to occur a narrow parameter window of implantation dose, implantation temperature, annealing temperature and time has to be defined since all these parameters depend strongly on the type of semiconductor material used for implantation [9]. The physical mechanisms leading to the process of layer splitting can be conveniently investigated by studying the development of surface blisters/exfoliation in hydrogen implanted and annealed but unbonded wafers [9]. Here an overview of the hydrogen implantation-induced blistering/exfoliation in GaN, AlN and ZnO has been presented. These semiconductors were implanted with 50 keV H+ ions at various fluences and after that annealed at higher temperatures up to 800 °C in order to observe the formation of surface blisters/exfoliation. The microscopic process leading to the formation of surface blisters/exfoliation has also been discussed.

2 Experiment

The samples used in this work were GaN and AlN epitaxial layers with a thickness of 4 and 2 µm, respectively, grown on 2-inch (0001) c-plane sapphire substrates. In case of ZnO, c-plane oriented bulk crystals having thickness of 500 µm were used. All these samples were implanted with 50 keV H+ ions with various fluences in the range of $5 \times 10^{16}$ to $6 \times 10^{17}$ cm$^{-2}$. It is to be mentioned here that in some cases we have used 50 keV H+ ions [15] while in other cases we used 100 keV H2+ ions [11,12,16–18] for implantation. But 100 keV H2+ ions are equivalent to 50 keV H+ ions with a dose that is two times of the latter case. Here, for the sake of consistency, we have presented all the results taking ion energy as 50 keV H+ in all the cases and have doubled the dose in those cases where we...
have used 100 keV H$_2^+$ ions. After implantation the samples were cut into different small pieces and annealed at higher temperatures up to 800 °C for 1 hour in air ambient. In order to check the optically detectable surface blisters/exfoliation in the samples, we used Nomarski optical microscopy. The surface morphology of the samples was studied using an AFM (digital Nanoscope III from Veeco in tapping mode). The microstructural characterization of the implantation-induced damage in these samples was performed using cross-sectional transmission electron microscopy (XTEM). The XTEM measurements were carried out by using a Philips CM20T machine operated at 200 kV.

3 Results and discussion

In case of GaN, the minimum hydrogen fluence required for the occurrence blistering to after post-implantation annealing was found to be 2.6×10$^{17}$ cm$^{-2}$ [11]. Figure 1 shows the Nomarski optical image of the GaN surface when the GaN layer was implanted with hydrogen and then annealed at 700 °C for 10 min. The size of the blisters varied between 2-6 µm. The blistering times were determined at various temperatures between 350-700 °C. The Arrhenius plot of the blistering time versus reciprocal temperature revealed two activation energies: 1.79 eV in the temperature range of 350-400 °C and 0.48 eV in the temperature range of 400-700 °C. The lower activation energy is associated with the free atomic diffusion of hydrogen in GaN while the higher activation energy is associated with the free atomic diffusion limited by trapping-detrapping of hydrogen in the implantation-induced defects [11]. This feature of blistering kinetics is similar to what has been previously obtained in case of hydrogen implanted silicon [9].

![Figure 1](image1.png)

Figure 1 Nomarski optical image of GaN surface after post-implantation annealing at 700 °C/10min [11]. The implantation was done with 50 keV H$^+$ ions at a fluence of 2.6×10$^{17}$ cm$^{-2}$.

The cross-sectional TEM image of the as-implanted GaN is shown in Fig. 2 wherein a damage band between 200-500 nm from the surface can be seen. Higher magnification TEM image of the damage band shows that this region is filled with nanovoids having dimensions of a few nanometers. These nanovoids upon high temperature annealing lead to the formation of nanocracks and micro-cracks inside the damage band (Fig. 3) that eventually lead to the formation of surface blisters [12-15].

![Figure 2](image2.png)

Figure 2 XTEM image of GaN implanted with 50 keV hydrogen ions at a fluence of 2.6×10$^{17}$ cm$^{-2}$. Inset shows high magnification image of a selected region in the damage band [15].

![Figure 3](image3.png)

Figure 3 XTEM image of microcracks formed inside the damage band in GaN implanted with 50 keV H$^+$ ions with a fluence of 2.6×10$^{17}$ cm$^{-2}$ and then annealed at 700 °C/1hr [12].

In case of hydrogen implanted AlN layers the minimum hydrogen ion fluence to observe blistering was found out to be 2×10$^{17}$ cm$^{-2}$ [16]. Figure 4 shows the blistering in hydrogen implanted and annealed AlN layers. The size of the blisters varied between 10-20 µm. From the blistering kinetics investigation of hydrogen implanted AlN, two activation energies were found: 1.16 eV in the temperature range of 450-550 °C and 0.44 eV in the temperature range of 550-750 °C. The XTEM image of the as-implanted AlN (Fig. 5) shows a damage band extending between 330-550 nm from the surface [16]. When a high magnification XTEM image (Fig. 6) of the damage was taken, it was found to be decorated with hydrogen filled nanovoids, as in the case of GaN. The number density of these nanovoids increases towards the end region of the damage band. Moreover, these nanovoids showed a tendency to agglomerate and line-up in the c-plane [17]. After annealing at higher temperatures, these nanovoids merged together.
leading to the formation of microcracks and ultimately to the optically observable surface blisters.

For ZnO(0001) bulk samples, the minimum hydrogen fluence required to observe surface blistering/exfoliation after post-implantation annealing was 5.0×10^{17} \text{cm}^{-2} [18]. It was observed that after post-implantation annealing of ZnO, large area exfoliation of the surface was observed. The entire top layer was removed and only a few island regions remained intact (Fig. 7). The XTEM image of ZnO in the as-implanted state showed the formation of a damage band extending between 200–600 nm from the surface (Fig. 8). This damage band was filled with nanovoids having size between 3-10 nm. Moreover, the nanovoid could also be observed in the top 200 nm layer of ZnO that was relatively much less damaged. Specifically, the nanovoids in the damage band showed a tendency of aligning along the c-plane. In addition, large area microcracks were observed in the damage band in the as-implanted state. The formation of microcracks in the as-implanted state was probably responsible for the large area exfoliation observed after high temperature annealing.

For GaN, AlN and ZnO after post-implantation annealing is quite higher than that for other semiconductors such as Si, SiC, InP and GaAs (for these semiconductors the minimum fluence is usually about 1.0×10^{17} \text{cm}^{-2}) [10, 19-21]. Specifically for ZnO the minimum fluence is about 5 times higher than that for Si or SiC. One potential reason may be due to the high radiation resistance of GaN, AlN and ZnO. It may also be related to other factors (that are yet to be explored with further detailed experimentation) such as higher formation energy of H\textsubscript{2} molecules [15], diffusivity of hydrogen (spe-
specifically for ZnO) [22] and details of the ion-defect interaction processes in these semiconductors. Nonetheless, for the technological application of thin film layer splitting of these semiconductors, the aforementioned implantation parameters are very useful.

4 Conclusions A brief overview of the hydrogen implantation-induced blistering/exfoliation in wide bandgap semiconductors, viz. GaN, AlN and ZnO has been presented. The implantation was performed with 50 keV H\textsuperscript{+} ions with fluences in the range of 5×10\textsuperscript{16} to 6×10\textsuperscript{17} cm\textsuperscript{-2}. The minimum fluences required to observe surface blistering/exfoliation in GaN, AlN and ZnO were 2.6×10\textsuperscript{17}, 2×10\textsuperscript{17} and 5×10\textsuperscript{17} cm\textsuperscript{-2}, respectively. The TEM investigations revealed the formation of a damage band in all the samples that was filled with nanovoids containing H\textsubscript{2} gas. These nanovoids served as precursors for the formation of microcracks inside the damage band after high temperature annealing eventually causing blistering/exfoliation. In combination with direct wafer bonding, the implantation parameters used in the present work for these semiconductors could potentially be utilised in the future for thin film layer transfer applications for fabricating inexpensive high structural quality templates.

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