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Investigation of blistering kinetics in hydrogen implanted aluminium nitride

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Abstract

Epitaxial layers of aluminium nitride (AlN) grown on sapphire by hydride vapour phase epitaxy (HVPE) were implanted with 100 keV hydrogen, H_2^+, ions with doses in the range of 5×10^{16}–2.5×10^{17} cm^{-2} and subsequently annealed in ambient air at temperatures between 450 and 750 °C in order to determine the kinetics of surface blister formation in AlN. The Arrhenius plot of the blistering time versus temperature shows two different activation energies for the formation of surface blisters: 0.44 eV in the higher temperature regime of 550–750 °C and 1.16 eV in the lower temperature regime of 450–550 °C. The implantation-induced damage was analyzed by cross-sectional transmission electron microscopy, which revealed a band of defects extending from 330 to 550 nm from the surface of AlN. The XTEM image of the implanted and annealed AlN displayed clearly the formation of microcracks that ultimately lead to the formation of surface blisters.

(Some figures in this article are in colour only in the electronic version)

Introduction

III–V nitrides have a wide range of applications in the field of optoelectronics as well as high frequency and high power electronic devices. In general, the epitaxial layers of these nitrides for various device applications are grown on lattice and thermal mismatched substrates such as sapphire and SiC. The growth of the epitaxial layers on foreign substrates is carried out since the single crystals of GaN and AlN are very expensive and are mostly available in small sizes [1–3]. In the case of AlGaN alloys, especially those with a high Al content, AlN offers a better lattice and thermal expansion match to AlGaN alloys in comparison to GaN. These high Al content AlGaN epitaxial layers are required for ultraviolet (UV) electro-optical applications such as UV light-emitting diodes, UV laser diodes and solar-blind UV photodetectors [4–7]. It has recently been shown that for the growth of high crystalline quality epitaxial layers required for these UV photonic devices, single crystal AlN substrates are very useful [6, 7]. But the single crystal substrates of AlN are extremely expensive. Recently, Crystal IS, Inc. USA has announced the growth of 2 inch diameter AlN wafers having ultra-low density of dislocations (~10^4 cm^{-2}) [3, 8]. A very promising method to fabricate low-cost and high structural quality substrates, comparable to single crystals of AlN substrates, for the epitaxial growth of high Al content AlGaN layers is direct wafer bonding and layer transfer of thin films of AlN via high-dose hydrogen implantation and layer splitting [9–11]. The free-standing AlN substrate can be utilized to transfer multiple layers on other foreign substrates. This process is based upon the agglomeration of hydrogen-implantation-induced platelets upon annealing and the subsequent formation of over-pressurized 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 [9–13]. 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 [14–16]. There are no reports in the literature regarding hydrogen-implantation-induced blistering in AlN. In the present investigation, we have performed a systematic study of the formation of surface blisters on hydrogen implanted and annealed AlN layers grown epitaxially on sapphire.

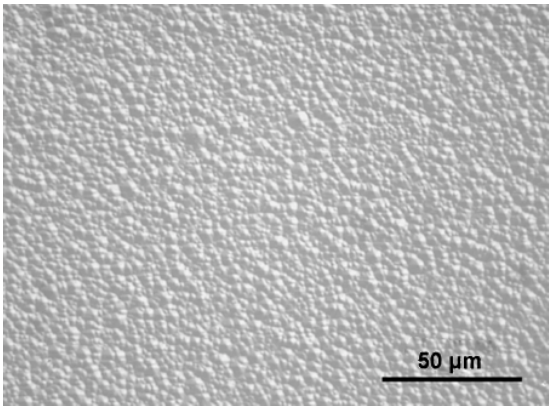

Figure 1. Nomarski optical image of the surface of a pristine AlN epitaxial layer.

Experimental details

AlN epitaxial layers about 2 μm in thickness were grown on 2 inch (0 0 0 1) *c*-plane sapphire substrates using metal hydride vapour phase epitaxy (HVPE). These AlN/sapphire wafers were purchased commercially from TDI, Inc. USA. The AlN epitaxial layers were implanted at room temperature with 100 keV H_2^+ ions with various doses in the range of 5×10^{16}–2.5×10^{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. The hydrogen implantation was performed at Ion Beam Services (IBS), France. After implantation the wafers were cut into small pieces (~3 × 3 mm^2) and annealed at different temperatures ranging from 450 to 750 °C. The annealing was carried out in an air ambient box-type furnace. The formation of optically detectable surface blisters on AlN epitaxial layers was observed using a Nomarski optical microscope. 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 450 to 750 °C. The microstructural characterization of the implantation-induced damage in AlN was performed using cross-sectional transmission electron microscopy (XTEM). The XTEM measurements were carried out using a Philips CM20T machine operated at 200 kV.

Results and discussion

The surface of the pristine AlN epitaxial layer was found to be quite rough, as shown in the Nomarski optical image of figure 1. The surfaces were found to have a large number of hillocks having the lateral size of a few micrometres. The typical RMS roughness of the surface, as measured by atomic force microscopy, was found to be about 20 nm on a 10 × 10 μm^2 scan area with a peak-to-valley height of about 140 nm, as shown in figure 2. In the case of hydrogen-implanted AlN, the wafers were implanted with a dose of 2.0×10^{17} cm^{-2} or higher exhibited surface blisters in the as-implanted state. In contrast, the AlN wafers that were implanted with a dose of 1.0×10^{17} or 1.5×10^{17} cm^{-2} showed surface blisters only after post-implantation annealing at higher temperatures. The sample implanted with a dose of 5.0×10^{16} cm^{-2} did not show any blistering even after post-implantation annealing up to 800 °C for 2 h. A typical Nomarski optical image of the AlN surface implanted with a dose of 1.0×10^{17} cm^{-2} and subsequently annealed at 500 °C for 1 h is shown in figure 3. The surface blisters have diameters in the range of 10–20 μm and their heights are about a few hundreds of nanometres (figure 3). A systematic blistering study was carried out for the AlN wafer that was implanted with a dose of 1.0×10^{17} cm^{-2}. The Arrhenius plot of the blistering time as a function of the reciprocal temperature is shown in figure 4. It can be clearly observed from this figure that there are two different activation energies for the formation of surface blisters. The activation energy is 0.44 eV in the higher temperature regime of 550–750 °C and 1.16 eV in the lower temperature regime of 450–550 °C. A similar kind of behaviour with two activation energies has been observed earlier in the case of hydrogen/helium implantation

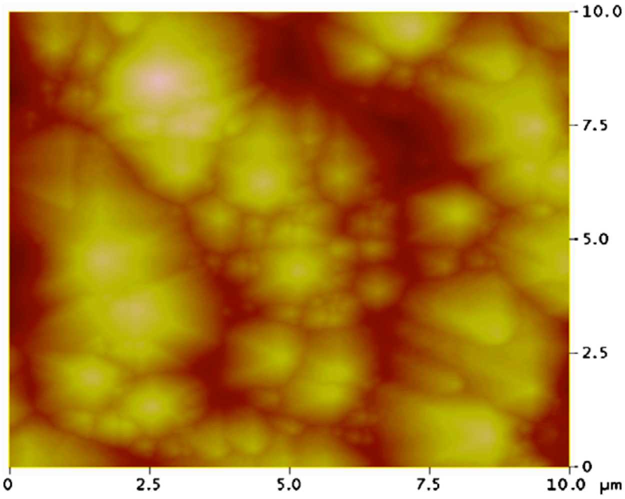

Figure 2. AFM image of the surface of a pristine AlN epitaxial layer. The RMS roughness of the surface is about 20 nm and the *Z* range is about 140 nm.

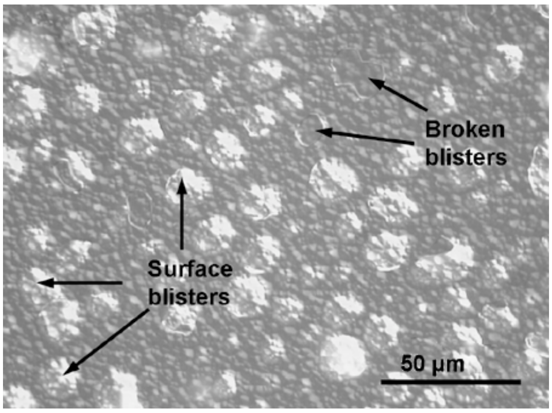

Figure 3. Nomarski optical image of the surface of an implanted and annealed AlN epitaxial layer. The implantation was performed with 100 keV H_2^+ ions with a dose of 1×10^{17} cm^{-2} and then the annealing was carried out at 500 °C for 1 h.

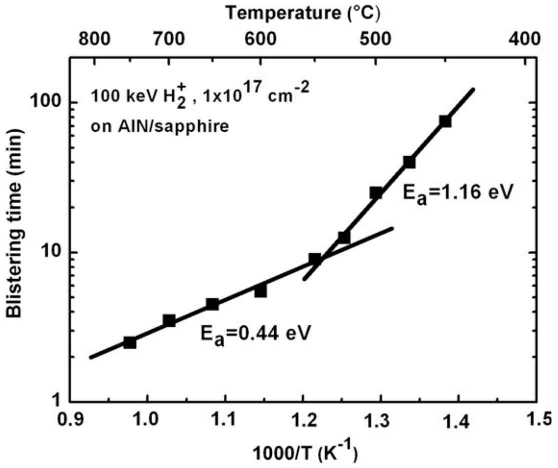

Figure 4. Arrhenius plot of the blistering time as a function of reciprocal temperature for AlN implanted by 100 keV H_2^+ ions with a dose of 1×10^{17} cm^{-2}.

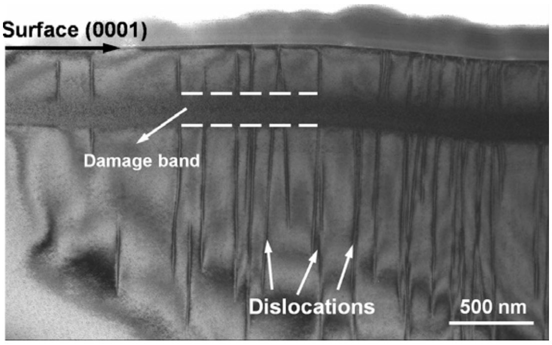

Figure 5. XTEM image of the as-implanted AlN with 100 keV H_2^+ ions with a dose of 1×10^{17} cm^{-2}. The linear defects running perpendicular to the surface are grown-in threading dislocations from the growth process having already been present before the hydrogen implantation.

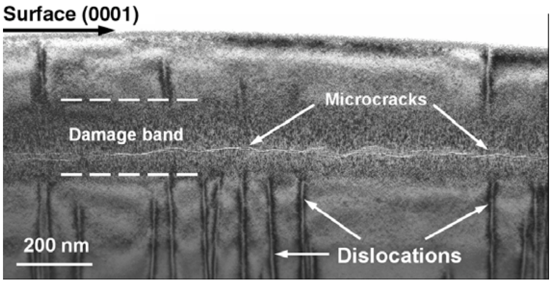

Figure 6. XTEM image of the AlN with 100 keV H_2^+ ions with a dose of 1×10^{17} cm^{-2} and annealed at 500 °C for 10 min.

of other semiconductors such as Si, SiGe, GaAs, InP and GaN [11–17]. As in other semiconductors, the lower activation energy appears to be correlated with the free atomic diffusion of hydrogen in the AlN lattice while the higher activation energy seems to be related to the diffusion of hydrogen limited by trapping–detrapping phenomena in the AlN [18].

A cross-sectional TEM image of the hydrogen as-implanted AlN sample is shown in figure 5. It shows a damage band consisting of defects such as clusters of vacancies and interstitials that are induced inside the AlN lattice due to the direct elastic collisions of the hydrogen ions with the AlN atoms. The linear defects running perpendicular to the surface are grown-in threading dislocations from the growth process having already been present before the hydrogen implantation. The damage band extends between 330 and 550 nm from the surface in the AlN sample. In comparison, the projected range and longitudinal straggling of 100 keV H_2^+ ions in AlN, as calculated using the Monte Carlo simulation program SRIM2006 [19], is 340 nm and 50 nm, respectively. Figure 6 shows the XTEM image of the hydrogen implanted and annealed AlN sample at 500 °C for 10 min (the blistering time at 500 °C is 12.5 min). A number of microcracks have formed inside the damage band and are mostly oriented parallel to the AlN(0 0 0 1) surface. These microcracks are ultimately responsible for the formation of surface blisters due to the hydrogen over-pressure inside the microcracks upon annealing at higher temperatures.

The minimum hydrogen dose required for the surface blistering in AlN is found out to be about 1.0×10^{17} H_2^+ cm^{-2}. In comparison to other semiconductors such as Si, Ge, InP, GaAs and SiC, this dose value is about three times higher [11–15]. For example, the minimum hydrogen dose required to observe surface blistering in Si, Ge or SiC is about 3×10^{16} H_2^+ cm^{-2} [11, 13, 14]. It is known from the literature that the group III nitrides such as AlN and GaN exhibit very efficient dynamic annealing of the implantation-induced defects [20–24]. In the process of blistering, the implanted hydrogen interacts with the implantation-induced damage inside the semiconductor lattice that ultimately leads to the formation of extended defects such as nanovoids/nanoplatelets [9, 10, 13, 25]. Upon thermal annealing of the hydrogen-implanted semiconductor, these nanovoids/nanoplatelets grow in size and agglomerate together due to the overpressure of hydrogen gas filled within them ultimately leading to the formation of large area microcracks. These microcracks subsequently lead to the formation of surface blisters upon annealing. Hence, a minimum amount of lattice damage is required in the semiconductor so that the hydrogen interaction process with the defects efficiently leads to the formation of nanovoids/nanoplatelets. Since in the nitride semiconductors, the dynamic annealing of the implantation-induced defects is very efficient, higher dose of hydrogen is required in comparison to other semiconductors to induce minimum damage inside the lattice. Similar to the case of AlN, GaN also exhibits an efficient dynamic annealing of the implantation-induced defects and hence the minimum hydrogen dose required for surface blistering in GaN is also quite high (~1.3×10^{17} H_2^+ cm^{-2}), as observed earlier by a few studies [16, 25, 26]. Thus, it is concluded that the III nitrides require higher values of minimum hydrogen dose in comparison to other semiconductors such as Si, Ge, GaAs, SiC and InP for the surface blistering to occur due to their higher radiation resistance.

Conclusions

AlN epitaxial layers were implanted with 100 keV H_2^+ ions at various doses and subsequently annealed at higher temperatures in order to observe the formation of surface blisters in AlN. The blistering time was determined at various temperatures between 450 and 750 °C for the AlN wafer implanted with a dose of 1.0×10^{17} cm^{-2}. The blistering kinetics studies revealed two different activation energies for the formation of surface blisters: 0.44 eV in the higher temperature regime of 550–750 °C and 1.16 eV in the lower temperature regime of 450–550 °C. The lower activation energy is related to the free atomic diffusion of hydrogen in AlN while the higher activation energy is related to the diffusion of hydrogen limited by the trapping–detrapping mechanism. The XTEM images of the implanted AlN layer showed that a damage band is formed in the AlN epilayer and after annealing at higher temperatures, large area microcracks are formed inside the damage band. These microcracks are ultimately responsible for the formation of surface blisters in the implanted AlN layers. It remains to be shown that, based on the results on hydrogen-implantation-induced blistering presented in this paper, thin layers of AlN can be transferred from free-standing AlN wafers to appropriate substrates by wafer bonding combined with hydrogen-implantation-induced layer splitting.

Acknowledgments

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