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Failure mechanism of AlN nanocaps used to protect rare earth-implanted GaN during high temperature annealing

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The structural properties of nanometric AlN caps, grown on GaN to prevent dissociation during high temperature annealing after Eu implantation, have been characterized by scanning electron microscopy and electron probe microanalysis. The caps provide good protection up to annealing temperatures of at least 1300 °C, but show localized failure in the form of irregularly shaped holes with a lateral size of 1–2 μm which extend through the cap into the GaN layer beneath. Compositional micrographs, obtained using wavelength dispersive x-ray analysis, suggest that these holes form when GaN dissociates and ejects through cracks already present in the as-grown AlN caps due to the large lattice mismatch between the two materials. Implantation damage enhances the formation of the holes during annealing. Simultaneous room temperature cathodoluminescence mapping showed that the Eu luminescence is reduced in N-poor regions. Hence, exposed GaN dissociates first by outdiffusion of nitrogen through AlN cracks, thereby opening a hole in the cap through which Ga subsequently evaporates. © *2006 American Institute of Physics*.
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The study of the optical emission properties of rare earth (RE) doped gallium nitride has attracted a great deal of interest due to the potential applications of such materials in optoelectronic devices.[1] The wide band gap of GaN ensures low thermal quenching of the RE emission, as shown by Favennec *et al.*[2]

Ion implantation and *in situ* doping during growth are the two methods mainly used to introduce REs into nitride hosts. The former shows several advantages over other doping methods but the damage introduced in the lattice during implantation poses a major problem. To remove it completely and fully activate the dopants, annealing temperatures as high as 1500 °C should be used, but, at temperatures higher than 1000 °C, unprotected GaN suffers dissociation. Zolper *et al.*[3,4] introduced the use of an AlN cap grown on GaN to allow higher annealing temperatures, up to 1400 °C, for optimal electrical activation of silicon implanted layers. This idea was later extended to Eu-implanted GaN by some of the present authors.[5,6]

When an AlN cap is grown prior to implantation it provides two benefits: first, it prevents the amorphization of the surface layer caused by implantation damage and, second, it allows annealing temperatures as high as 1300 °C, which substantially increases the intensity of RE-related luminescence. However, some localized failures of the AlN caps are observed; several groups have reported pitted surfaces in Si-implanted AlN capped GaN after annealing at temperatures higher than or equal to 1300 °C.[3,7–9] The structure of these pits and the mechanism that leads to their formation has not been fully explained. In this letter, we present the microscopic study of the failure mechanisms of such caps in relation to the protection that they provide during high temperature annealing of RE implanted GaN epilayers providing clear indications for producing caps with a higher resistance to degradation. Nondegraded caps would allow studies at higher annealing temperatures with no localized failures, important not only for rare earth implantation but also for implantations for electrical doping, fabrication of integrated circuits, and so on.

The epitaxial growth of molecular beam epitaxy (MBE)[10,11] and metal organic chemical vapor deposition (MOCVD)[12,13] AlN on GaN has been investigated in some detail recently. The lattice mismatch is 2.4%, resulting in a quite small critical thickness for plastic relaxation, around 1–3 nm, when AlN is grown on GaN.[11] AlN annealing caps tend to be somewhat thicker than this. AlN caps with thicknesses of tens of nanometers were grown by MOCVD on 2-μm-thick GaN-on-sapphire (0001) templates. Three AlN-on-GaN hosts were used for implantation and annealing, referred to by substrate numbers 326, 474, and 475 hereafter.

Wavelength dispersive x-ray analysis (WDX) profiling can be used to estimate the cap thickness of each sample.[14] Figure 1 plots the ratio of the Al K_α x-ray intensity to that measured for a pure Al standard for beam energies from 5 to 15 keV, together with line fits generated by Monte Carlo simulations for different AlN thicknesses. From the fits, cap thicknesses of 9, 11, and 25 nm are inferred for 326, 474, and 475, respectively.

The implantation of Eu ions was carried out at an energy of 300 keV to a dose of 1×10^{15} cm^{-2} through the AlN caps, as detailed elsewhere.[5] Annealing was performed at 1200 and 1300 °C in a conventional tube furnace under a moderate overpressure of 4 bar of N_2.

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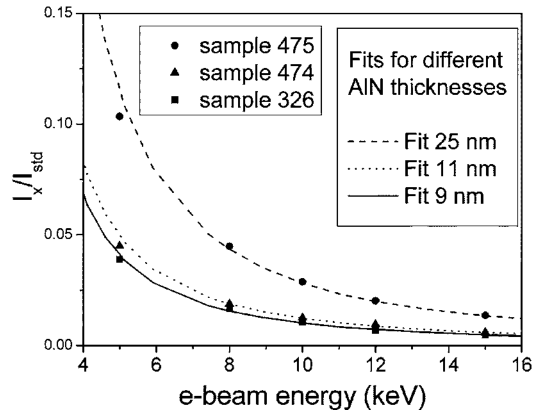

FIG. 1. Dependence of the ratio of the Al K_α x-ray intensity measured from the samples to that of a pure Al standard on the electron beam energy for samples 475 (circle), 474 (triangle), and 326 (square), and the corresponding Monte Carlo fits for thicknesses of 25 nm (dashed line), 11 nm (dotted line), and 9 nm (solid line).

The microstructural characterization was done with a field emission gun scanning electron microscope (FEGSEM) and a modified Cameca SX100 electron probe microanalyzer. With some modifications introduced to the latter, room temperature cathodoluminescence (CL) spectroscopy can be performed simultaneously with WDX and energy dispersive x-ray microanalysis.[15] Using a cooled charge coupled device, CL spectra are acquired at each pixel of the SEM image and maps of the integrated intensity of different emission peaks obtained.

Figures 2(a)–2(c) show FEGSEM secondary electrons micrographs of the surfaces of samples 326, 474, and 475, respectively, before implantation. Differences between the samples can be clearly observed. Samples 326 and 474 (respectively, 9 and 11 nm thick) show much lower crack densities than 475 (25 nm thick). The three AlN caps are all well in excess of the critical thickness for plastic relaxation and the features observed are typical for such structures.[10,12,13]

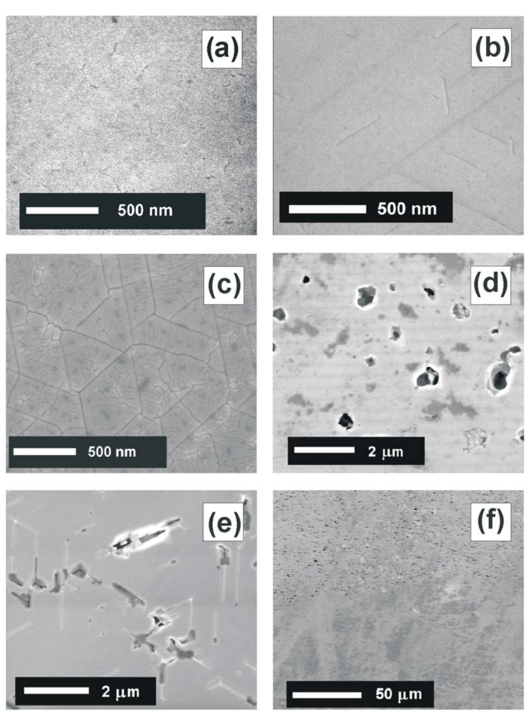

FIG. 2. SEM images of the surface of samples (a) 326, (b) 474, (c) 475, (d) 326ia, Eu implanted, and annealed at 1300 °C, (e) 474ia, Eu implanted, and annealed at 1200 °C and (f) 326ia at the border of implanted (upper half) and unimplanted (lower half) regions.

Figures 2(d) and 2(e) show the secondary electron FEGSEM images of the two thinner samples after implantation and annealing at 1300 °C [sample 326ia, Fig. 2(d)] and 1200 °C [sample 474ia, Fig. 2(e)]. Both samples show holes in the surface whose structure and origin will be discussed later. The more resistant sample is 326, the thinner one with smaller initial cracks [Fig. 2(a)], which withstands annealing temperatures of 1300 °C with only localized damage. Sample 475 is the least robust of the three, in spite of being thickest, due to the presence of large cracks. Large scale deterioration occurs at 1200 °C in this sample (image not shown); at 1300 °C it is completely destroyed.

The influence of the implantation damage on the formation of surface holes has also been studied. Before annealing, no differences were found in the topographic images of as-implanted and unimplanted samples. Figure 2(f) shows the annealed sample 326ia in an area with two well differentiated regions: the upper one has been implanted while the lower one has not. A much higher surface density of holes is found in the implanted region, which suggests that implantation damage leads to increased sample deterioration during annealing. Similar results were found for samples 474 and 475. However, some holes are also found in the unimplanted regions of these samples, which have their origin in the larger cracks present before implantation.

Annealing of AlN-capped GaN produces pitted surfaces when temperatures above 1300 °C are used; this is not an unexpected result. However, no systematic description of the pitting has been given. The AlN caps used in previous studies, deposited by sputtering[3,4,9] or MBE (Refs. 7–9), had thicknesses of 50 or 120 nm, much larger than those used in our study. Cao *et al.*[9] discussed the possible influence of residual H_2 bubbles in the AlN layer as a source of occasional localized cap fractures. Zolper *et al.*[4] suggested that the AlN cap on Si-implanted GaN might fail due to poorly defined stoichiometry, or the evolution of hydrogen from the GaN that could break the AlN during escape. None of these explanations pertains to our materials. We now describe a study of the microcomposition of the damaged caps, in particular in the vicinity of the holes appearing in them, in the hope of discovering clues to the nature and origin of the damage.

Figure 3 shows a backscattered electrons (BSE) image and two compositional maps acquired with WDX (Ga L_α and N K_α) signals from sample 474ia. In areas where no cracks are present, the AlN provides good protection. No loss of N or Ga is evident. In the vicinity of damaged regions, however, the composition map shows that N is lost all along the cracks, while Al and Ga are deficient only when holes are formed. A similar result was obtained for sample 326ia. Thus, the dissociation mechanism has a first step, in which N outdiffuses through cracks, and a second one, where a breach is created in the AlN cap, by attrition of Al, through which the Ga from the underlayer is also lost. It is in fact well known that there is preferential N_2 loss[16] during GaN dissociation at temperatures higher than 1000 °C, which agrees with our results where nitrogen is lost preferentially through cracks.

The composition of the material that remains around the cracks and the holes formed during the annealing influences

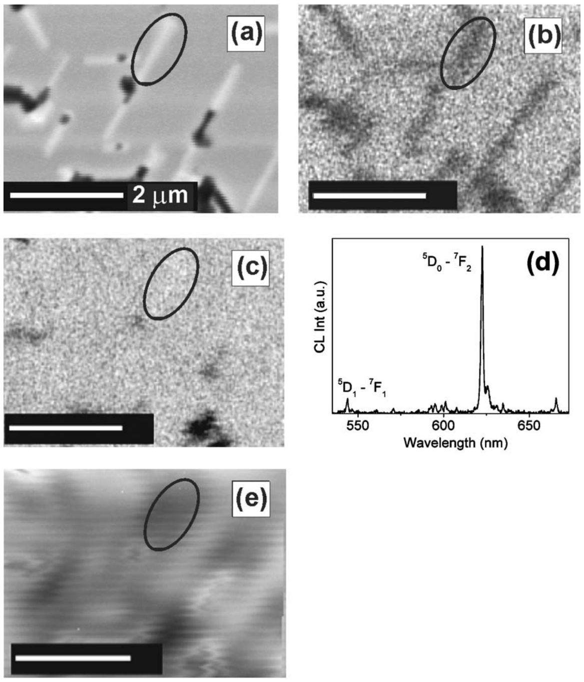

FIG. 3. (a) BSE image of sample 474ia, implanted with Eu and annealed at 1200 °C, and corresponding compositional mappings obtained with WDX of (b) N and (c) Ga signals. (d) Spectrum obtained in this area showing the typical sharp emissions related to Eu^{3+} intra $4f$ electronic transitions. (e) CL mapping of the integrated intensity from the transition $^5D_0-^7F_2$ corresponding to the same area (dark, 1500 counts, bright, 5500 counts). The ellipse shows a N-poor area which is associated with a decreased emission efficiency.

the Eu luminescence. Figure 3(d) shows CL emission from the area shown in Fig. 3(a). The CL map of the intensity of the emission line related to the $^5D_0—^7F_2$ Eu^{3+} intraionic transition in the same area is shown in Fig. 3(e). It is clear that the emission intensity is reduced in the regions where nitrogen is severely deficient, below the AlN cracks. It has to be mentioned that the Eu signal (map not shown in Fig. 3) is not reduced in the N poor areas around the cracks but only where holes are formed. Thus, the decrease in the CL intensity is related not to Eu loss but to N deficiency. Somewhat surprisingly, an increase of CL intensity is sometimes observed around the holes. A possible influence on the emission properties of a different composition or structure of the material in these regions requires further investigation.

In the light of the present results, we may suggest ways to reduce the degradation of samples which is observed during high temperature annealing. Surface damage can be avoided to some extent by using a proximity cap during annealing, as discussed by Fellows *et al.*[7] In Fig. 4 we compare the surfaces of one piece of sample 474ia with another treated in the same way but with an AlN proximity cap in position during annealing. Although cracks are observed in the surface, no holes are formed in this sample. At higher temperatures, however, this method does not completely avoid the formation of holes in our samples, although their number is greatly reduced. Second, we may seek to improve the robustness of the as-grown cap. Preliminary results indicate that an AlN/GaN multilayer grown on GaN with each layer below the critical thickness is almost completely crack-free and should withstand high annealing temperatures without any local failures.

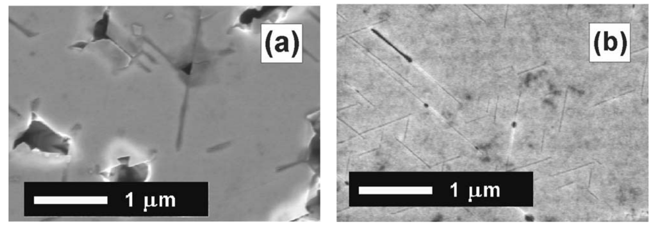

FIG. 4. SEM images from (a) sample 474ia and (b) a sample treated in the same conditions but with an AlN proximity cap during the annealing. A strong improvement of the surface has been obtained in the latter, which does not show almost any holes formation.

In summary, we have presented a microscopic study of MOCVD AlN caps grown on GaN for implantation of Eu and subsequent annealing at high temperatures. It has been found that the most critical factor leading to local dissociation of material is the presence of extended defects, mainly cracks, in the AlN cap. These allow local dissociation of GaN, which produces micron-sized holes. The two steps leading to the formation of the holes have been elucidated and found to be in agreement with previous studies of GaN dissociation. Spatially resolved room temperature CL spectra have been studied and correlated with WDX results, showing that the intensity of the Eu^{3+} related emission decreases in the surroundings of the cracks, where the N content decreases.

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