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HIGH TEMPERATURE SURFACE DEGRADATION OF III-V NITRIDES

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ABSRACT

The surface stoichiometry, surface morphology and electrical conductivity of AlN, GaN, InN, InGaN and InAlN was examined at rapid thermal annealing temperatures up to 1150 °C. The sheet resistance of the AlN dropped steadily with annealing, but the surface showed signs of roughening only above 1000 °C. Auger Electron Spectroscopy (AES) analysis showed little change in the surface stoichiometry even at 1150 °C. GaN root mean square (RMS) surface roughness showed an overall improvement with annealing, but the surface became pitted at 1000 °C, at which point the sheet resistance also dropped by several orders of magnitude. and AES confirmed a loss of N from the surface. The InN surface had roughened considerably even at 650 °C, and scanning electron microscopy (SEM) showed significant degradation. In contrast to the binary nitrides the sheet resistance of InAlN was found to increase by ~ 10^2 from the as grown value after annealing at 800 °C and then remain constant up to 1000 °C, while that of InGaN increased rapidly above 700 °C. The RMS roughness increased above 800 °C and 700 °C respectively for InAlN and InGaN samples. In droplets began to form on the surface at 900 °C for InAlN and at 800 °C for InGaN, and then evaporate at 1000 °C leaving pits. AES analysis showed a decrease in the N concentration in the top 500 Å of the sample for annealing ≥800 °C in both materials.

INTRODUCTION

Much progress has recently been made in the areas of growth, dry etching and implant isolation and doping of the III-V nitrides and their ternary alloys. This has resulted in nitride-based blue/UV light emitting and electronic devices.[1-3]. High temperature annealing is necessary in many of the processing steps for these devices, including activation of implanted ions,[4] maximization of implant isolated regions[5,6] or high temperature alloying of metal contacts.[7] A key issue is the question of surface degradation of the III-V nitrides during these high temperature anneals.[8]

In all of this previous work the equilibrium N_2 pressures above the solid (or solid plus liquid) have been the focus. In many process steps rapid thermal annealing (RTA) using the proximity geometry is employed, and this is a non-equilibrium situation. Zolper et. al.[9] observed that the luminescence and surface morphologies of GaN annealed in flowing N_2 actually improved for RTA temperatures up to 1100 °C. Similar results were obtained at lower temperatures by Lin et. al.[10]

In this paper we report on an investigation of the thermal stability of AlN, GaN, InN, InAlN and InGaN during rapid thermal annealing. the electrical conductivity, surface morphology and surface stoichiometry have all been measured as a function of annealing temperature. The In-containing materials are found to be substantially less

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thermally stable than either GaN or AlN, and loss of nitrogen creates a thin n-type surface layer in all three binary nitrides.

EXPERIMENTAL

The GaN, AlN, InN, InGaN and InAlN samples were grown using Metal Organic Molecular Beam Epitaxy (MO-MBE) on semi-insulating, (100) GaAs substrates or Al_2O_3 c-plane substrates in an Intevac Gen II system as described previously.[11] The group-III sources were triethylgallium, trimethylamine alane and trimethylindium, respectively, and the atomic nitrogen was derived from an ECR Wavemat source operating at 200 W forward power. The layers were single crystal with a high density (10^{11} - 10^{12} cm^{-2}) of stacking faults and microtwins. The GaN and AlN were resistive as-grown, and the InN was highly autodoped n-type (>10^{20} cm^{-3}) due to the presence of native defects. InAlN and InGaN were found to contain both hexagonal and cubic forms. The $In_{0.75}Al_{0.25}N$ and $In_{0.5}Ga_{0.5}N$ were conducting n-type as grown (~ 10^{19} cm^{-3}) due to residual autodoping by native defects. The samples were annealed in a rapid thermal anneal (RTA) system (AG 410T) face down on a GaAs substrate for 10 s at temperatures between 650 - 1150 °C in a N_2 atmosphere.

RESULTS AND DISCUSSION

The sheet resistance normalized to the as grown value for all of the nitride samples is shown in Fig. 1 as a function of annealing temperature. The values for the GaN, AlN and InN are found to drop by approximately three orders of magnitude with annealing, up to 900 °C. The material becomes strongly n-type in all cases, even in the GaN and AlN which were resistive as grown. The sheet resistance for AlN continues drop steadily with anneal temperature until 1100 °C. AlN shows only a small loss of N from the surface as determined by AES. However the electrical measurements are more sensitive to small changes in the composition than the Auger. Here we believe the N vacancies created by the loss of N from the surface are creating shallow donors. This agrees with the theoretical prediction of Maruska and Tietjen.[12] The actual values of sheet resistance for AlN are much higher than the GaN up to 900 °C, and significantly higher than InN at all temperatures. The data in Figure 1 is in agreement with the melting point and vapor pressure curves for these materials. AlN is predicted to be stable under N_2 gas up to ~2500 °C,[8] and to melt at ~ 3700 °C at atmospheric pressure[8]. GaN is predicted to melt at ~3000 °C and InN at only ~2400 °C[8] and to degrade at 600 °C AES has confirmed loss of N from the annealed GaN sample which would suggest that N vacancies are contributing to the conductivity. At 1150 °C the sheet resistance for the GaN drops sharply indicating that N is being lost at a much greater rate than the Ga. Groh et. al.[13] showed loss of nitrogen beginning at 710 °C in vacuum annealed GaN, with significant loss at ≥ 980 °C. The sheet resistance for the InN drops steadily over the temperature range, which correlates to the problems of nonstochiometry in InN. The large size difference between the N and In make the material less stable.

The sheet resistance for InGaN and InAlN on the other hand, increases with annealing. The InAlN sheet resistance increases by 10^2 from the value for the as grown material when annealed at 800 °C. Its resistance then remains constant to 900 °C, and then decreases slightly at 1000 °C. For InGaN the sheet resistance remains constant up to

700 °C and then increases rapidly with increasing temperature. This suggests that simple N vacancies are not the cause of the residual n-type conductivity in these samples since at the highest temperatures we are losing N from the surface, as described below. However these samples become less conducting, suggesting creation of compensating acceptors or annealing of the native donors is occurring.

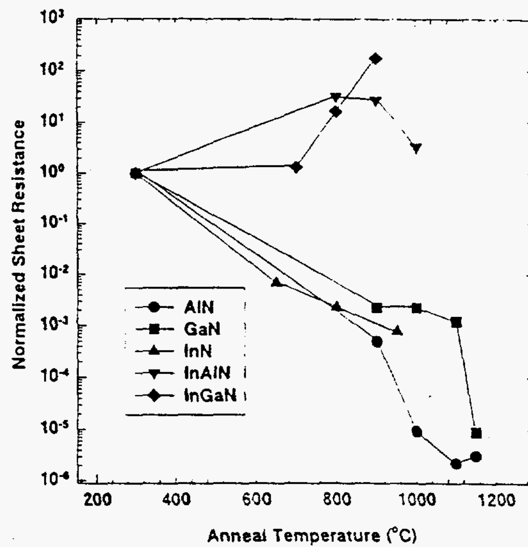

Figure 1. Sheet resistance normalized to the as grown value for AlN, GaN, InN, InAlN and InGaN as a function of annealing temperature.

The RMS data normalized to the as grown roughness as a function of anneal temperature is shown in Fig. 2 for AlN, GaN and InN. The AlN is still smooth at 900 °C, but becomes quite rough at 1000°C. Further surface reconstruction continues at higher annealing temperatures. At 1150 °C the sample becomes smooth again- in fact slightly smoother than the as grown sample. GaN shows no roughening, becoming smoother with annealing due to defect annealing and surface reconstruction. InN on the other hand is a factor of two rougher than for as grown samples at 650 °C, indicating the weaker bond strength of this material.

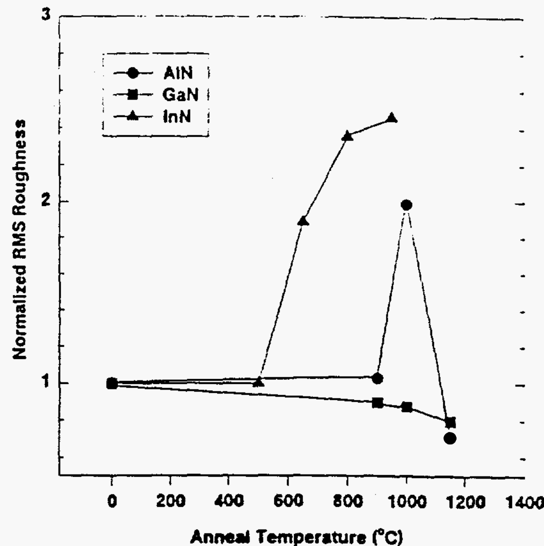

Figure 2. The RMS data normalized to the as grown roughness as a function of anneal temperature for AlN, GaN and InN.

In Fig. 3 the RMS roughness for InAlN and InGaN are shown as a function of rapid thermal anneal temperature. We see that the InAlN remained smooth until 800 °C, and at 900 °C has increased an order of magnitude in roughness. At 1000 °C the RMS roughness returns to a value close to that of the value for the as grown material. We found this to be a result of In droplets forming on the surface above 800 °C and then evaporating above 900 °C. The InGaN surface was unchanged at 700 °C, with the roughness increasing above that temperature. In Fig. 4 the individual AFM scans are shown for the ternaries. We see the surface of the samples becoming coarser above 800 °C, with large droplets forming. In the case of InAlN these droplets are removed by annealing at 1000 °C, where the surface evaporation is more congruent.

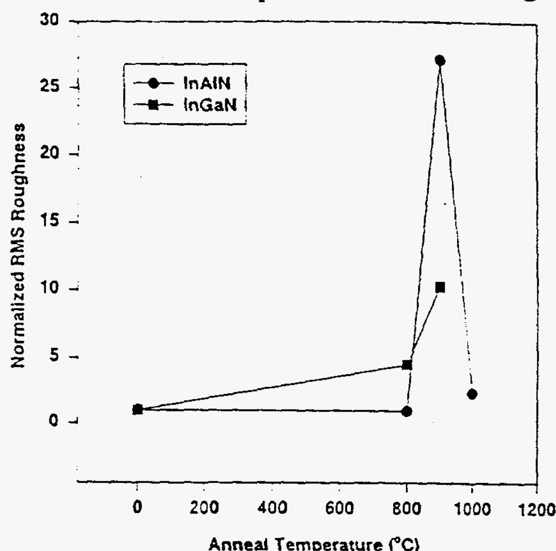

Figure 3. The RMS data normalized to the as grown roughness as a function of anneal temperature for InAlN and InGaN.

For GaN, the Ga/N ratio measured by raw AES counts increased from 1.73 on the as-grown samples to 2.34 after 1150 °C annealing, indicating that nitrogen was indeed lost from the surface. Similar results were obtained for for InAlN and InGaN (Fig.5) as grown and annealed at 1000 °C and 800 °C respectively. Both materials showed a definite decrease in the amount of N at the surface of the samples after anneal. In the case of InGaN there was also a reduction in In, which could be related to the changes in the electrical properties. The surfaces of all the samples show a loss of N, consistent with the SEM, AFM and EDAX results.

CONCLUSION

The III-V nitrides are thermally stable to relatively high temperatures. AlN and GaN remain smooth and stochiometric at 1000 °C, InAlN and InGaN up to 800 °C, and InN up to 600 °C. Above these temperature capping is necessary to prevent the loss of N and, sometimes, In. Consistent with the predicted melting temperatures and thermal stabilities of the nitrides, we found AlN to be somewhat more stable than GaN, and much more stable than InN. InAlN was found to be more stable than InGaN, as expected from a consideration of the binary component N_2 vapor pressures. AlN may prove to be a good capping material for the other nitrides, because of its high stability and the fact that it can be selectively removed by wet etching in KOH based solutions.

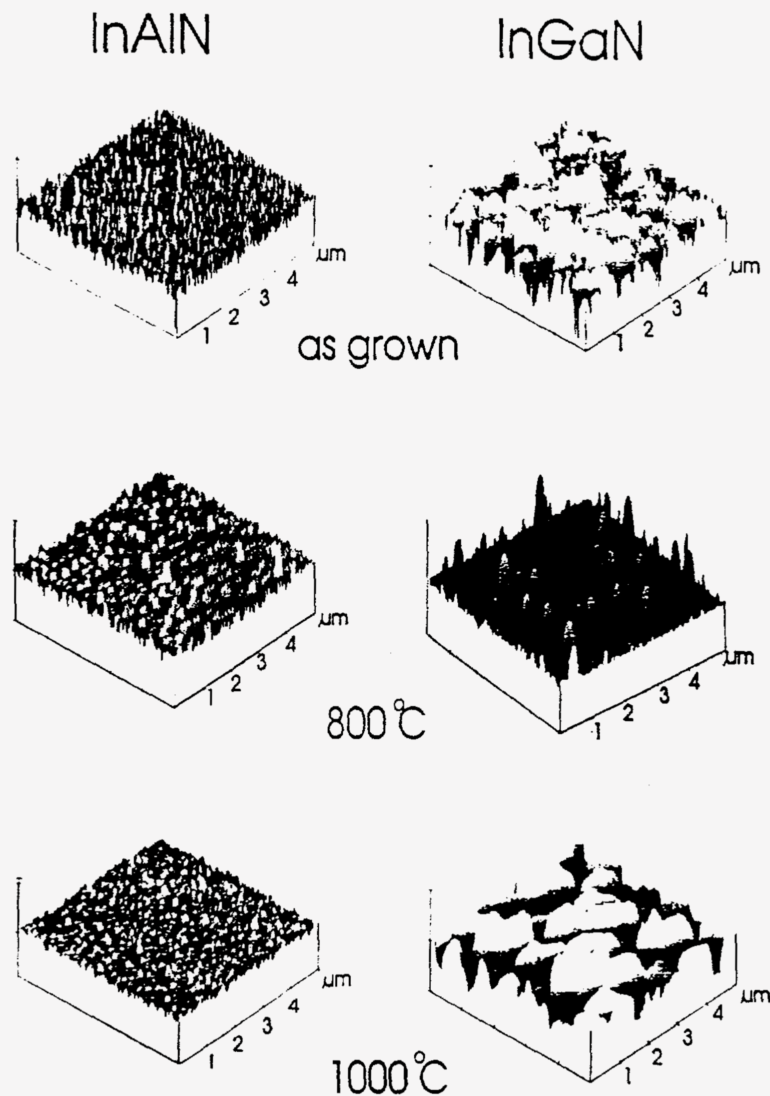

Figure 4. Individual AFM scans of InAlN and InGaN. Vertical scale is 100 nm per division.

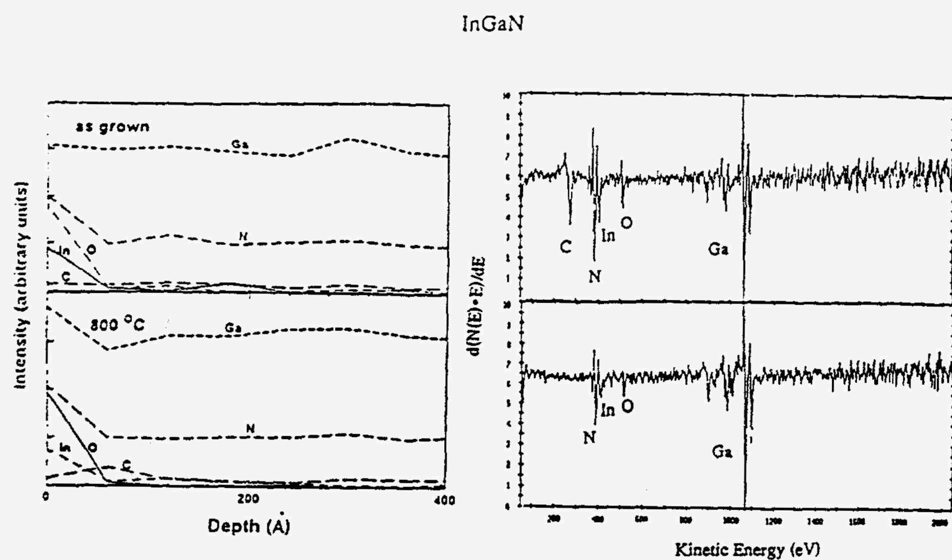

Figure 5. AES surface scans and depth profiles for InGaN as grown and annealed at 800 °C.

ACKNOWLEDGMENTS

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