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High Resistivity $Al_xGa_{1-x}N$ Layers Grown by MOCVD

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Abstract

Undoped $Al_xGa_{1-x}N$ layers with good surface morphology and very low electron concentration have been grown by MOCVD on sapphire substrates. The observed electrical and optical properties depend strongly on the growth temperature. Layers grown at 1000 °C exhibited low resistivity and strong optical absorption below the bandgap. In contrast,layers grown at 1050 °C had low carrier concentrations and good mobilities. Virtually no optical absorption near the band edge was observed as opposed to the usual situation in $Al_xGa_{1-x}N$. The electrical properties of these layers can be explained by the presence of donor centers whose energy increases with composition, and deeper lying compensating defects. The interaction of these centers renders the samples with x<0.2 highly resistive, with room temperature resistivity higher than 10^6 ohm-cm. SIMS data strongly suggest that the electrically active centers in our AlGaN layers are native defect-related. Implantation of Si ions into $Al_{0.12}Ga_{0.88}N$, and subsequent annealing at 1140 °C resulted in layers with electron concentration of 4.6 x 10^{17} cm^{-3}.

1. Introduction

Due to the large number of potential applications in optoelectronics and high-temperature electronics, considerable research has been directed at the growth and characterization of GaN epitaxial layers. The related materials $Al_xGa_{1-x}N$ and $In_xGa1_{-x}N$ necessary for heterojunction devices have also been studied, although less intensively. In this paper, we report our recent work on the growth of $Al_xGa_{1-x}N$ by reduced-pressure MOCVD. We also present initial results on doping of this material by ion implantation.

2. Growth of undoped AlGaN

Epitaxial layers of $Al_xGa_{1-x}N$ were deposited by MOCVD on basal plane sapphire substrates using trimethylgallium (TMG), trimethylaluminum (TMA) and ammonia precursors. Growth was performed in a horizontal two-inlet reactor at 76 torr with hydrogen carrier gas. Substrates were prepared by degreasing in organic solvents, followed by an etch in hot H_2SO_4:H_3PO_4. The substrates were annealed in hydrogen at 1100 °C for 10 minutes followed by 3 minutes in ammonia; 700Å thick AlN buffer layers were then deposited at 500°C, after which the temperature was ramped to the growth temperature of1000 or 1050 °C. Growth was initated after a 1 minute anneal in ammonia. Type A samples were grown at 1000 °C with a growth rate of approximately 1 µm/hr, and type B samples were grown at 1050

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°C with a growth rate of approximately 0.7 μm/hr. All layers studied were approximately 1 μm in thickness.

Composition of the resulting layers was determined from X-ray diffraction measurements of the c lattice parameter. Electron concentrations and mobilities were determined from Hall effect measurements between room temperature and 140 °C, using the van der Pauw technique. Optical transmission spectra were measured at room temperature and reduced to determine the absorption coefficient α. SIMS measurements were performed in order to determine the concentrations of impurities (C, Si, H, O, S, and Se).

Figure 1 shows the measured (300 K) electron concentration and Hall mobility as a function of aluminum fraction x. For both A and B series, similar results were obtained for GaN, with electron concentrations near 10^{15} cm^{-3}. The measured mobilities were reasonable (≈500cm^2/Vsec) although not as high as reported by some workers [1] [2]. For x>0, very different results were obtained for these two series. The A series showed electron concentrations of order 10^{18} cm^{-3} for most of the composition range, with the electron concentrations decreasing for x>0.5. Similar behavior has been reported in $Al_xGa_{1-x}N$ by a number of researchers [3] [4] . The mobilities in this series were quite low (≈10 cm^2/Vsec). In contrast, the B series exhibited much lower electron concentrations- indeed, at x=0.05-0.08 the electron concentration was not measurable in our apparatus. The electron concentration reached a peak value of near 10^{15} cm^{-3} before declining for x>0.3. Mobilities in this series of samples are much higher (200-500cm^2/Vsec).

We will now discuss possible interpretations for these results in terms of unintentional impurities and native defects. We first consider the possibility that the poor characteristics of the A series can be explained by higher impurity concentrations. The most likely donor and acceptor contaminants in MOCVD are Si, C, and O. The concentrations of these impurities measured by SIMS are presented in Table 1. Carbon is likely to be the major acceptor impurity as our system has never been used to grow p-type material; and silicon and oxygen the dominant donor impurities. The results in Table 1 show a higher concentration of carbon acceptors in the A series, inconsistent with the observed higher electron concentrations. Similarly, the silicon concentrations appear to be approximately the same (except forAlN samples), and the oxygen contamination is greater in the B series. While the measured impurity concentrations are high enough to account for the high electron concentration in the A series, the results of the B series can only be explained if there is an extremely large change in impurity activation for a small change in growth conditions. Thus it does not appear likely that the observed differences are due to contamination.

It is more likely that the explanation involves different concentrations of native defects. In order to explore this possibility, temperature-dependent Hall effect measurements were used to extract the activation energies for the electron concentration. Assuming that the Fermi level is pinned by a trap level, the activation energy provides an indication of the location of the trap level. The results of this analysis are presented in Figure 2, where energies are measured with respect to the top of the valence band. For the type A samples, the activation energies are quite low until x>0.5, when the pinning trap level drops into the energy gap. In type B samples, the activation energy is quite high for the x=0.12 sample. This has been observed repeatedly in a number of samples grown with this composition, and is consistent with the semi-insulating behavior observed in resistivity measurements. For higher x, the pinning trap level is quite close to the conduction band until x=0.3, and then falls into the energy gap for higher x.

The behavior of both type A and B samples can be quite nicely explained by invoking the calculated energy levels of the nitrogen vacancy by Jenkins et al. [5] if we suppose that the concentration of compensating acceptors is smaller in the type B samples [6] . In such a situation, the Fermi level would be pinned by the nitrogen vacancy T2 (single donor) state in type A samples and by the A1 (double donor) state in type B samples. However, a very different value for the A1 energy level is obtained in more sophisticated calculations [7] , and it therefore appears unlikely that this simple explanation is correct.

The behavior of the type B samples can be reasonably well explained using the position of the T2 state from the more complete calculations of Neugebauer and Van de Walle [7] . Taking into account relaxation in the neighborhood of the nitrogen vacancy, the T2 state in GaN is calculated to lie at E_C+0.8 eV [7] . If we suppose that the T2 state is pinned to the vacuum level, then the T2 state would emerge into the gap at approximately x=0.5, in fair agreement with measurements on the B series. Some experimental evidence for the dependence of the T2 level on composition can be obtained from studies of the pressure dependence of donor levels in GaN [8] [9] . It was found that pressures sufficient to increase the bandgap of GaN to 3.7-4.2 eV (corresponding to x=0.1-0.3) cause the donor state to emerge into the energy gap. For a further increase in pressure, the donor level was observed to remain unchanged with respect to the valence band, which is qualitatively consistent with the B series data. Such a picture also helps to explain the composition dependence of photoluminescence measurements [10] . It needs to be noted, however, that a rather high formation energy of the nitrogen vacancy has been calculated [7] and so for growth under equilibrium conditions the density of these defects would be quite small. But MOCVD growth takes

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place away from equilibrium conditions. If a significant density of nitrogen vacancies are generated during growth, we would then suppose that the Fermi level is pinned by different defects in the A series. These defects could be vacancy-impurity complexes.

In any case, optical transmission measurements provide additional evidence that the deep acceptor concentration is higher in the type A samples. Figure 3 shows the square of the absorption coefficient α for type A and B samples. Type A samples exhibit a more pronounced band edge absorption tail, consistent with a higher density of deep defects.

3. Ion implantation doping of AlGaN

Ion implantation is an essential process step in the fabrication of many semiconductor devices. Although the use of Be and N implantation to compensate n-type conductivity in AlGaN has been reported [11] , there appear to be no reports of the successful activation of implanted shallow dopants in AlGaN. In this section, we report initial results on the ion implantation doping of AlGaN.

Experiments were performed on 1 μm thick $Al_{0.12}Ga_{0.88}N$ layers grown under the same conditions as the type B layers discussed above. As noted above, the carrier concentrations obtained under these growth conditions are low ($\approx 10^{11}$ cm^{-3}), facilitating studies of implantation doping. Si, Mg,and C were implanted to a dose of 5×10^{14} cm^{-2}, with energies of 110, 100, and 50 keV, respectively. In the case of Mg, P was co-implanted at an energy of 130 keV and dose of 5 x 10^{14} cm^{-2}, following a procedure used in GaN [12].

A 1 s rapid-thermal activation anneal was performed at 1150 °C in nitrogen. Then samples were annealed for 1 hr in ammonia face-to-face with an unimplanted sample, followed by a treatment at 800 °C for 0.5 hr in nitrogen to remove any possible hydrogen passivation associated with the ammonia. Ammonia anneals were performed at 1050, 1100, and 1140 °C and Hall effect measurements of carrier concentration and mobility were obtained after each anneal. Depth profiles were measured by SIMS after implantation and after the final 1140 °C anneal.

Redistribution of implanted impurities is undetectable except in the case of Mg, where the profile is only slightly broadened. The minimal redistribution observed is consistent with earlier results on GaN [13] . The measured SIMS profiles for Si are illustrated in Figure 4.

The resistivities of all as-implanted layers were very high, estimated to be of the order of 10^{12} Ω/square. For C and Mg there was no evidence of dopant activation, with the resistivity even increasing after the highest temperature anneal at 1140 °C. In the Si implanted sample, there was no change in resistivity after the 1050 °C anneal, while the 1100 C anneal returned the resistivity to approximately its pre-implantation value (n=9×10^{10} cm^{-3}, μ_n=250cm ^{2}/Vsec). The sample became highly conducting after the 1140°C anneal. Assuming the width of the implanted region was 0.2 μm, the average electron concentration was 5 x 10^{17} cm^{-3} and the mobility n$\approx$24 cm^2/Vsec. Measurement of the temperature dependence of the electron concentration yielded an activation energy of 0.04 eV, in good agreement with that expected for Si donors in $Al_{0.12}Ga_{0.88}N$ [14].

The increased electron concentration could be attributed to the creation of nitrogen vacancies during the high-temperature annealing. However, an unimplanted $Al_{0.12}Ga_{0.88}N$ sample subjected to the same annealing treatment showed no change in carrier concentration or mobility. So the decreased conductivity can be attributed to activation of the implanted silicon, although the doping efficiency is low (less than 10% of the implanted silicon is activated). Possibly nitrogen vacancies are created during implantation and the Si subsequently is redistributed between the III and V sublattices, leading to self-compensation. The low mobility observed suggests that appreciable implantation damage remains even after the 1140 °C anneal.

4. Summary

We have reported the growth of undoped GaN and AlGaN epitaxial layers on sapphire by MOCVD. In contrast with much previous work, high resistivity AlGaN was obtained for growth at 1050 °C. Good mobilities (200-500cm^2/Vsec) were also observed for growth at 1050 °C. The energy of the pinning trap level was extracted as a function of composition, and can be explained by the expected composition dependence of the T2 nitrogen vacancy (single donor) trap level.

High resistivity samples with x=0.12 were used to explore doping by ion implantation. Carbon and magnesium

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could not be activated at anneal temperatures below 1140 °C. In contrast, some activation (≈10%) of silicon donors was observed after annealing at this temperature. The low activation together with the low mobility suggests that significant implant damage remains.

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Table 1

Concentration of some impurities [cm^{-3}] in GaN, $Al_{0.12}Ga_{0.88}N$, andAlN grown at 1000 °C and 1050°C.

impurity	GaN 1000 °C	GaN 1050 °C	AlGaN 1000 °C	AlGaN 1050 °C	AlN 1000 °C	AlN 1050 °C
C	2.5×10^{18}	1.5×10^{18}	5×10^{18}	1.5×10^{18}	$2\text{-}3\times10^{19}$	1.5×10^{18}
O	6×10^{17}	5×10^{17}	1×10^{19}	3×10^{19}	$2\text{-}3\times10^{20}$	3×10^{19}
Si	2×10^{18}	2×10^{18}	2×10^{18}	2×10^{18}	1×10^{19}	2×10^{18}

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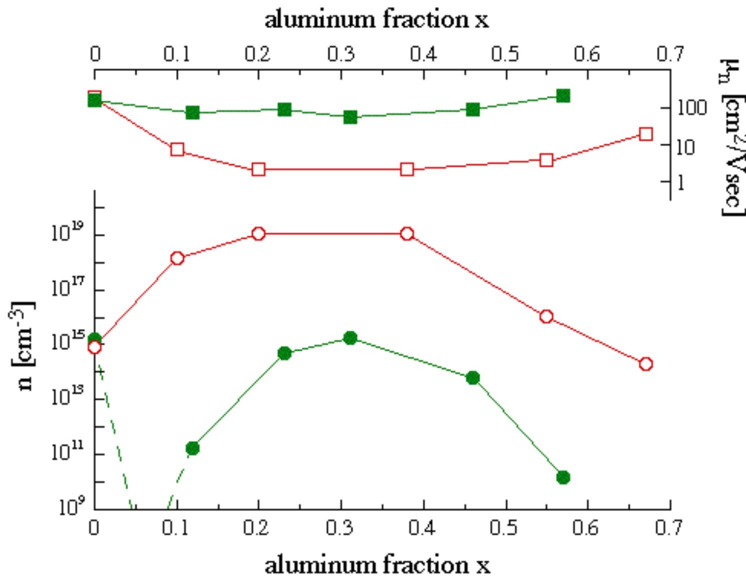

Figure 1. Hall mobility (top) and electron concentration (bottom) as a function of aluminum fraction x for samples of the A (open points) and B(solid points) series.

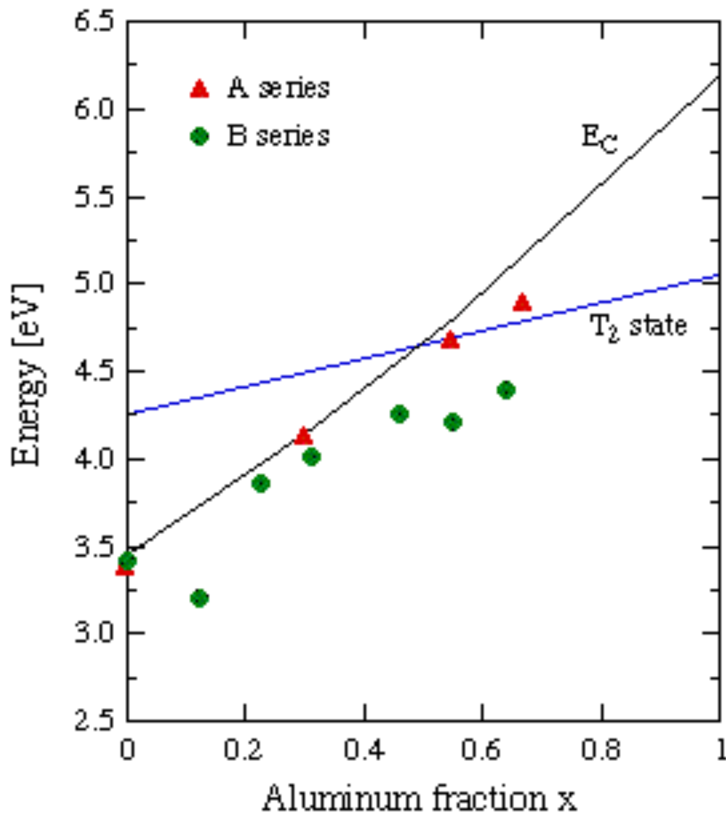

Figure 2. Measured pinning trap level for type A (triangles) and B(circles) samples. The reference level is the valence band. Also shown are the conduction band edge and the extrapolated position of the T2 level assuming it is pinned to the vacuum level.

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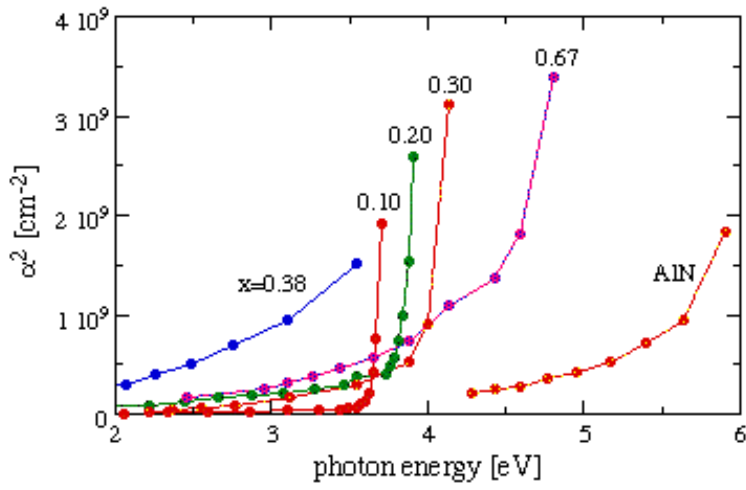
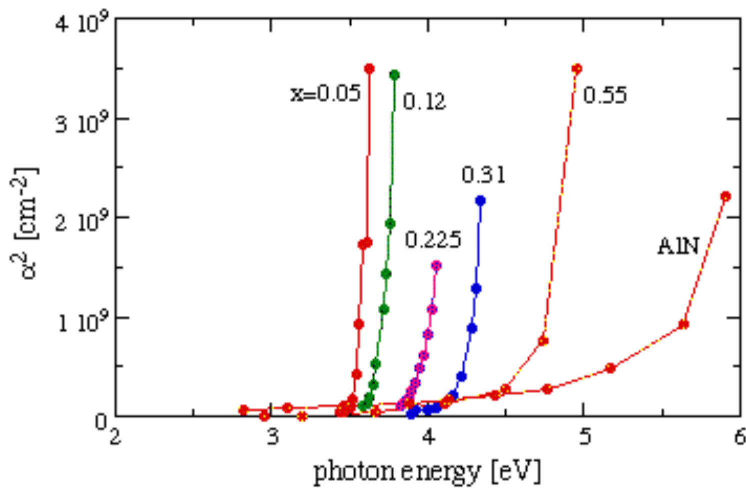


Figure 3. Squared absorption coefficient (α^2) as a function of photon energy for various samples of series A (top) and B(bottom).



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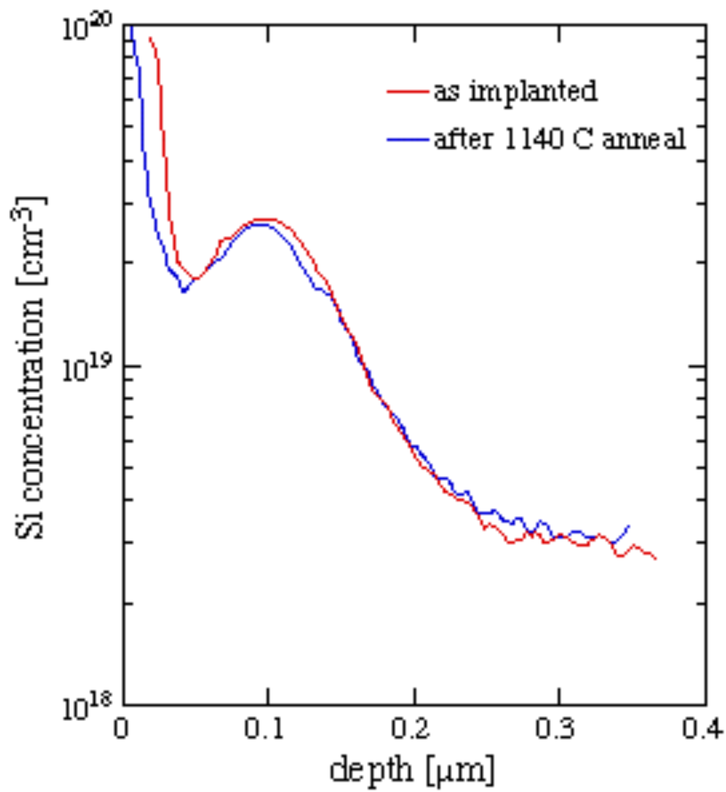

Figure 4. SIMS profiles of Si in as-implanted $Al_{0.12}Ga_{0.88}N$ and after annealing at 1140 °C.

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