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Short communication

Gallium and oxygen accumulations on gallium nitride surfaces following argon ion milling in ultra-high vacuum conditions

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Abstract

Metallic gallium was observed on the surfaces of GaN commercial samples following argon ion milling. SIMS measurements confirmed that the commercial GaN had approximately 0.02% bulk oxygen present. The SIMS signal was standardized using a specimen of known oxygen content, as determined by elastic recoil detection analysis using 200 MeV heavy ions of ^{197}Au. Despite this 2–5% oxygen was observed by XPS in the bulk of the GaN after the argon ion milling. This oxygen is believed to be from the original surface oxide that re-cycles on the GaN surface during the ion milling.
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1. Introduction

Gallium nitride is an important material for the production of optoelectronic devices and high power transistors [1]. There now seems to be some consensus that oxygen in bulk gallium nitride may act as a shallow dopant [1], or, for gallium-rich material, it can be active in the formation of neutral complexes [2]. In contrast, the influence of the surface oxide on device operation is not understood. The beta form of gallium oxide—the most usual form of the oxide—is itself a wide band-gap (~4.8 eV) n-type semiconductor. The presence of this oxide at surfaces or interfaces following device processing may therefore have a strong influence on the operation of devices.

Using X-ray photoelectron spectroscopy (XPS) depth profiling and angle resolved XPS, we report on the observation of oxygen on the surface of commercial gallium nitride samples after argon ion milling in an ultra-high vacuum environment. Secondary ion mass spectroscopy (SIMS) results for the commercial sample were used to establish its bulk oxygen content, which was compared with a standard sample grown with a known amount of oxygen, as determined separately by heavy ion elastic recoil analysis.

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2. Experimental

Commercial Emcore samples of nominally undoped GaN were used for all the XPS measurements described in this paper. The samples were single crystal GaN grown on sapphire substrates. Although the samples were nominally undoped they had sufficient n-type conductivity to eliminate problems with sample charging during SIMS measurements. The XPS results were obtained using two spectrometers: a Kratos XSAM800 pci instrument (1990), and a Kratos Axis Ultra (1999). The majority of the XPS measurements were carried out using the second instrument. For this spectrometer the energy scale was calibrated using the Au $4f_{7/2}$ photoelectron peak at a binding energy (E_B) of 83.98 eV. Spectra were charge corrected using the C 1s photoelectron component peak corresponding to C–C species at a binding energy, $E_B = 285.0$ eV. High resolution elemental region spectra were acquired for the Ga 3d, N 1s and O 1s photoelectron peaks using an analyzer pass energy of 20 eV with an Mg Kα X-ray source. The area of analysis was approximately $700\,\mu m \times 300\,\mu m$. The relative sensitivity factors supplied with the instrument control software were used for element quantification. Depth profiling was performed by argon ion milling between repeated photoelectron peak area measurements. The argon ion source was differentially pumped and the chamber pressure was maintained at 1.6×10^{-5} Pa with the argon gas present in the system. The base pressure of this system before introduction of the argon was 5.1×10^{-7} Pa.

The Kratos Axis Ultra system also had a sample preparation chamber connected to the main analysis chamber. The samples could be introduced into this chamber from the analysis chamber and heated to 650 °C whilst mass analysis was carried out on desorbed species. Gallium desorption was studied in this manner.

A Cameca 5f SIMS instrument was used for dynamic SIMS measurements of an Emcore GaN sample and a standard sample with known oxygen concentration. A Cs ion beam was used as the primary ion source during the SIMS measurements. Quantitative SIMS require standards for comparison. A high oxygen content was required for the standard sample so that an accurate determination of the atomic percent of oxygen present could be made. Elastic recoil detection analysis (ERDA) using 200 MeV heavy ions of ^{197}Au was used to determine the elemental content of the standard sample. The heavy ions were supplied by a 14UD Pelletron accelerator. The ERDA system is housed at the Australian National University and is particularly well-suited to the detection and analysis of light elements such as nitrogen, oxygen, and hydrogen [3].

3. Results

Fig. 1 shows the results for ERDA measurements of the GaN standard sample later used for SIMS comparison. There was nitrogen loss, and to a lesser extent hydrogen loss, during the measurement period. However, by extrapolating back to zero ion dose the original atomic concentrations of the film could be determined. These are shown in the inset of the figure. The oxygen content was determined to be 2.4% averaged over the analysis volume, or approximately 9×10^{20} oxygen atoms per cm^3. Fig. 2 shows a comparison between the oxygen SIMS signal for the standard sample and that for an Emcore sample. The measurement shows that the bulk oxygen content of the Emcore sample is extremely low at between 10^{18} and 10^{19} oxygen atoms per cm^3, and this value may be even lower depending on how strongly the standard was influenced by oxygen related matrix effects during the SIMS measurements. The atomic concentrations of oxygen in the Emcore sample are typical for undoped commercial GaN. Converting to an atomic percentage value, as is used for XPS analysis, it is evident that the Emcore sample had approximately 0.02% oxygen present in the bulk, a value well below the detection limit for XPS. The surface oxide was evident in the XPS results, and not in the SIMS results of Fig. 2, because the XPS has higher surface sensitivity with an analysis depth of approximately 2 nm. However, in both the XPS systems used detectable amounts of oxygen were measured even after etching into the bulk of the material. The difference between the SIMS and XPS results occurs because the SIMS analyses material removed from the surface by ion milling, while the XPS examines material left on the surface after milling. This effect was noted first in the Kratos XSAM800 pci instrument. However, the sensitivity to oxygen at levels below 10% was found to

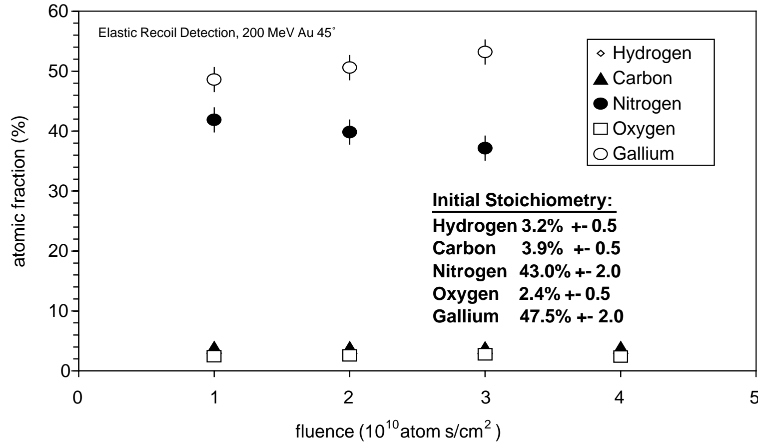

Fig. 1. Elastic recoil detection analysis of standardized GaN sample.

be quite poor. The Kratos Axis Ultra instrument, with better elemental sensitivity, was employed.

Fig. 3 shows a depth profile for the elements of interest collected using the Kratos Axis Ultra instrument. C 1s due to adventitious hydrocarbons was observed on the surface but was not significant in the material bulk (measured using an Al Kα X-ray source, so as to avoid the Ga Auger line which overlaps with the C 1s photoelectron peak when using an Mg Kα X-ray source) and is consequently not shown. The accelerating potential used for the argon ion source at the various stages of milling is shown on the top of the plot. After milling past the oxide layer into the bulk material it was observed that there was a slight increase in the oxygen, when using 2.5 keV ion milling compared to 5 keV ion milling. This phenomenon was observed in both XPS systems and could be reproduced, regardless of how much milling had previously taken place.

Despite the apparent disparity between the Ga and N signals in Fig. 3, the data does not supply conclusive evidence of a gallium-rich surface. The vendor-supplied sensitivity factors of 0.736, 0.505, and 0.439 for the O 1s, N 1s and Ga 3d photoelectrons, respectively, are provided on the basis of measurements in pure

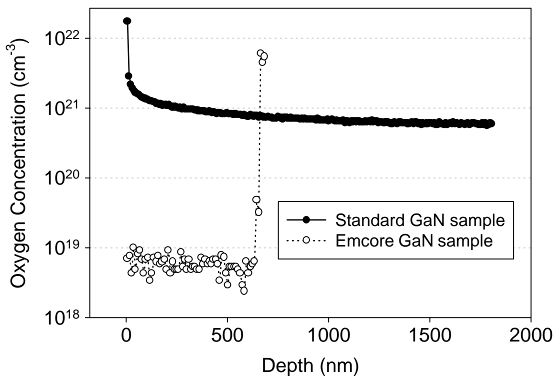

Fig. 2. Oxygen levels determined by SIMS for standard GaN sample (independently calibrated using elastic recoil detection analysis) and GaN sample from Emcore.

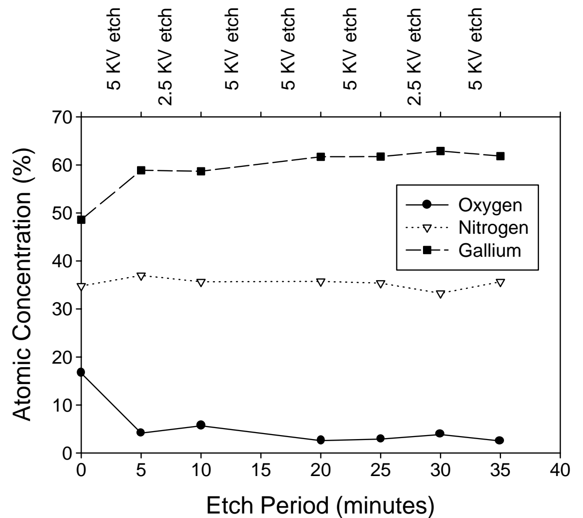

Fig. 3. XPS analysis of Emcore GaN sample after etching with argon ions at various energy. Higher oxygen levels are apparent after etching with 2.5 keV argon ions.

elements, or in compounds unrelated to this study. Mixing nitrogen and gallium may severally affect the photoelectron escape depth for one or both components, so that the sensitivity factors may not provide accurate quantification. Nevertheless the possibility of preferential removal of nitrogen during the milling, and particularly for milling with the higher energy (5 keV) ions, is quite high given the low vapor pressure for nitrogen, and the fact that the ion cascade during milling breaks bonds below the milled surface [4]. This is believed to be significant since the presence of free liquid gallium metal at the milled surface might mask the presence of oxygen recycled at the surface of the gallium nitride. Greater masking of oxygen might be expected after 5 keV milling since the higher energy ions create more subsurface damage than 2.5 keV ions, resulting in greater amounts of free gallium present on the surface.

Since the SIMS results had shown that the Emcore sample had bulk oxygen levels well below the detection limit of XPS, the oxygen found in the sample after argon milling was due either to low level contamination in the ultrahigh purity argon gas that supplied the ion beam, oxygen recycled at the surface during the milling process, or oxygen gettered from the chamber. The former is unlikely given the purity of the starting gas, and also given that the system was differentially pumped. With regards to oxygen gettering from the chamber, the base pressure of the analysis system was 5.1×10^{-7} Pa before introduction of the argon gas. This equates to a potential gas bombardment of the sample surface from background species of approximately 1.4×10^{12} molecules/(cm^2 s). At this bombardment rate it would take over 2 h to build a monolayer of surface oxide given 100% oxygen absorption at the surface. Therefore it is unlikely that background contaminates in the system could contribute substantially to the oxide seen on the Emcore GaN sample. Oxygen is known to recycle on the surfaces of samples that have a high affinity for oxygen [5] and this appears to be the most likely candidate for the source of oxygen seen on the sample surface. Table 1 shows the atomic percentage of Ga 3d, O 1s and N 1s observed at normal and at 60° to normal incidence. Care was taken during these angle resolved measurements to ensure that the analysis area was wholly within the etch crator (hence the small analysis area used). The measurements taken at 60° are analyzed at a shallower depth compared to the normal measurement position because the photoelectrons had to traverse twice the distance to escape the sample and subsequently be detected by the analyzer. Comparing the 60° and normal measurements it is clear that there is a larger amount of oxygen at the surface of the GaN and that the surface is depleted of nitrogen after the milling. However, the Ga signal does not appear to change between the 60° and the normal analysis orientations when the sample had been milled with the 2.5 keV ions, whereas after milling with the 5 keV ions the Ga signal was notably stronger for the 60° measurement. This result supports the belief that free Ga is on the sample surface. The presence of the free metal is apparently strongest for the 5 keV ion milling. However, it may also be present for the 2.5 keV milling given that the increase in the oxide concentration, if present as Ga_2O_3, requires less gallium in this compound. The fact that there is no change in the gallium content for the 2.5 keV milling may not necessarily indicate that there is no increase in the amount of free gallium present.

Table 1
Atomic percentage of elements observed by XPS at normal and 60° analysis angles

	Element		
	Ga 3d (%)	N 1s (%)	O 1s (%)
Normal analysis after 2.5 keV milling	62.9	33.2	3.8
60° Analysis after 2.5 keV milling	63.0	28.1	8.9
Normal analysis after 5 keV milling	61.8	35.6	2.5
60° Analysis after 5 keV milling	65.8	28.0	6.2

To further test the possibility of gallium metal accumulating at the sample surface, a sample that had undergone milling was transferred—while being maintained in a ultra-high vacuum environment—from the analysis chamber into the sample preparation chamber. The sample was then initially heated to 560 °C over a period of 25 min and then subsequently heated to 650 °C over a further 40 min period to drive away any excess gallium, since at these temperatures free gallium may be desorbed [6–8].

The sample was then subsequently returned to the analysis chamber after each heat treatment for re-analysis. A mass spectrometer was used to monitor the gallium desorption during heating, and an increase

Table 2
Atomic percentage of elements prior to and subsequent to heat treatment

	Element		
	Ga 3d (%)	N 1s (%)	O 1s (%)
Atomic concentration before heat treatment	67.2	27.8	5.0
Atomic concentration after 560 °C heat treatment	57.8	36.2	6.0
Atomic concentration after 650 °C heat treatment	55.7	37.4	6.9

in the gallium signal of over two orders of magnitude was observed during the heating. Table 2 compares the atomic percentage of gallium, nitrogen, and oxygen observed by XPS before and after this annealing process. From the changes observed in Table 2 after heating it is apparent that a substantial amount of free gallium was desorbed from the sample surface. On removal of this gallium both the oxygen and nitrogen signals increased while maintaining approximately the same concentration ratio. The change after heating to 560 °C was quite strong, while the subsequent change after heating to 650 °C for a longer period of time was much smaller, indicating that the initial treatment had removed most of the free gallium present on the sample surface. Interestingly even after heating there was still a large disparity in the calculated values of atomic percent concentration between the gallium and nitrogen, whereas if all the free gallium had been removed fairly good stoichiometry between the nitrogen and gallium should be expected (albeit that the oxygen has a small bearing on this). Again this relates to the inaccuracies involved in use of the sensitivity factors for determining the concentrations, as discussed above. In fact, the stoichiometry of the gallium and nitrogen is probably considerably better than indicated since there is unlikely to be any free gallium still resident on the sample surface after the heat treatments.

The decrease in the gallium content indicated in Table 2, is greater than the change seen when switching between 5 and 2.5 keV milling, indicating that even in the case of 2.5 keV milling there is free gallium metal accumulating on the sample surface. This may have significant implications for device processing. Though reactive ion etching is more commonly used than ion milling during GaN device processing, the ion energies present are still significant in that case so that great care must be taken to ensure that the reaction chemistry is sufficient to remove free gallium metal.

The recycling of oxygen at the ion milled surface of the GaN may also have been enhanced by the presence of the free gallium accumulations on the GaN surface. The Ga may mask the oxide beneath, but even as the milling continued the reservoir of free gallium would strongly getter any oxygen released from the nitride surface, whereas nitrogen would be removed without any gettering effect. Oxygen accumulations on GaN sample surfaces may therefore also be problematic for device processing and should be carefully monitored.

4. Conclusions

The low oxygen content of commercial samples of GaN was established to be 0.02% or less using SIMS and by comparison with a standard sample previously analyzed with ERDA. Despite this 2–5% atomic oxygen was observed on the surface of the GaN samples after ion milling into the bulk of the material. The observed oxygen was found to originate from the original surface oxide of the material, which was believed to be recycling at the sample surface. The surface oxide was found to increase after 2.5 keV ion milling when 5 keV had been used previously. This effect was highly reproducible. It was found to be related to the formation of accumulations of free gallium at the sample surface that form as a result of preferential removal of the nitrogen component during milling. The presence of the free gallium was confirmed by angle resolved XPS and by analysis following sample heat treatment. The free gallium metal was shown to mask some of the oxide signal with more of the signal being masked following milling with 5 keV ions.

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