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Accurate ultra-low-energy secondary ion mass spectrometry analysis of wide bandgap GaN/In$_x$Ga$_{1-x}$N structures using optical conductivity enhancement

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Ultra-low-energy secondary ion mass spectrometry has been used to undertake a structural analysis of GaN–In$_x$Ga$_{1-x}$N ($x \sim 0.25$) quantum wells used in optoelectronic devices. The high resistivity of intrinsic GaN–In$_x$Ga$_{1-x}$N restricts the necessary electrical path between the analyzed area and the instrument ground potential resulting in surface charge accumulation. Consequently, unstable and unrepresentative depth profiles tend to be produced. A technique known as optical conductivity enhancement (OCE) has been used during depth profiling to reduce the material resistivity. This creates an electrical path between the sample and holder, eliminating charge build up and resulting in accurate depth profiles.

Wide bandgap nitride semiconductor materials are currently being explored for a number of optoelectronic device applications, e.g. solar cells, LEDs, and lasers.[1–3] One particular material of interest is GaN with differing levels of indium incorporation, as this affords the ability to engineer bandgaps from $E_g \sim 0.7$–3.4 eV which span the entire solar spectrum,[4] improving flexibility and efficiency, for example in solar cell applications. To create the most efficient device structures, combinations of thin (nm) layers that vary in elemental composition, e.g. quantum wells, and dopant concentration, are being investigated. Nanometre-scale interface sharpness and control of the doping distribution are essential. Ultra-low-energy (i.e. sub-keV) secondary ion mass spectrometry (uleSIMS) offers quantification of both the composition and the doping levels (ppb/ppm) as well as their distributions with the necessary depth resolution,[5] so long as the optimal measurement conditions and quantification protocols are established. The inherently large resistivity of intrinsic nitride semiconductors,[6] and the insulating substrates (e.g. sapphire)[7] typically used, make this type of sample structure susceptible to 'charging'.[8,9] This occurs when charge accumulates on the sample surface because of a restriction in the conductive path between the injected primary ions (i.e. ion current) and the instrument ground potential. The result is a lensing effect[10] just above the sample surface which modifies the local surface electric fields, changes the ion trajectories and shifts the secondary ion energy spectrum. This produces an unstable instrument collection efficiency resulting in a distorted/erratic profile,

signal suppression or in the worst case a complete loss of secondary ion collection. Co-bombardment with electrons is often used to combat these effects, but this can be problematic with resistive, as opposed to insulating, layers, as an overabundance of negative charge flowing through the changing spreading resistance under the crater, i.e. as the thickness between the crater bottom and insulating substrate is reduced the ohmic resistance along the crater base increases,[11] will also cause the surface potential to be unstable.[12]

Another common approach is to coat the sample surface with a conductive layer, e.g. gold,[11] but this may degrade the depth resolution and for this reason it was not adopted.

EXPERIMENTAL

The sample used for this work was a five period GaN–In$_x$Ga$_{1-x}$N ($x \sim 0.25$) quantum well structure grown by metalorganic vapour phase epitaxy (MOVPE). Figure 1(a) shows a schematic of the intended structure and Table 1 summarizes the intended layer thicknesses and their composition. This type of layer structure is analogous to those currently being developed for certain solar cell applications.[7] The uleSIMS measurements were carried out with an Atomika 4500 SIMS profilometer (CAMECA, Gennevilliers, France) using an O$_2^+$ primary beam over a range of sub-keV beam energies (175, 250, 375 and 500 eV) with measured beam currents at the sample of 40, 45, 60 and 70 nA, respectively. All the profiles were taken within 1° of normal incidence using a raster size of 250 × 250 µm with an ion collection gate of 3.52%. This combination of energies and angle was chosen as part of an investigation into the effect of beam energy in the sub-keV regime on depth resolution[5] (important to establish given the nanometre scale layers being investigated). Prior to inserting the sample into the

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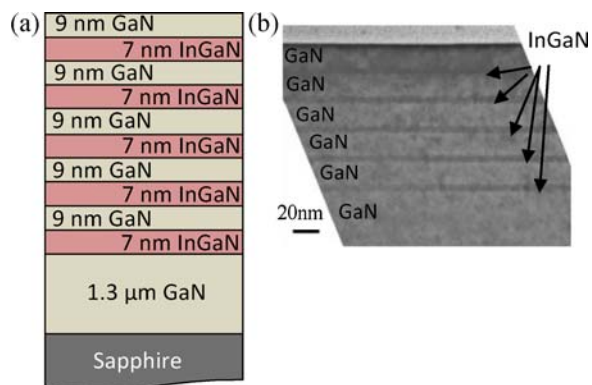
Figure 1. (a) Schematic of the intended GaN–In$_x$Ga$_{1-x}$N sample structure. (b) Cross-sectional TEM of the five-period GaN–In$_x$Ga$_{1-x}$N quantum well structure.

Table 1. Intended layer thicknesses and stoichiometry as well as the measured layer thicknesses using cross-sectional transmission electron microscopy (XTEM)

Layer	Intended layer Composition	Intended layer thickness (nm)	Measured layer thickness (nm)
1	GaN	9	12.9 ± 0.3
2	In$_{0.25}$Ga$_{1-0.25}$N	7	3.5 ± 0.3
3	GaN	9	12.0 ± 0.3
4	In$_{0.25}$Ga$_{1-0.25}$N	7	3.8 ± 0.3
5	GaN	9	12.2 ± 0.3
6	In$_{0.25}$Ga$_{1-0.25}$N	7	3.6 ± 0.3
7	GaN	9	12.2 ± 0.3
8	In$_{0.25}$Ga$_{1-0.25}$N	7	3.5 ± 0.3
9	GaN	9	12.2 ± 0.3
10	In$_{0.25}$Ga$_{1-0.25}$N	7	3.8 ± 0.3

SIMS instrument, the surface was cleaned with 2-propanol and dried using dry N$_2$. For the optical charge compensation a blue continuous-wave GaN laser (supplied by Laser 2000, Ringstead, UK) with a photon energy of 3.1 eV (wavelength 405 nm) and a maximum output power of 25 mW was used. Atomic force microscopy (AFM) measurements using a Veeco multimode AFM system (Veeco Instruments Inc., Santa Barbara, CA, USA) and a Nanoscope 3A controller (Veeco) were performed in tapping mode with images of 5×5 µm obtained using a scan rate of 1 Hz.

RESULTS AND DISCUSSION

Figure 1(b) shows an (004) cross-sectional transmission electron microscopy (XTEM) image of the sample from which the five-period GaN–In$_x$Ga$_{1-x}$N quantum well structure is visible. From this image an ion intensity scan was taken and the layer thicknesses ascertained (see Table 1 for the actual values). Figure 2 shows the uleSIMS depth profiles (without any charge compensation) obtained for the four different primary beam energies. The ^{69}Ga signals show a large amount of instability which increased as we decreased the primary beam energy while the ^{115}In signals show a significant amount of unsystematic variation in magnitude and shape as a function of energy. For the lowest beam energy (175 eV) the quality of the ^{115}In signal meant that the In$_x$Ga$_{1-x}$N layers could not be distinguished. The instabilities observed for all the profiles shown in Fig. 2 are indicative of charging. Furthermore, a decrease in the primary ion beam energy corresponds to a reduced ion voltage and so the ion trajectories become more susceptible to variations in the surface potential; hence the enhanced distortion observed.
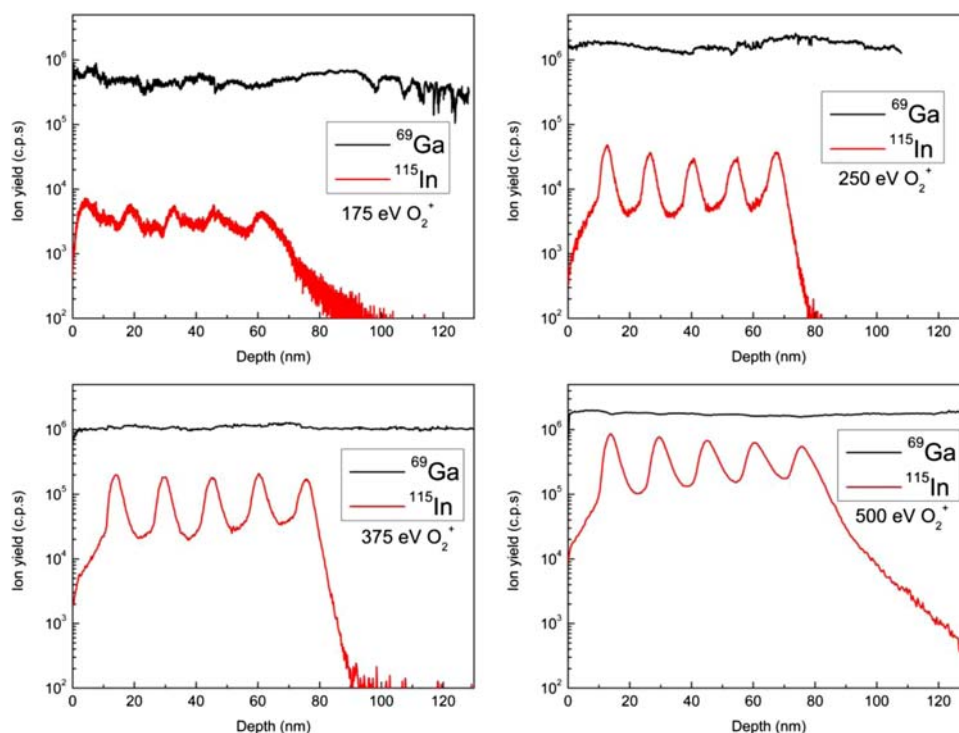

Figure 2. uleSIMS depth profiles of the five-period GaN–In$_x$Ga$_{1-x}$N quantum well structure without any charge compensation.
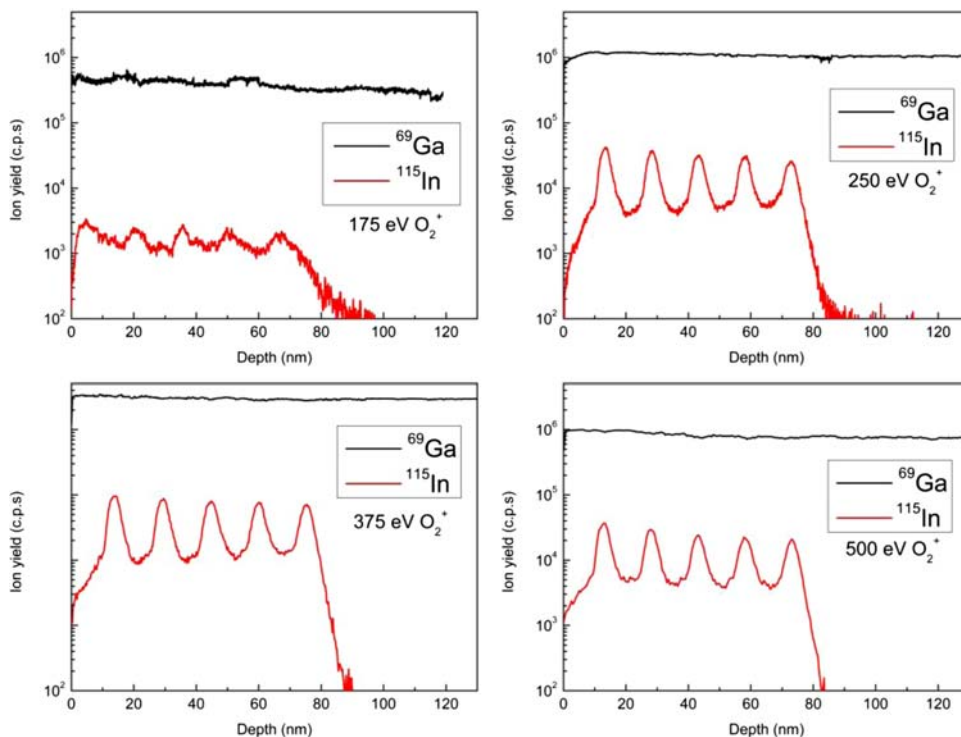
Figure 3. uleSIMS depth profiles of the five-period GaN–In$_x$Ga$_{1-x}$N quantum well structure using simultaneous red laser OCE charge compensation.

A similar problem is encountered in the SiGe system, and is especially pronounced in intrinsic SiGe which has a smaller bandgap ($\sim$0.7–1.1 eV). A technique termed by the authors ''optical conductivity enhancement (OCE)''[11] was developed to overcome this as the sample impedance precluded the use of coincident bombardment with low-energy electrons.[9] The OCE technique works by exciting electrons from the valence band (or doping levels) into the conduction band, thus enhancing the (surface) conductivity of the material. If this conductivity can be increased sufficiently, a conductive (electrical) path between the bombarded area and the sample holder can be achieved with charge build
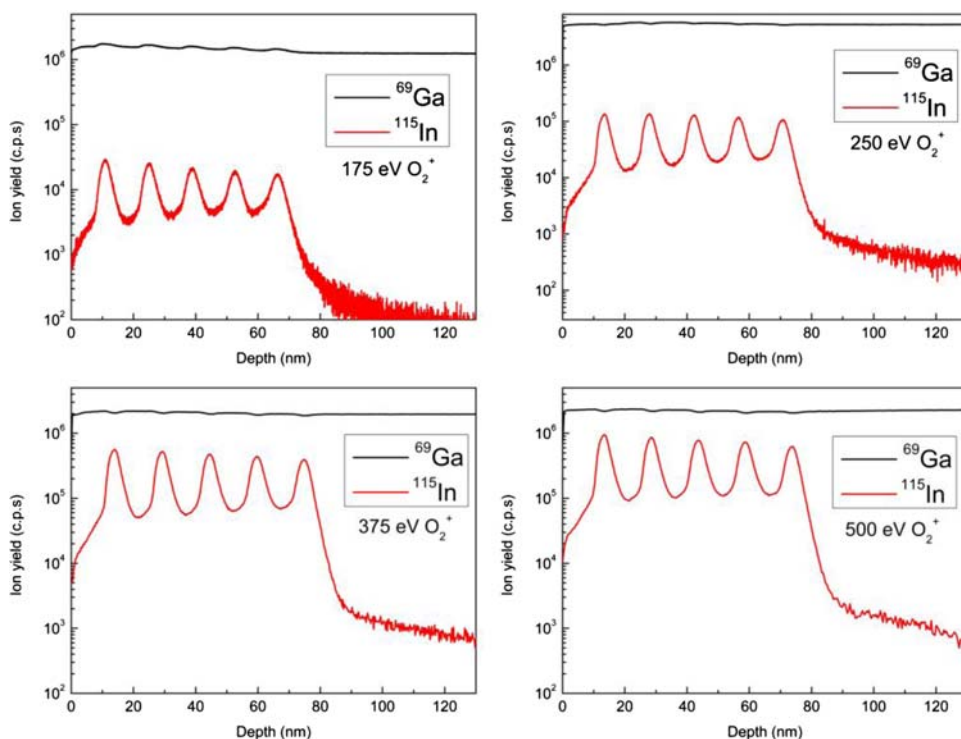

Figure 4. uleSIMS depth profiles of the five-period GaN–In$_x$Ga$_{1-x}$N quantum well structure using simultaneous blue laser OCE charge compensation.
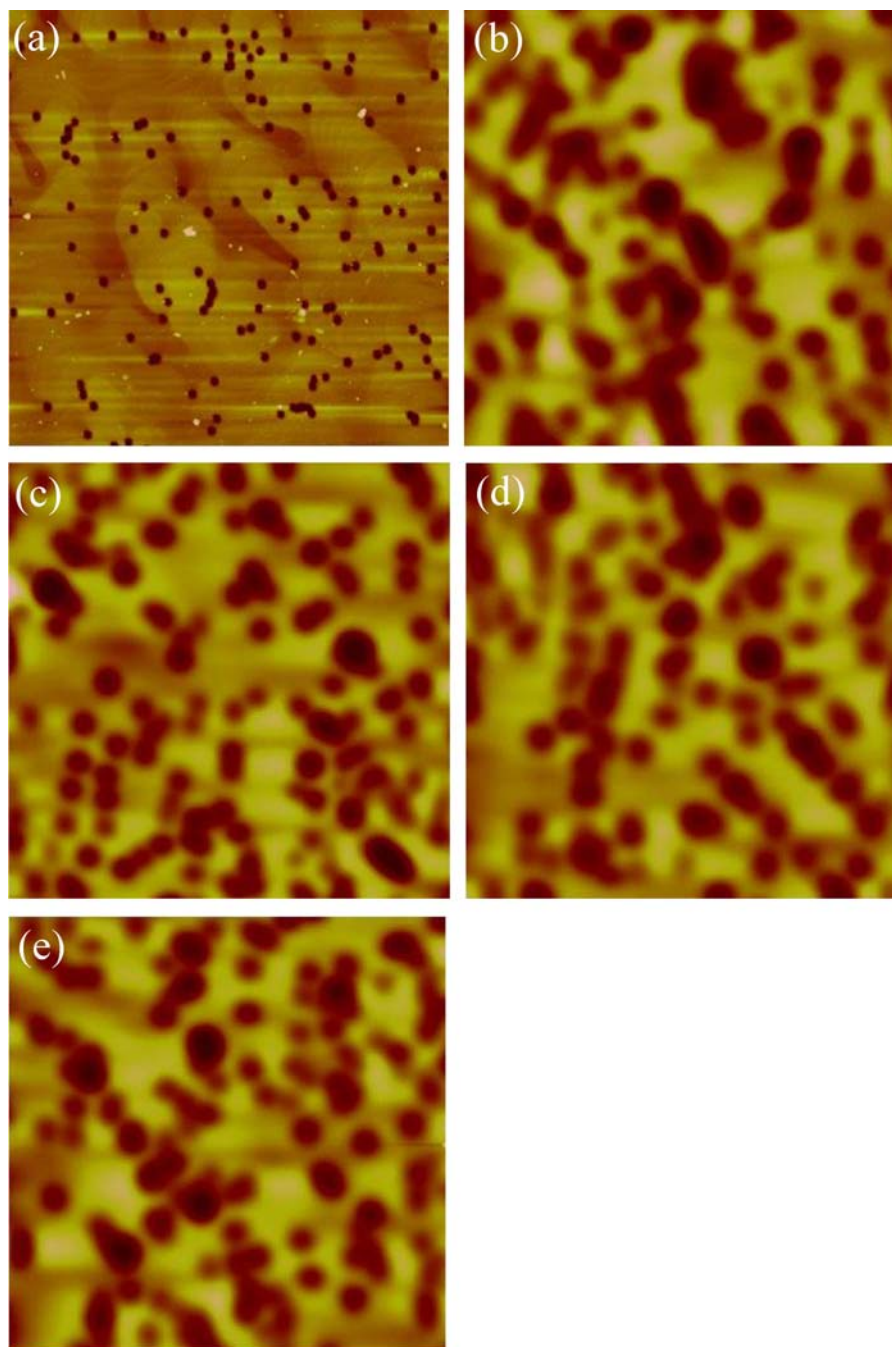
Figure 5. AFM images (5 × 5 μm) taken from (a) sample surface, (b) 175 eV crater, (c) 250 eV crater, (d) 375 eV crater, and (e) 500 eV crater.

up (and changes in the collection field) avoided. In SiGe we have previously found that a red laser (λ = 635 nm; hυ = 1.9 eV) was sufficient to stabilize the surface and enable accurate SIMS profiles to be obtained. It was also suggested[13] that OCE could be applied to a variety of other materials, especially wide bandgap semiconductors, as long as the wavelength of the illuminating light was sufficient to generate electron-hole pairs and had enough power to maintain stability for the particular ion current used.

MOVPE-grown GaN typically crystallizes in the wurtzite structure[1] with an intrinsic (300 K) bandgap of 3.4 eV.[14] Zinc blende is the other form of GaN and it has a (300 K) bandgap of 3.3 eV.[14] The introduction of indium at matrix levels reduces the bandgap until, at a composition of InN, the lowest bandgap of around 0.7 eV[14] is achieved. For OCE to work effectively, the wavelength of the light must be sufficient to stimulate an electron across the bandgap at or near the sample surface, and in this case it should be of the order of 3.4 eV. In this experiment, a blue GaN laser diode (BLD) of wavelength 405 nm and power 25 mW was used, with the illumination being defocused so that it projected onto both the sample surface and the holder simultaneously in order to generate a conductive surface path between the two. This sample dispersive method[12] was adopted as the laser stimulates surface conductivity, but the bulk of the sample remains highly resistive or insulating. It should be noted that an initial set of profiles (see Fig. 3) using a red laser (λ = 635 nm; hυ = 1.9 eV) were found to be unstable,

Table 2. RMS roughness values from the sample surface and different beam energy SIMS craters measured by AFM

Scanned region	RMS roughness (nm)
Surface	2.2 ± 0.2
175 eV crater	2.1 ± 0.2
250 eV crater	2.8 ± 0.2
375 eV crater	2.7 ± 0.2
500 eV crater	2.8 ± 0.2

suggesting that there were no (or not enough) low-energy excitable states present near the surface. Figure 4 shows the measured depth profiles using the BLD. It can be seen that the ^{69}Ga signal is stable and remains constant within the GaN regions, while small variations are observed within the quantum well regions where the In has displaced some of the Ga. Furthermore, the improved quality of the ^{115}In signal and its similarity at different energies meant that the five $In_xGa_{1-x}N$ alloy layers are resolved even down to 175 eV. From these profiles it is believed that quantitative information could be obtained if reference samples were profiled under the same conditions.

The wavelength (405 nm) of the blue laser diode used here should only be capable of generating electron-hole pairs within a material that has a bandgap of ≤ 3.1 eV according to:

$$E_g = \frac{1.24}{\lambda} \qquad (1)$$

where E_g is the bandgap of the material in eV, λ the wavelength of the incident photons in nm and the constant 1.24 in μm is derived from Planck's constant ($h = 6.626 \times 10^{-34}$ J/s) multiplied by the speed of light in vacuum ($c = 3 \times 10^8$ m/s) divided by the electron charge constant ($e = 1.6 \times 10^{-19}$ C). This gives a value slightly less than the bandgap for intrinsic GaN which was present between the $In_xGa_{1-x}N$ layers and beyond the final $In_xGa_{1-x}N$ quantum well. However, we found that the measured ^{69}Ga signal when profiled using coincident blue laser OCE also remained stable in these regions and appeared free from charging effects. Possible reasons for this include: (i) an unintentional indium background; (ii) trace amounts of a dopant(s) previously deposited in the MBE system (i.e. growth system memory effects);[15] (iii) a high background concentration of donors from native defects;[7] and (iv) sufficient excitation of carriers due to the combined effects of the ion beam and the laser light, e.g. through direct excitation of carriers by the ion beam, allowing charge to leak back to smaller band-gap layers where conductivity can be sustained by the laser alone. The latter is the most likely in our view, although further work is clearly required to identify the exact mechanisms at work here.

Figure 5 shows some representative AFM images taken from the sample surface and SIMS craters. The surface image revealed that the sample contained a high density of pinholes. Subsequent roughness analysis showed no measurable beam-induced roughening at 175 eV while a small but similar increase was evident at 250, 375 and 500 eV. Table 2 summarizes the typical root mean square (rms) roughness values obtained from the surface and different

beam energy SIMS craters. From the AFM images the most notable effect from the beam sample interaction process was the lateral enlargement of these pinholes. Moreover, pinholes will have a detrimental effect on the SIMS depth resolution. Thus, to perform an accurate study of the effect of beam energy on depth resolution, similar samples without pinholes are required.

CONCLUSIONS

We have used uleSIMS to depth profile a GaN–$In_xGa_{1-x}N$ quantum well structure. Without charge compensation, the intrinsically high resistivity led to surface charging during ion bombardment and resulted in unreliable and unquantifiable profiles. The level of instability within the signals was found to increase as the primary beam energy was lowered, with a complete loss of layer resolution at 175 eV. OCE with a blue laser was successfully used during profiling as the photon energy of this laser corresponds to the bandgap in the target material. Consequently, stable and reproducible profiles were measured with all the $In_xGa_{1-x}N$ quantum wells resolved, even for the lowest primary beam energy (175 eV) used. Hence, by using a combination of OCE, reference materials and, provided that the In yield is monotonic with concentration, accurate matrix and dopant quantification of GaN–$In_xGa_{1-x}N$ layer structures using uleSIMS can be achieved.

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