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ORIGINAL ARTICLE

Comparison of different X-ray-based scanning electron microscopy methods to detect sub-nanometre ultra-thin InAs layers deposited on top of GaAs

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Abstract

We compare three different methods of X-ray analysis in a scanning electron microscope (SEM): energy-dispersive X-ray spectroscopy (EDX), wavelength-dispersive X-ray spectroscopy (WDX) and micro X-ray fluorescence (μXRF). These methods are all applied to the same gallium arsenide (GaAs) wafer with a 0.8 nm layer of indium arsenide (InAs) on top. All methods allow detection and quantification of the indium L-line intensity from the thin InAs layer. EDX is the easiest to perform, WDX is the most sensitive and μXRF a novel technique where a poly-capillary optics is used to focus an X-ray beam from a high-voltage X-ray tube onto a small spot several micrometres wide and the characteristic X-rays produced are detected by a solid-state silicon detector similar to that used in EDX. It is to our knowledge the first time a sub-nanometre layer is reliably detected and analysed using μXRF in an SEM.

KEYWORDS

detection limit, energy-dispersive X-ray spectroscopy (EDX), indium gallium arsenide (InGaAs), micro X-ray fluorescence (μXRF), sensitivity, wavelength-dispersive X-ray spectroscopy (WDX)

1 | INTRODUCTION

Surface analysis of thin films can be achieved by different techniques where those that yield ultra-low (parts-per-million, ppm) sensitivity often have low penetration (e.g. secondary ion mass spectroscopy, SIMS) or low escape depths (e.g. Auger electron spectroscopy, AES) and so typically need to be combined with destructive depth profiling[1,2] while those with high penetration (e.g. proton-induced X-ray generation, medium energy ion scattering)[3] are often hard to quantify. X-ray photoelectron spectroscopy (XPS) lies somewhere in-between but usually does not yield any lateral resolution as would be needed for characterising laterally inhomogeneous systems.

Techniques that rely on X-ray generation and detection and can be incorporated into a scanning electron microscope (SEM) to yield non-destructive compositional mapping across surfaces with a lateral sub-μm-scale resolution include energy-dispersive X-ray spectroscopy (EDX), wavelength-dispersive X-ray spectroscopy (WDX) and micro X-ray fluorescence spectroscopy (μXRF). Of course, scanning AES and nanoSIMS can also achieve chemical mapping with sub-μm lateral resolution but require rather specialised instrumentation that is not

available in most laboratories (and neither at University of Sheffield).

SEM-EDX has been shown to be sensitive in the few at. ‰ range,[4] while SEM-WDX[5] and μXRF[6,7] can both reach 10 ppm level sensitivity for heavy elements.

For very thin surface layers on bulk substrates the penetration depth of the electrons and the interaction volume for X-ray generation will always be much larger than the layer thickness so quantification in top-down geometry is tricky. A previous top-down investigation of several thin In(Ga)As layers grown on GaAs has been able to detect indium in various In(Ga)As layers as thin as an individual unit cell even in a simple Hitachi 3030+ tabletop SEM with tungsten filament and 30 mm^2 Bruker XFlash 430 SDD (15 kV, ~1 h acquisition time).[8] We have previously checked the appropriateness of In L/As L X-ray line ratios for quantification of EDX with the help of an InAs wafer sample, which is not discussed here but in detail in Ref. (8). For InAs bulk where absorption in the sample is dominant, experiment and simulation differ systematically by 7%–8% if the differences between the detector windows used in our SEM-EDX experiment (ultrathin window of type Moxtek AP3.3) and in simulations (thicker Al coating but thinner parylene polymer) are taken into account.

Here we compare quantification of EDX at 5 or 15 kV in this instrument to WDX in a dedicated JEOL JXA 8530F+ electron microprobe equipped with four crystal spectrometers using Rowland circle geometry and operated at 5 kV where beam current is more than an order of magnitude higher and the penetration depth smaller. Finally, for μXRF a Quantax X Trace 2 system with an X-ray tube with Rh target[9] has been used where penetration at higher voltage of 25–50 kV will be an order of magnitude deeper. Our study builds on a more theoretical comparison of WDX and μXRF methods reported earlier by Procop and Hodoroaba[10] who assessed the quantifiability of the latter by modelling analytically photo-ionisation cross-sections, Bremsstrahlung and characteristic X-ray intensities for K- and L-lines in XRF. Our contribution is an experimental comparison of detection and sensitivity limits of three SEM-based techniques applied to an InGaAs semiconductor wafer. Such samples are relevant for optoelectronics as thin strained InAs layers deposited on GaAs(001) can relax some of the compressive strain by spontaneous quantum dot formation on the surface and simultaneous segregation and interdiffusion.[11,12]

2 | SIMULATIONS

Figure 1 shows results from Monte–Carlo simulations of electron scattering and X-ray generation and detection using the CASINO software v2.42.[13] While 5 kV acceleration voltage will produce In L counts preferentially near the surface, which should be beneficial for thin surface layer detection, the absolute number of counts produced is low because the over-voltage is only slightly above that required to produce In L X-rays, all of which lie in the 3.3–3.9 keV range. For 10–20 kV, electron penetration and X-ray generation volume both increase with acceleration voltage but the number of In L X-rays produced near the surface is almost constant and about twice as high as at 5 kV. For EDX, 15 kV is therefore a good compromise between sufficient X-ray production yield and penetration while for WDX, where the background is lower and the signal-to-noise ratio thus better, 5 kV may be a better choice.

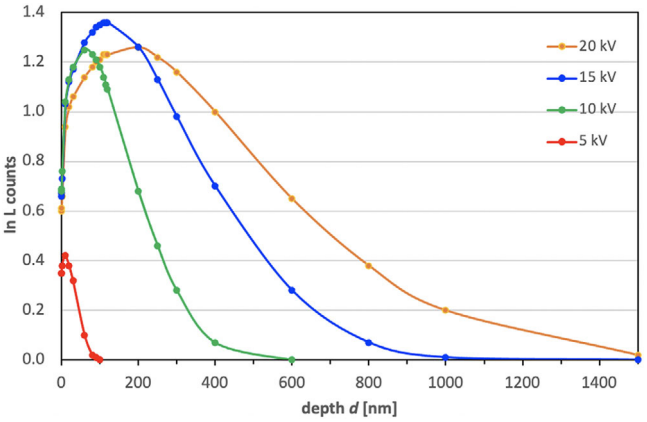

FIGURE 1 Simulation of number of In L counts produced from a 1 nm thin InAs layer embedded in GaAs as function of depth below the surface for different acceleration voltages for a nominal take off-angle (ToA) of 25°.

3 | EXPERIMENTS

Below, we will correlate measurements of the same wafer sample by EDX, WDX and μXRF in different scanning electron microscopes. Wafer pieces were investigated in top-down geometry without any specimen preparation apart from cleaning with HPLC-grade acetone (99.9% pure, Sigma-Aldrich, Burlington, MA).

The indium signal from the In Lβ line coincides with the position of possible sum peaks from Si K (see Figure 2), which, together with the high Bremsstrahlung background, ultimately limits the detection of very small amounts of indium in EDX. The In Lα line is barely visible upon the background in EDX at 5 kV acceleration voltage (cf. Figure 3). It is clearly visible at 15 kV, the In Lβ being only marginally detectable. So, in agreement with the previous study[8] we evaluate the In_L/As_L ratio at 15 kV, the longer acquisition time of ~2 h used here giving us a

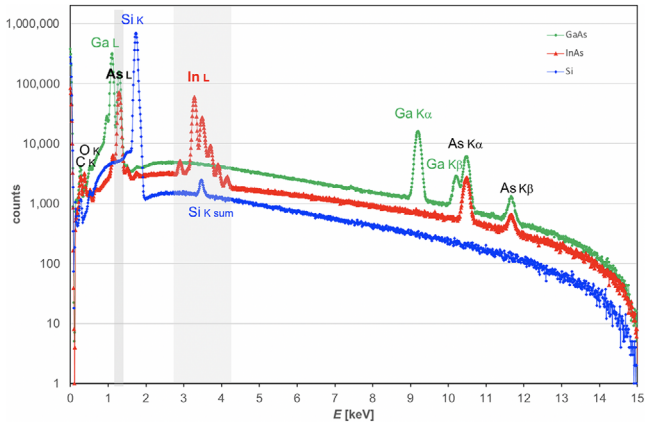

FIGURE 2 Experimental EDX spectra of GaAs, InAs and Si reference samples at 15 kV. Relevant peaks are labelled. ToA of 22°.

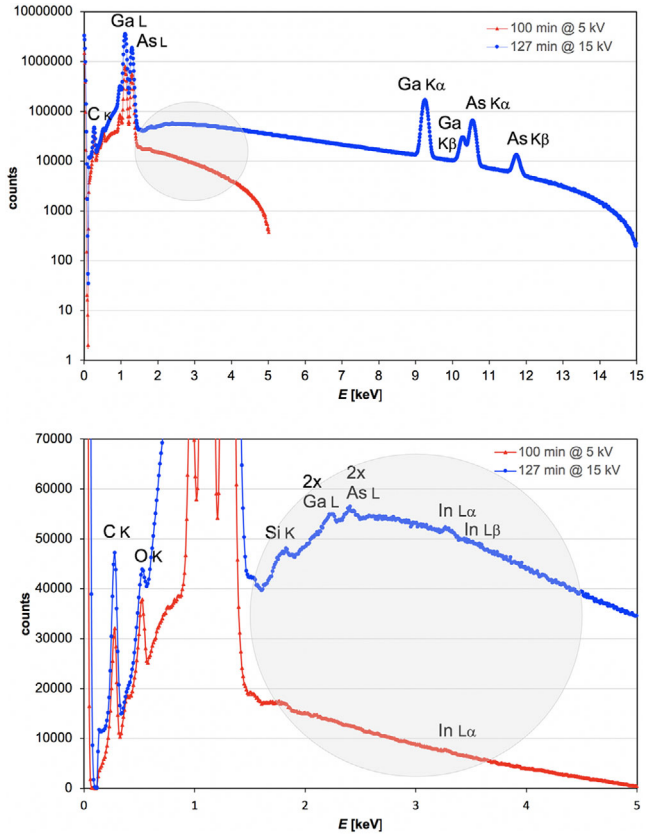

FIGURE 3 EDX spectra on log scale (above) and on shrunken linear scale (below) of EDX spectra of InAs-on-GaAs sample AF9151 at 5 kV (lifetime: 49 min, 1.4% deadtime) and 15 kV (lifetime: 113 min, 11.3% deadtime). Relevant peaks are labelled where the prefix 2× refers to (weak) sum peaks. ToA of 22°.

slightly improved detection limit. Numbers given in the following are net intensities after background subtraction from the 15 kV spectra shown in Figure 3, as measured by Bruker's Quantax 70 software. From the count ratio $In_L/As_L = (24{,}239 \pm 5000)/(13{,}581{,}340 \pm 7000) = 1.78 \pm 0.37$ ‰, we get 0.88 ± 0.18 nm or 2.9 ± 0.6 ML equivalent of

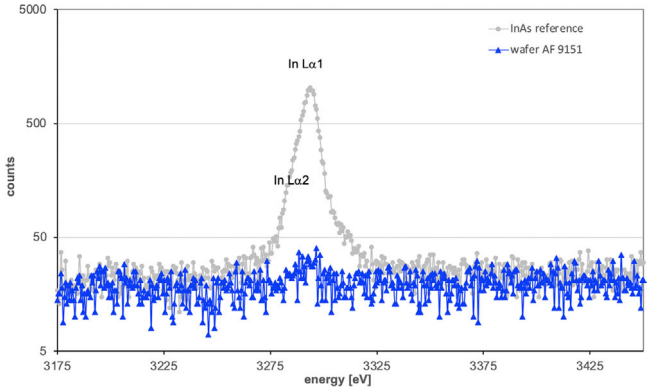

FIGURE 4 WDX spectra of In L taken at 5 keV of an InAs reference sample (grey) and the InAs-on-GaAs sample AF9151 (blue) recorded on channel 4 using a PET-L detector, displayed on log scale. The In L peak counts of ~1000 for InAs and 29 for InAs-on-GaAs are the results from 4s integration. As L and Ga L signals were recorded simultaneously using additional TAP and TAP-H analyser crystals, respectively. Total recording time was 33 min for each of two scans, one using a 2 µm and the other a 4 µm large probe. ToA of 40°.

InAs, where the error bar is a little smaller than previously reported (2.7 ± 0.8 ML) due to doubling of the acquisition time and a little increase in beam current, however, the error bar will ultimately be limited by background fitting at this stage and will likely not reach what WDX can achieve (see below). A monolayer (ML) equivalent is another way to express the chemical width a very thin layer, by multiplying its physical width in monolayers (here: single group-III metal layers in the sphalerite lattice, spaced a distance $a/2$ along the [001] growth direction) with the fractional chemical occupancy of that layer: one complete atomic layer would give the same chemical signal as n layers wherein only $(1/n)^{th}$ of each was occupied by the atomic species in question. A unit cell of InAs is 0.60 nm thick and thus would make up 2 ML equiv. of indium and 2 ML equiv. of arsenic.

Quantification of the complete WDX spectra for In L (shown in Figure 4) and As L, scanning a 2 µm or a 4 µm large defocused 5 keV electron beam with 15 nA current over the surface of sample AF9151, gave indium weight percentages of 0.52 ± 10 wt% and 0.44±0.05 wt%, respectively, whose weighted average would be 0.46 ± 0.04 wt%. Taking the different atomic weights of Ga, As and In into account, this would mean 0.29 ± 0.02 at. % indium for an ideal $In_xGa_{1-x}As$ alloy, that is, $x = 0.0058 \pm 0.0005$. Comparing again CASINO Monte–Carlo simulations of both an $In_{0.0058}Ga_{0.4942}As$ bulk with a thin pure InAs film (density ρ = 5.68 g/cm) on GaAs bulk (substrate, density ρ = 5.32 g/cm) imaged at 5 kV, a 40° take-off angle would suggest both to give ratios of $In_L/As_L = 1.15$‰ and $In_L/Ga_L = 0.93$‰ for an InAs film thickness of

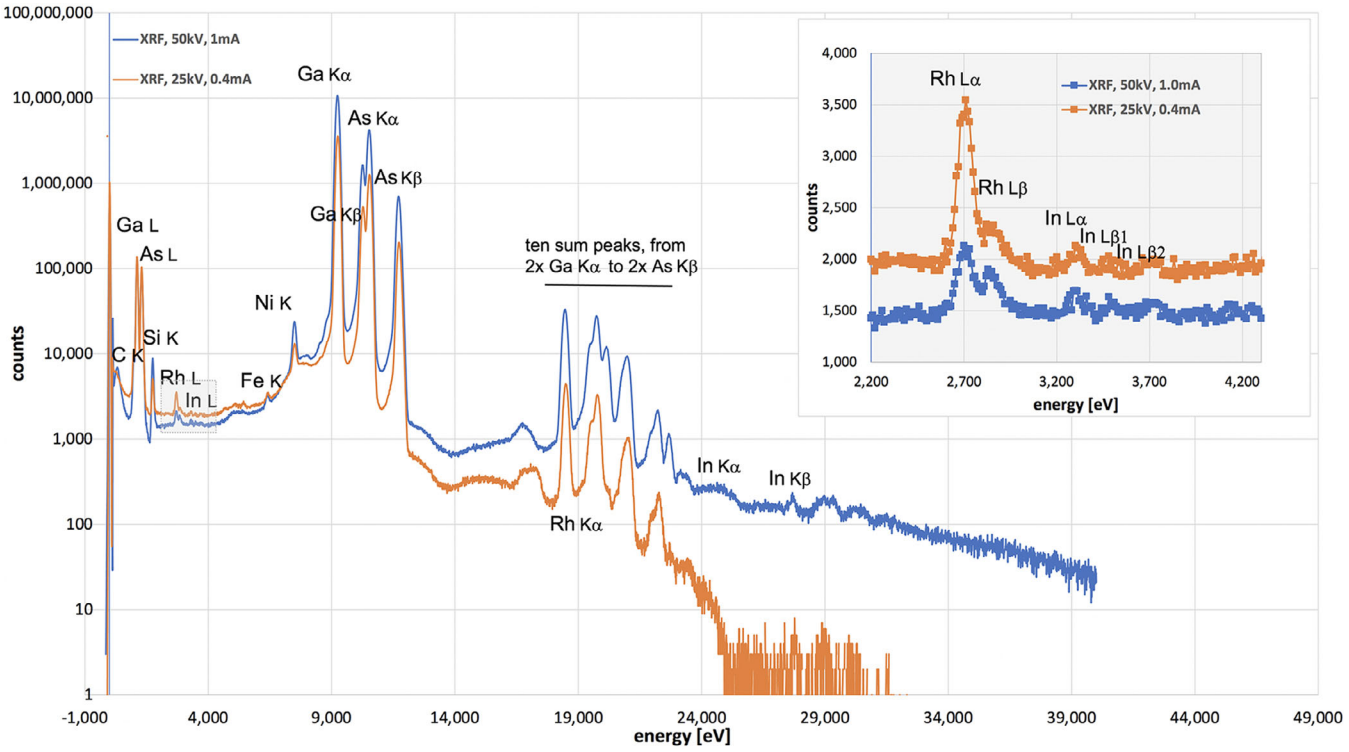

FIGURE 5 Micro-XRF spectra of InAs-on-GaAs sample AF9151 at 25 kV (with a 60 mm^2 SDD) and 50 kV (with a 30 mm^2 SDD). The area of 2.2–4.2 keV around the Rh L and In L lines is shown enlarged in the top right. Acquisition time for 50kV: 76 min total, 58 min live time.

0.78 ± 0.10 nm. Using the lattice parameter of a_{InAs} = 0.606 nm, which corresponds to 2 d_{002} monolayers (ML), WDX quantification finally yields 2.5 ± 0.3 ML equivalent of pure InAs.

Micro X-ray fluorescence (μXRF) has been measured in a SEM with Quantax X Trace 2 using a poly-capillary X-ray optics coupled with a Rh target. The SEM functionality was only used for navigation and focusing. In the μXRF spectra in Figure 5, one can see that detection of the In L signal interferes with the Rh L signal from the X-ray source, which could be suppressed by a thin aluminium foil as filter commonly applied at the exit of the X-ray tube to avoid diffraction (but wasn't used here). In K signals at 24–28 keV cannot be generated by 25 kV electrons or X-rays at all, and stay weak even at 50 kV electron acceleration voltage, but the In L signals from the Lα, Lβ_1 and Lβ_2 sub-lines are all well visible. Their integrated net signal amounts to about 1400 counts here. Their quantification, however, is difficult. The InL/AsL and InL/GaL line intensity ratios of 2.15‰ and 1.46‰ measured at 50 kV are similar to what EDX and WDX observe. Full quantification necessitates, however, a comparison with either experimental XRF spectra from pure elements or calculated standards taken at the same acceleration voltage. For 50 kV, Bruker uses a database for a 60 mm^2 SDD with experimental intensities for the Ga K-line from a metallic gallium standard and for the In L-line an interpolated value for metallic indium. Correcting for the different densities between metals used as standards and semiconductors measured here, taking into account the smaller SDD used for the 50 kV measurement as well as the acquisition live time, gives an estimate of the indium thickness on the surface of 0.8 nm, with a relative error of up to 25%, corresponding to 0.8 ± 0.2 nm, or 2.6 ± 0.7 ML equivalent of pure InAs. This value lies between the earlier results from EDX and WDX, and error bars overlap.

4 | CONCLUSION

EDX, WDX and μXRF in an SEM are all able to detect a 0.8 nm thin InAs on a GaAs(001) wafer, and quantification results are consistent within the error bars. The sensitivity is best in WDX because of its low background signal. EDX has a worse sensitivity due to the high bremsstrahlung background, which makes detecting tiny peaks on top difficult. To the authors' knowledge this is the first time a sub-nm surface layer has been reliably detected and quantified by μXRF in an SEM.

The absolute quantification errors are small, with standard RMS errors for EDX and μXRF of 0.6–0.7 ML equivalent (and half of that for WDX) while the relative errors are large because they are limited by both intrinsically poor counting statistics from very thin surface layers

as well as systematic errors due to background subtraction (EDX only) and the reliability of the reference material standards because of the unavoidable slight surface oxidation of compound semiconductors as well as pure metals (used for μXRF).

Regarding practical implementation, this study strengthens the case for using SEM-EDX despite its lowest sensitivity, as this is a method commonly found in industrial and research cleanrooms, while WDX and μXRF are more elaborate techniques not normally used in cleanrooms environments. If one used a field emission SEM with higher beam current than the tungsten filament in our tabletop SEM then similar experiments could be conducted within ~10–15 min rather than 2 h, making them useful for quality control and feedback during growth and device processing.

Our comparison of the surface analysis capability of three imaging methods based on scanning electron microscopes has here only been performed for one type of material but should be extendable to all types of single layers that contain at least one chemical element that produces detectable X-rays above 100 eV (i.e. not H, He or Li) and does not occur in the underlying substrate. For native oxide layers on silicon wafers one of the authors has already shown that SEM-EDX yields sub-nm sensitivity and high accuracy.[14] A transfer to multilayers, however, would only be possible under very specific additional conditions regarding their chemistry and repetition that would require detailed modelling.

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