Surface and buried interface layer studies on challenging structures as studied by ARXPS

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Abstract

Previous extensive studies were performed at Surface Science Western on the treatment of III-V semiconductors to produce surfaces suitable for subsequent epitaxial growth. XPS was used to study oxide formation, capping techniques and to monitor changes that would occur upon thermal desorption. The effects of a remote plasma on these surfaces was studied as well as to apply thin dielectric films of Si$_3$N$_4$ in order to study interfacial properties. ARXPS was performed in many cases to ascertain oxide layer thickness, uniformity and structure. For the types of surfaces studied – mirror finished semi-conductors, ARXPS is straightforward and the angular dependence is obtained by physically altering the surface orientation with respect to the analyser. While the sample can be repositioned with care to analyse the same spot, changing the angle will effectively change the sampling area, further, surface topography can preclude the use of ARXPS. Use of parallel angle-resolved XPS (PARXPS), now available on recent instrumentation, can alleviate these problems. In this case photoelectrons are collected simultaneously from a large angle. A multichannel detector allows this to be split into smaller angles thereby giving the PARXPS spectra without physically tilting the sample. Further, since the sample is not tilted, topographical effects are minimised allowing meaningful data to be extracted from not so perfect samples. To illustrate this a detailed PARXPS study on a gallium Indium eutectic (EGaIn) will be presented. Various methods of extracting the depth information from these spectra will be discussed. Finally, the application of using PARXPS to study buried interfaces will be briefly discussed.
1. Introduction

Previous extensive studies were performed at Surface Science Western (SSW) on the treatment of III-V semiconductors – mainly GaAs and InP in order to produce surfaces for suitable for subsequent epitaxial growth. The primary analytical technique used was X-ray photoelectron spectroscopy (XPS), which allowed a convenient means to study oxide formation – both native and sacrificial, capping, as well as to monitor changes that would occur upon thermal desorption such as stoichiometry, defect formation and band bending.\cite{1-6} Construction of a remote plasma enhanced chemical vapour deposition (RPECVD) reactor allowed for in-situ studies on the effect of the remote plasma on the substrate as well as the application of a thin dielectric film of Si$_3$N$_4$ to study the interfacial properties (chemical structure, Fermi level position and so forth) of both the film and its interaction with the substrate.\cite{7} The reactor was also utilised for the H-plasma assisted decapping of both sacrificial oxide-capped and As-capped surfaces of InGaAs.\cite{4}

Since the oxide surface and interfacial region is of the order of just a few nanometers, XPS is an ideal technique to study the interfacial region being able to analyse down to a depth of 7 – 10 nm. While shifts in the Fermi level position can give an indication of the introduction/removal of defects, angle resolved XPS (ARXPS) can provide a means of performing non-destructive depth profiling to ascertain such parameters as oxide layer thickness and structure, uniformity of applied over layers, and the surface/interface composition after various treatments. For example, in an XPS study on InP treated surfaces\cite{1}, curve-fitting yielded three oxidized components for In in its 3d$_{5/2}$ spectra whose relative intensity did not vary with angle thereby implying an homogenous distribution within the oxide layer. However, the corresponding P component showed a variation of angle between the two oxidised components that could be fitted to the envelope suggesting a layered structure with the higher oxidised component closer to the surface. In a similar manner, ozone-formed oxides on GaAs\cite{6} showed a non-uniform distribution in three As-oxide components whereas the 2 Ga components were not sensitive to depth.

The thickness of the oxide layer can be calculated by implying a Beer-Lambert type expression:

\[ I = I^0 \exp \left( - \frac{d}{\lambda \sin \theta} \right) \]

[1]
Where \( I \) is the measured intensity, \( I^0 \) is the concentration found in a pure layer, \( d \) is the overlayer thickness, \( \lambda \) is the electron inelastic mean free path and \( \theta \) is the take-off angle (relative to the surface). Thus a model can be built up, namely:[8]

\[
\frac{I_B}{I_A} = \frac{I_B^0 \cdot f \left( 1 - \exp \left( -\frac{d}{\lambda \sin \theta} \right) \right)}{I_A^0 \cdot \left[ (1 - f) + f \cdot \exp \left( -\frac{d}{\lambda \sin \theta} \right) \right]} \quad [2]
\]

Where \( f \) accounts for the uniformity of the coverage. In most cases \( f \) is taken as 1, as was the case when Flinn and McIntyre[5] performed calculations on the UV/Ozone oxidation of GaAs using a modified version of the Laplace Transform model of Bussing and Holloway[9]. It was observed that UV/ozone treatment of <100> GaAs surfaces prepared by thermal desorption produced uneven oxide films yielding poor ARXPS profiles. Inclusion of the uniformity factor, \( f \), may have corrected for this.

In a similar manner, Lau et al.[10] calculated the overlayer thickness of polysulphide-treated InP surface assuming a uniform layer-by-layer structure. This is in contrast to calculations performed on \((NH_4)_2S\) passivated of GaP surfaces[11] where a dramatic increase in estimated thickness was observed with angle when a uniform coverage was assumed. Following work of McKeown et al.,[12] \( f \) was varied until a consistent average value was obtained with angle.

For the types of samples studied above – mirror finished, flat semi-conductors, ARXPS as conducted was straight-forward and angular dependence could be obtained by simply changing the take-off angle of the emitted photoelectron by physically altering the surface orientation of the sample with respect to the analyser. However, while the sample can be repositioned with care to analyse the same spot,[13] changing the angle will effectively change the sampling area. Further, surface topography or non-uniform overlayer thickness[5] can preclude the use of ARXPS where the sample has to be physically shifted. Many of these problems can be overcome by use of parallel angle resolved XPS (PARXPS). In this case photoelectrons are collected simultaneously over a large angle. A 2-d multichannel detector allows the energy spectrum to be collected in one axis while the other axis splits the angular acceptance into smaller angles[13] thereby giving ARXPS without physically tilting the sample. Further, since the sample is not tilted,
To illustrate the application of PARXPS on challenging structures, the results from a detailed study on a eutectic alloy of gallium and indium (EGaIn) will be presented. Interest in the development of liquid metal-based platforms, where the passivating oxide is important, include heat-free solders, flexible electronics, electro-actuation, and as electrodes to study charge transport across self-assembled monolayers. One such system is EGaIn (eutectic gallium indium). Under atmospheric conditions its surface oxidises rapidly to form a protective oxide skin, which can be drawn into a tip. The goal of this work was to estimate the composition, thickness and reproducibility of the protective layer on this electrode. As discussed, ARXPS allows a non-destructive means of estimating the thickness and composition of an interface, but since the tip has a small radius of curvature its use is precluded in this case. A large drop has a much larger radius of curvature and is thus relatively flat at the apex; however, since physical tilting is still not valid, use of PARXPS, where the sample is not physically tilted, is required for this type of measurement. In this paper, various methods of extracting depth information from these spectra are presented. Finally, the application of PARXPS to study buried interfaces will be briefly discussed.

2. Materials and Methods

Parallel angle-resolved XPS (PARXPS) was performed on a large droplet of a eutectic alloy of gallium and indium (EGaIn) having a composition (relative atomic %) of 78.7% Ga and 21.3% In placed on an as-received Si wafer. The size of the droplet was ~10 mm diameter, ~ 2 mm thick. The PARXPS spectra were obtained with a Thermo Scientific Theta Probe XPS system (Thermofisher Scientific, E. Grinstead, UK) located at the University of Toronto using the monochromatic Al K$_\alpha$ source with a spot size of 400 $\mu$m centred on the apex of the drop. It was assumed that the radius of curvature would be large enough for ARXPS to be valid with any effects to be further nullified since the spectra were collected in parallel mode from the same spot without physically tilting the sample. Following an initial survey spectrum (pass energy - 200 eV, total acceptance angle - 60$^\circ$), moderately high-energy resolution spectra (50 eV pass energy) for the Ga 2p, O 1s, C 1s and the Ga 3d / In 4d spectral regions were obtained with the total acceptance angle of 60$^\circ$ being divided into 16 channels.

Since the Ga 3d and In 4d lines overlap, high energy spectra were obtained on a similar large drop using a Thermo Scientific K-Alpha XPS system (Thermofisher Scientific, E.
Grinstead, UK) also located at the University of Toronto. As with the Theta Probe, a monochromatic Al Kα source with a spot size of 400 μm centred on the apex of the drop was used, however, the emitted photoelectrons were collected normal to the sample surface using a pass energy of 5 eV. Prior to this, a survey spectrum was obtained on the same area using a pass energy of 150 eV. All spectral collection and processing with the K-Alpha were performed using software provided with the instrument (Avantage - Thermofisher Scientific, E. Grinstead, UK) as was also the case with the spectra obtained on the Theta Probe. The higher resolution obtained with the K-Alpha allowed for an unambiguous fit, the separations of which where fixed when applied to the spectra obtained on the Theta Probe, as well as the spin-orbit (S-O) parameters.

3. Results and Discussion

3.1 XPS Results

The survey spectrum for the EGaIn drop obtained on the K-Alpha with the spectral regions of interest labeled is shown in Figure 1. As well as the expected peaks from EGaIn/oxide, some adventitious C was present. The high resolution fit of the Ga 3d / In 4d region as obtained on the K-Alpha is shown in Figure 2. A Shirley background[19] was applied to the peak, which itself, was on top of a continuous sloping background. The observed peaks can be assigned to those associated with In metal, In oxide, Ga metal and both a Ga oxide and sub-oxide. Both the Ga and In metal spin-orbit are clearly resolved as is the In oxide component, thereby allowing for an unambiguous fit. The Ga oxide and sub-oxide were not deconvoluted into their respective S-O components as they were well separated from other components and use of the appropriate sensitivity factors would yield the correct relative atomic concentrations.

Since the signal obtained with the PARXPS is split between 16 channels, a compromise has to be made between resolution and count-rate. Figure 3 shows the Ga 3d / In 4d spectrum obtained at a take-off angles of 44.375° relative to the normal. The inferior resolution is clearly apparent from the Ga 3d metal peak. However, application of the separations obtained from the K-Alpha high-resolution spectrum allows for a satisfactory deconvolution. Also shown in Figure 3 are the respective fits for the O 1s and C 1s regions obtained at the same take-off angle.

An overlay of all 16 angles for the Ga 3d/In 4d region is shown in Figure 4. It is clear that as the take-off angle relative to the normal increases, the Ga oxide peak increases relative to the metal peaks. The variation in relative atomic % of the components with
angle is also shown both with and without C/O, the latter to emphasize the metal/oxide layer variation.

3.2 Extraction of Depth Information
3.2.1 Relative Depth Plot (RDP) and Thickness Calculations from ARXPS
The RDP method\textsuperscript{[14]} provides a simple means of estimating depth distribution in a multilayer system which is independent of any model or material properties. For each species the ratio of the log of peak intensity at near grazing is taken to that at near normal emission. While it does not give thickness or depth values, the positions are related to the “average” depth of that species and, as such, by showing the ordering of the layers, provide a good starting point for subsequent thickness calculations. Figure 5 shows the RDP plots for the EGaIn/oxide structure. Also shown is the proposed ordering of the oxide structure on top of the eutectic.

Thus the following model can be proposed:

Adventitious C: Predominantly C (though some C-O bonding apparent from XPS)
Oxide: Ga$_2$O$_3$
Ga$_{(2-x)}$In$_x$O$_3$
Eutectic: EGaIn

Because of the large radius of curvature, the area at the apex can be considered relatively flat, thereby allowing one to estimate the overlayer thickness by application of the typical 2-layer model

\[
\frac{I_B}{I_A} = \frac{I_B^0 \cdot (1 - \exp \left(-\frac{dB}{\lambda_B \cos \theta} \right))}{I_A^0 \cdot \exp \left(-\frac{dB}{\lambda_A \cos \theta} \right)} \quad [3]
\]

which is Equation [2] with \( f = 1 \) (i.e. uniform coverage) and the take-off angle, \( \theta \), taken relative to the normal as opposed to the surface. \( I_B \) and \( I_A \) are the measured intensities of the selected peaks for the overlayer and substrate respectively, while \( I^0 \) denotes the respective intensities found in a thick/pure layer. \( \lambda_B \) and \( \lambda_A \) are the respective inelastic mean free paths through an overlayer of thickness \( dB \). The values used in this paper have been estimated from Tanuma \textit{et al}\textsuperscript{[20]} and should be adequate for the purposes of this study.
The calculation can be done in two stages where the substrate and overlayer are defined as follows:

- Substrate is the oxide layer, while the overlayer is adventitious C.
- Substrate is the eutectic, with the overlayer being the oxide layer. The adventitious C layer is ignored since it will affect both underlayers.

**Adventitious C layer:** Looking at the C 1s spectrum, there is little C-O functionality compared to the hydrocarbon peak and so \( I_C^0 \) is taken to be 100%.

The variation of \( O/Ga(\text{ox+sub}) \) with angle is shown in Table 1 and is relatively constant. Taking average value of \( O1s(\text{met})/Ga(\text{ox+sub}) \) between angles 36.875° and 63.125°, a composition of this “pure” layer can be obtained, namely Ga\(_{18.4}\)O\(_{24.4}\). This is assuming that the amount of In oxide is small and can be ignored. Thus a value of 43% is obtained for \( I_{\text{ox}}^0 \).

The values for \( I^0 \) can now be substituted into Equation (3), which can be re-arranged and upon taking the ln yield a plot with slope \( d/\lambda \) as can be seen in Figure 6. The curve shows slight deviation from a straight line at high take-off angles (relative to the normal), possibly due to the slight curvature of the actual sample, and these points (1/cos \( \Theta \) > 3) have been ignored in obtaining the slope. \( \lambda \) has been assumed to be the same for C and Ga (they will vary between 2.5 and 3 nm) in order to simplify the expression. They will vary between 2.5 and 3 nm and thus an estimate of 0.64 – 0.77 nm is obtained for the C overlayer.

**Oxide thickness:** This can be obtained in a similar manner by considering the variation of intensity of Ga in the metal with that in the oxide as the angle is changed. Since the adventitious C will affect both layers, it can be ignored. \( I_{\text{ox}}^0 \) (43%) was obtained above, and \( I_{\text{met}}^0 \) was obtained from the eutectic composition (78.7%). The resulting plot is shown in Figure 7. Taking \( \lambda \) as 3 nm gives an estimated oxide thickness of 0.7 nm.

3.2.2 Thickness Calculations from differences in escape depth.

Given that there is still some curvature on the large drop, is PARXPS still valid? Depth information can be obtained as well by utilizing the different kinetic energies of the Ga 2p\(_{3/2}\) and Ga 3d photoelectrons. The Ga 2p\(_{3/2}\) region was also collected, and as for the 3d could be fitted with 3 components (Figure 8). Table 2 summarises the relative atomic peak intensities for the 3 components for both the Ga 2p\(_{3/2}\) and Ga 3d spectra collected with the same pass energy. Of interest is the attenuation of the Ga metal signal. By ratioing the Beer-Lambert type expression for each level:
\[ \frac{I_{2p}}{I_{3d}} = \frac{I_0 \exp \left(-\frac{d}{\lambda_{2p}} \cos \theta \right)}{I_0 \exp \left(-\frac{d}{\lambda_{3d}} \cos \theta \right)} \]

where, \(\lambda\) has been taken to be 1.2 nm for the 2p electron and 3 nm for the 3d, a thickness of 1.32 nm is obtained which in excellent agreement with the PARXPS results, since it is going through both the oxide and adventitious C overlayer.

Further corroboration of the oxide thickness has been provided by TEM studies of 2 adjoining EGaIn particles where the thickness across them was ~1.2 nm translating to an individual oxide thickness of ~0.6 nm.[21]

The primary motivation for this work was the development of liquid metal electrodes to study charge transport across self-assembled monolayers.[18] As the tips were ~ 100 \(\mu\text{m}\) in diameter this proved to be a very challenging surface and PARXPS was not appropriate and so the drop was used to model the oxide structure/thickness. However, does the tip form a similar oxide? The Ga 2p/3d peaks were compared for an unused tip, a 25x-cycled tip and the drop. In each case the spectra were comparable.

3.2.3 Optimisation of profile by a Maximum Entropy Model.

So far we have ignored the formation of In oxide – Ga preferentially oxidises, with the RDP plot indicating formation of some In oxide at the eutectic surface. This has also been observed with GaInSn[20+2] where it was stated that In (and Sn) were almost stable in their metallic state. It is thus unlikely that the In forms a separate oxide phase, albeit small, but is rather part of the Ga suboxide phase and hence can be ignored in the thickness estimates. However, is it possible to generate a more optimized depth profile from the ARXPS data and thus extract more meaningful information? One such approach is the Maximum Entropy Model.[14,23]

Originally suggested by Smith and Livesey[23] as a means of extracting depth profile information from ARXPS data, the Maximum Entropy Model allows for a plausible solution albeit by no means unique.[14] Briefly, generate a trial profile and calculate the ARXPS data using the usual Beer Lambert expression (Equation [1]). Minimise the error between the observed and calculated data while maximizing the entropy term, which is done by maximizing the joint probability function.[14, 24] As mentioned, it allows for a plausible solution, however, constraints can be added to prevent chemically
unreasonable solutions. These will include knowledge of the substrate composition, selection of like stoichiometric components and addition of terms to allow for variations from stoichiometry. While other approaches exist for modeling ARXPS data, including more complex structures, these go beyond the intended scope of this study. A review of the current state-of-the-art and future prospects can be found in a report on the 47th International Union for Vacuum Science, Technique and Applications (IUVSTA) workshop on ARXPS and references therein.\[25\]

The results from one model fit are shown in Figure 9, which shows the peaks profile as well a fit unit profile. The layered structure is indicated below the fit unit profile and confirms the presence of a Ga$_2$O$_3$ layer on top of an interfacial region. No attempt has been made to fully optimize this region and it has simply been assigned as Ga$_{1(2-x)}$In$_x$O$_3$. Two forms of O are implied in the adventitious C layer from this plot. “B” is likely associated with the hydrocarbon, whereas “A” could reflect surface –OH groups and/or O-containing organic functional groups, which can H-bond to the oxide/OH surface.

3.3 Buried Interfaces
In evaluating the composition and thickness of the oxide skin on the eutectic surface, the adventitious C overlayer could be ignored, as it would affect the signal from both the substrate and the overlayer. This could equally be applied to systems with buried interfaces. Capping/decapping\[26\] of surfaces may be required in cases where it is not possible to prepare and measure the surface properties in situ, or to transfer the sample under vacuum or inert atmosphere. If the cap is thin enough, it is then possible to study the interfacial region, as was the case in the RPECVD of Si$_3$N$_4$ on III-V semiconductors.\[7\] While ARXPS can still be used to study the interfacial region, PARXPS allows any variation in cap thickness to be ignored. Such work is currently underway to study oxide thickness on III-V semiconductors following various passivation treatments and capping with alumina.\[27\]

4. Conclusions
PARXPS provides a powerful means of estimating film thickness on surfaces, which cannot be analysed by the more usual method of physically tilting the sample. Use of a simple Beer-Lambert type expression allowed for the estimation of the film thickness by assuming that the oxide was predominantly Ga$_2$O$_3$ + sub-oxide and it was calculated to be of the order of 0.7 nm. A model based upon the Maximum Entropy method allowed
the oxide structure to be ascertained more accurately. The results confirmed the prediction of the RDP that the oxide, while predominantly Ga$_2$O$_3$ was on top of an interfacial layer given by Ga$_{2-x}$In$_x$O$_3$. Finally, the profile of the adventitious C overlayer suggested that it consisted of O-functionalised hydrocarbon and surface –OH and/or O-organic functional groups, which could H-bond to the oxide/OH surface.

References


[27] R.N.S. Sodhi, D. Lynall and H. Ruda (to be published)

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### Table 1:

Variation of O/Ga(Ox+Sub) with angle. Taking an average value of the O1s(met)/Ga(Ox+sub) ratio between angles 36.875° and 63.125° (1.33 +/- 0.06) yields a composition of Ga18.4O24.4 for this “pure” layer. Sensitivity factors of 2.93 and 1.085 were used for O 1s and Ga 3d respectively.

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<th>Ga(Ox+Sub)</th>
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Table 2: Relative Atomic % for the Ga oxide, sub-oxide and metal taken from the Ga 2p$^{3/2}$ and 3d spectral regions.

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<th>0.651</th>
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**Figures Captions**

Figure 1. Survey XPS spectrum for EGaIn obtained on the Thermo Scientific K-Alpha. Spectral regions of interest are labeled.

Figure 2. High-resolution spectrum (pass energy – 5 eV) and fit of the Ga 3d / In 4d region obtained on the K-Alpha. S-O denotes the d_{5/2} – d_{3/2} spin-orbit pair.

Figure 3. Ga 3d / In 4d, C 1s and O 1s XPS spectra (pass energy – 50 eV) obtained on the Theta Probe. The take-off angle (relative to normal) was 44.375°.

Figure 4. PARXPS spectra (16 angles – 3.75° increment) for the Ga 3d / In 4d region of EGaIn. The solid lines indicate the two extreme take-off angles (with respect to the normal). The variation of the relative atomic % with angle with and without C and O contributions is also shown.

Figure 5. Relative Depth plot for EGaIn / oxide structure. The proposed oxide structure on top of the eutectic is indicated.

Figure 6. Estimation of the thickness of adventitious C layer from Equation \([3]\), which has been re-arranged to give a plot with slope d/\(\lambda\) (see text for details).

Figure 7. As Figure 6 but for the oxide thickness.

Figure 8. Ga 2p_{3/2} region for EGaIn showing a 3-component fit. The relative atomic peak intensities for both this region and the Ga 3d spectrum are presented in Table 2.

Figure 9. Results for one Maximum entropy model fit. Both the peaks profile and a fit unit profile are shown. The layered structure is indicated below the fit unit profile.