Application Note

AR-XPS at environmental conditions

Angle-resolved x-ray photoelectron spectroscopy (AR-XPS) can be used for non-destructive sample depth profiling. Here we demonstrate the power of this technique for determination of thicknesses of thin films with sub-nanometer resolution under high vacuum (HV) conditions as well as under environmentally relevant conditions (0.1 Torr). The experiments where performed on native silicon oxide using a differentially pumped Scienta Omicron R3000 HP analyser and a high pressure adapted Scienta Omicron MX650 monochromated aluminium K α x-ray source, at the Philadelphia environmental XPS (E-XPS) system. The data are presented in Review of Scientific instruments (F. Mangolini, 83 (2012) 093112).

Angle-resolved XPS (AR-XPS) relies on the acquisition of XPS spectra at different emission angles (i.e., the angle between the surface normal and the direction of the photo-emitted electrons), thus allowing the characterisation of the sample with different surface sensitivities and in a nondestructive manner. Parallel acquisition systems have opened the possibility of collecting data at different emission angles simultaneously, allowing AR-XPS analysis without tilting the sample to be performed. Compared to conventional angle-resolved XPS, which is performed by tilting the sample to change the emission angle, acquiring XPS data in parallel mode permits the analysis of large samples, performing small-area analysis without difficulties in aligning the specimen and without any change of the analysed area during the measurements.

To demonstrate the possibilities of the angle-resolved E-XPS instrumentation a well known sample was used. The native oxide of silicon is highly studied and the thickness of the oxide layer is well known. Angular measurements of this system were performed for several sample to spectrometer tilt geometries under HV conditions as well as environmental conditions of 0.1 Torr nitrogen pressure (Figure 1). As the nitrogen does not react with the surface it is possible to compare the performance of the E-XPS under these two different pressure conditions.
As seen in Figure 1 the intensity of the Si and SiO_2 changes with emission angle (Θ) due to the electron escape depth. This behaviour results in a maximum of bulk intensity contribution for normal emission (NE) and an enhancement of the surface species intensity for grazing emission.

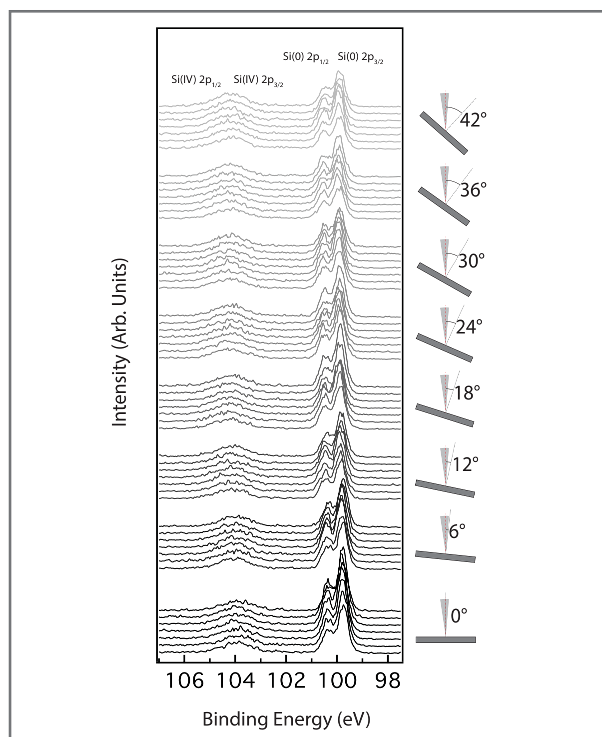

Figure 1: A set of angular resolved Si 2p spectra from silicon oxide recorded at different tilt angles, as indicated in figure. Each series has a 14 degree angular span and each spectra is integrated over 2 degrees.

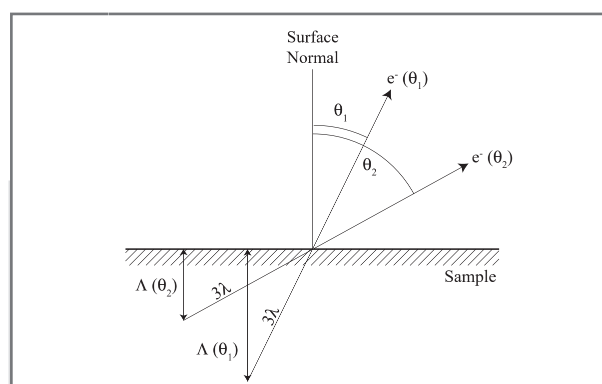

Figure 2: Schematic illustration of a thin film sample.
The intensity of the bulk and surface features in an XPS spectrum is dependent upon the mean free path of the electrons and show cosine behaviour with respect to Θ. Two different emission angles Θ1 and Θ2 are shown in the figure, where Θ1 is more bulk sensitive than Θ2 due to the different distances the electrons travel inside the material.

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For the silicon oxide we can use a simplified and well established equation for depth determination, as the photoelectrons have similar energies, when determining the oxide thickness using the elemental Si and oxidised Si 2p peaks (see Figure 1). The thickness of the oxide layer (dSiO2) can in this case be expressed as in Equation 1:

$$d_{SiO2}=L_{SiO2}\cos\Theta\ \ln\left[1+\frac{R}{R_\infty}\right] \qquad \text{(Eq 1.)}$$

Where $LSiO_2$ is the attenuation lengths of the Si 2p photoelectrons in SiO_2. The attenuation length of the electron is the probability e^{-1} of an electron that is ionised to exit the material without being inelastically scattered. Here we use 3.485 nm for $LSiO_2$ as suggested in the ISO/DIS 14701 standard.

R is the ratio between the intensities of the oxidised ($ISiO_2$) and elemental silicon (ISi) peaks for the studied sample ($R=ISiO_2$ / ISi), which is compared with the ratio ($R\infty$) of the intensities measured on a pure silicon sample and a pure silicon oxide sample. The peak intensities for bulk samples can be measured on freshly-grown surface (i.e., without any contamination). For Silicon oxide $R\infty$, following the ISO/DIS 14701 standard, has a value of 0.9329.

Plotting the logarithmic function appearing in equation (1) as a function of the inverse of the cos Θ will produce a line whose slope is the ratio of the thickness of the oxide layer and the photoelectron attenuation length (d_{SiO2} / $LSiO_2$). d_{SiO2} is here calculated for each set of angle resolved spectra, measured at different tilt angles. The resulting film thicknesses are displayed in Figure 3. Here it is seen that the thickness of the oxide film is determined to be 1.3-1.4 nm in HV and 0.1 Torr, which is well in agreement with values reported in literature. These measurements show that it is very powerful to use the angular resolved mode of the analyser to perform depth profiling experiments in a non destructive way.
This is very promising for future experiments performed under environmental conditions (0.1 Torr), as the depth profile can be recorded in a single spectrum without having to change tilt angle.

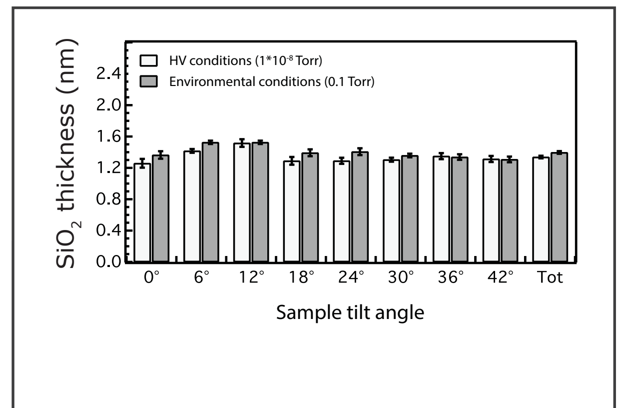

Figure 3: Calculated SiO_2 film thickness for HV and environmental pressure conditions according to Equation 1 using series of spectra shown in Figure 1.

This is especially useful when measure a series of spectra during film deposition, heating experiments, etc.

The experiments presented here have been performed in a joint collaboration between the Carpick group of University of Pennsylvania and Scienta Omicron at the E-XPS instrument situated in Philadelphia and the results is presented in Review of Scientific instruments (F. Mangolini, 83 (2012) 093112). The E-XPS consists of a differentially pumped Scienta Omicron R3000 HP analyser and a high pressure adapted MX650 monochromated aluminium Kα x-ray source. This type of analyser is capable of measuring angular resolved spectra with a 14 degree acceptance angle and an angular resolution better than 0.5 degrees.

This application note was made in collaboration with Filippo Mangolini and Robert Carpick at University of Pennsylvania, USA.
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