

Central Lancashire Online Knowledge (CLOK)

| | |
|----------|--|
| Title | Thin film structural analysis using variable-period x-ray standing waves |
| Type | Article |
| URL | https://clock.uclan.ac.uk/24365/ |
| DOI | https://doi.org/10.1103/PhysRevB.98.165402 |
| Date | 2018 |
| Citation | Gibson, Joshua S., Syres, Karen orcid iconORCID: 0000-0001-7439-475X, Buckley, Matthew, Lee, Tien-Lin, Thakur, Pardeep K. and Jones, Robert G. (2018) Thin film structural analysis using variable-period x-ray standing waves. Physical Review B, 98 (16). ISSN 2469-9950 |
| Creators | Gibson, Joshua S., Syres, Karen, Buckley, Matthew, Lee, Tien-Lin, Thakur, Pardeep K. and Jones, Robert G. |

It is advisable to refer to the publisher's version if you intend to cite from the work.
<https://doi.org/10.1103/PhysRevB.98.165402>

For information about Research at UCLan please go to <http://www.uclan.ac.uk/research/>

All outputs in CLOK are protected by Intellectual Property Rights law, including Copyright law. Copyright, IPR and Moral Rights for the works on this site are retained by the individual authors and/or other copyright owners. Terms and conditions for use of this material are defined in the <http://clock.uclan.ac.uk/policies/>

Supplementary Material

Thin film structural analysis using variable period X-ray standing waves

Joshua S Gibson¹, Karen L Syres^{1,3}, Matthew Buckley¹, Tien-Lin Lee², Pardeep K Thakur² and Robert G Jones¹

¹ School of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK

² Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK

³ Current address: Jeremiah Horrocks Institute, University of Central Lancashire, Fylde Road, Preston, PR1 2HE

A. X-RAY CONSTANTS

Sample 1 consisted of a thin layer SiO₂ (layer 2) on bulk Si (layer 3). The values of β and δ ¹ used to calculate the electric field intensity of the standing wave in layer 2 and in the substrate layer 3 are shown in Table A1.

Sample 2 consisted of H₂O-CHCl₃-[OMIM][BF₄] (layer 2) on SiO₂-Si (layer 3). The δ values of H₂O, CHCl₃ and [OMIM][BF₄] are sufficiently similar, table A1, that the δ value for [OMIM][BF₄], which was the dominant material in the adlayer, was used for layer 2. Similarly, the δ values for SiO₂ and bulk Si are sufficiently similar, table A1, with bulk Si the dominant material, and sufficiently different to the δ values of layer 2, that the β and δ value for Si was used for layer 3.

Table A1

X-ray constants β , δ ¹ and critical angles α_c calculated at 3000 eV for elements and compounds in this work using the given density.

| | $\beta / 10^{-6}$ | $\delta / 10^{-5}$ | $\alpha_c / ^\circ$ | density / g cm ⁻³ |
|--------------------------|-------------------|--------------------|---------------------|------------------------------|
| Si | 7.4998 | 5.4303 | 0.5828 | 2.3289 |
| SiO ₂ | 4.1625 | 5.1740 | 0.5971 | 2.2 |
| [OMIM][BF ₄] | 51.271 | 2.7828 | 0.4274 | 1.08 |
| CHCl ₃ | 6.5462 | 2.9501 | 0.4401 | 1.49 |
| H ₂ O | 0.6445 | 2.6159 | 0.4144 | 1.0 |

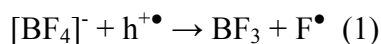
The densities used to calculate the X-ray constants in table A1 are room temperature values. For a given atomic composition the β and δ values scale linearly with density,

hence changes in density due to temperature (thermal expansion), phase change or porosity will alter the value. In this work the 90 K measurement temperature amounts to a density change of $< +1\%$ for Si and SiO_2 , $\approx +5\%$ for CHCl_3 and $[\text{OMIM}][\text{BF}_4]$, and $\approx -8\%$ for water, over the room temperature values for perfectly ordered materials. However some level of porosity is expected for the organic materials due to the deposition method at low temperature, which would tend to decrease the density, in opposition to the increase due to lower temperature. With no accurate measure of the porosity available, we have simply used the room temperature density values. For water, with its decrease in density at 0°C and decrease due to any porosity, the room temperature value used may be too large. However, the water layer is thin, so any inaccuracy in the density and hence X-ray constants has little effect on the calculations.

For porous materials (e.g. metal organic frameworks (MOFs)) where the pores in one material were filled with a second material, then the total density and the relative atomic proportions of absorbent and absorbate would be required to calculate the X-ray constants.

B. POSSIBLE DESORPTION OF BF_3 DAMAGE PRODUCT FROM A 90 K SURFACE

Reference ² describes how radiation damage produces holes, $\text{h}^{+\bullet}$, and electrons, e^\bullet which then interact with ionic liquids. $[\text{BF}_4]^-$ reacts with a hole to produce BF_3 and F^\bullet



the fluorine atom then reacts with available C-H groups to produce HF. At 90 K HF (boiling point 292.7 K) will not evaporate and will remain in approximately the location it was formed in the IL slab, as described for other damage products in the main paper. However, BF_3 (boiling point 172.8 K) would be expected to evaporate from a surface at 90 K. The Antoine equation for the vapour pressure of BF_3 is

$$\log_{10}(P) = A - (B/(T+C)) \quad (2)$$

where the units of P and T are bar and Kelvin respectively and $A=4.68215$, $B=663.463 \text{ K}$ and $C=-30.795 \text{ K}$ for $118.5 < T < 172.5$, ³. Extrapolating this to $T=90 \text{ K}$ gives $P=3 \times 10^{-7} \text{ bar}$, i.e. $3 \times 10^{-4} \text{ mbar}$. This is much higher than the 10^{-10} mbar at which the experiments were carried out so bulk BF_3 would evaporate. Should the BF_3 be stabilised by dipole or van der Waals interactions with surrounding IL material, it

would still likely have a vapour pressure greater than 10^{-10} mbar and hence would still desorb.

C ESTIMATE OF ERRORS IN FITTINGS

Sample 1: SiO₂/Si

Figure A1 shows the experimental data for the bulk Si substrate (Si 2p_{3/2} bulk and Si 2p_{1/2} bulk) and the SiO₂ overlayer (Si 2p_{3/2} SiO₂, Si 2p_{1/2} SiO₂ and O 1s SiO₂) with VPXSW simulations for the bulk and overlayer for overlayer thicknesses of 0, 10, 20, 30 and 40 Å. $\lambda = 58$ Å for photoelectron transmission through both the Si substrate and the SiO₂ overlayer and all simulations have been shifted by 0.025 ° to align the angular scales. The error in the thickness determination is estimated ± 10 Å for both, though for the bulk signal it probably slightly smaller.

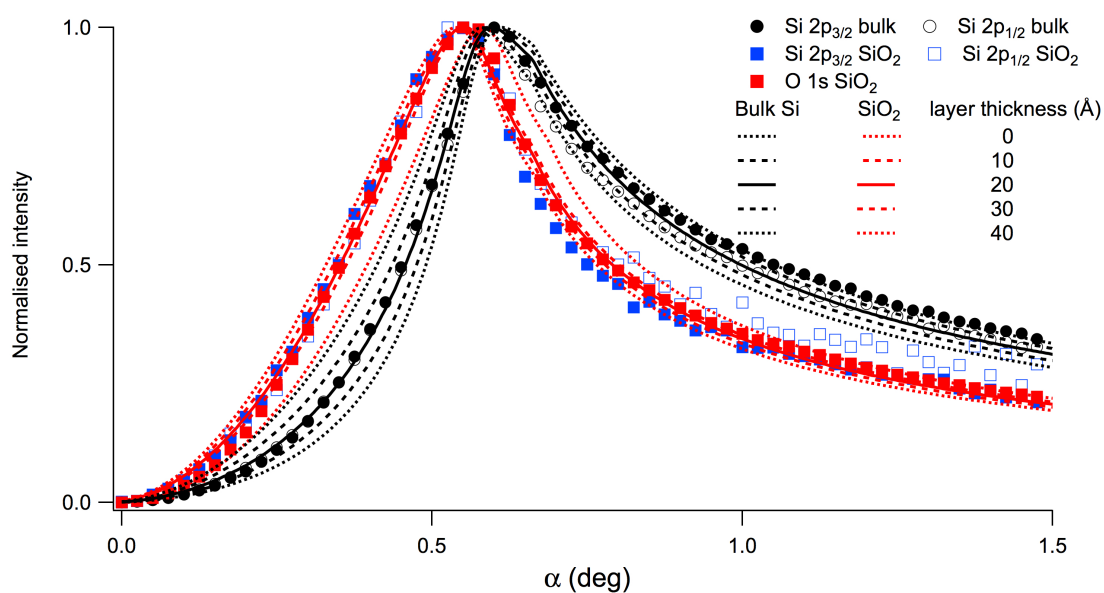


Figure A1. VPXSW scans of the O 1s, Si 2p_{1/2} and Si 2p_{3/2} for Si bulk and SiO₂. The simulations for bulk and oxide layer (normalised to 1 and corrected for footprint and path length) are for an oxide layer thicknesses of 0, 10, 20, 30 and 40 Å thick, see cartoon in Fig. 6 of paper.

Sample 2

CHCl₃-H₂O marker layer.

The accuracy of the fitting parameters for the marker layer containing the CHCl₃ and H₂O have been determined as follows. The middle of the marker layer is at position

z_0 and has thickness $\pm t/2$ either side of this position. Here we use the marker layer thickness, t and the total thickness of the adlayer, d_2 . Figure A2 A shows the chloroform (Cl 1s_{tot}) and water (O 1s_{tot}) data and simulations showing the effect of increasing the total thickness (d_2) of the organic layer for a fixed marker layer thickness of 12 Å using $\lambda = 9$ Å for the Cl 1s_{tot} signal. The fit is 223 ± 15 Å. Figure A2 B shows the effect of varying the marker layer thickness for a fixed total thickness of 223 Å. There is hardly any change on going from 2 Å to 40 Å. This arises because the value of λ is very small, which means only Cl 1s electrons from the top $\approx 3\lambda$ (27 Å) contribute significantly to the measured signal. Thus any further increase in marker layer thickness beyond 27 Å provides little extra signal and hence no change in the profile of the curves. So the outermost part of the CHCl₃ marker layer can be located at 223 ± 15 Å from the SiO₂ substrate, but its thickness can only be determined as > 2 Å.

For H₂O the O 1s photoelectrons have $\lambda = 55$ Å, making them far more penetrating than the Cl 1s photoelectrons. Figure A1 B shows a VPXSW simulation for a total thickness $d_2 = 223$ Å and a marker layer thickness of $t = 12$ Å, using $\lambda = 55$ Å. It is indistinguishable from the $\lambda = 9$ Å plot. The water layer is expected to be on top of the chloroform layer and rather thin, so a thin combined layer of chloroform and water is consistent with the lack of sensitivity to λ and the close similarity of the two experimental curves for chloroform and water. So both water and chloroform are contained within a thickness of 12 ± 10 Å with the outmost part at 223 ± 15 Å. It is not possible to distinguish whether the water is above, or mixed with the chloroform.

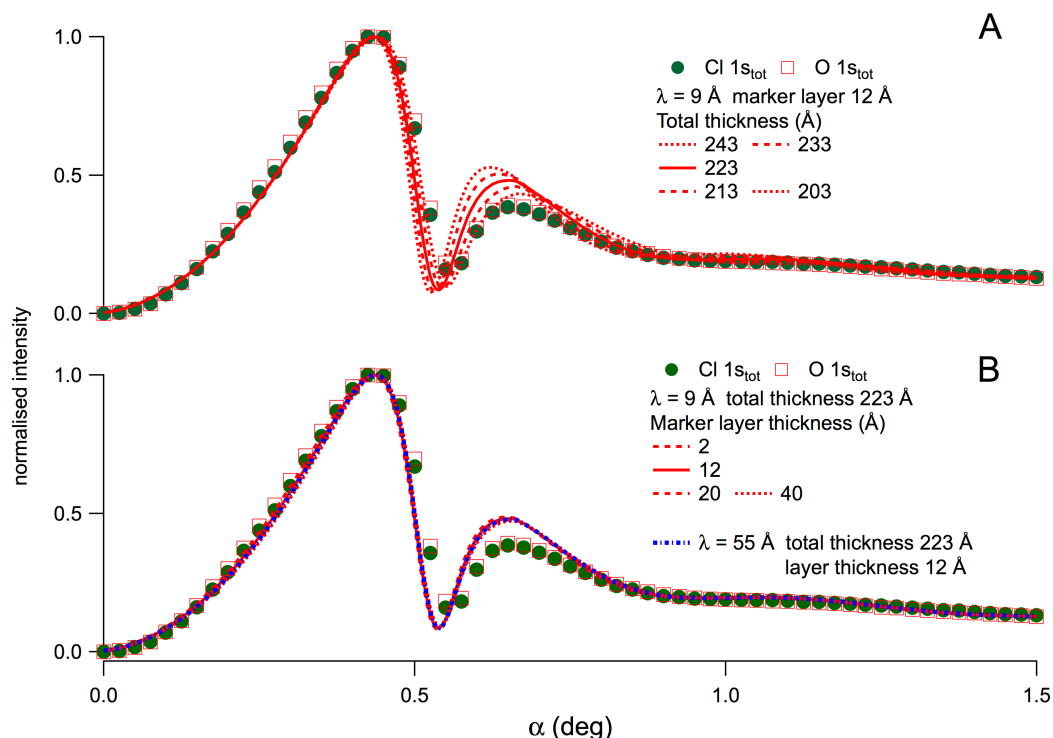


Figure A2. A, Cl 1s_{tot} and O 1s_{tot} VPXSW data with simulations using a 12 \AA thick marker layer and total thicknesses of 203, 213, 223, 233 and 243 \AA . B, Cl 1s_{tot} and O 1s_{tot} VPXSW data with simulations using a total thickness of 223 \AA and marker layer thicknesses of 2, 12, 20, and 40 \AA . All simulations used $\lambda = 9 \text{ \AA}$ except for one plot in B which used $\lambda = 55 \text{ \AA}$. All simulations are footprint and path length corrected and have been shifted by 0.025° .

[OMIM][BF₄] spacer layer

Figure A3 shows the C 1s_{tot} VPXSW data, as representative of the N 1s_{tot} and F 1s_{tot} data, with VPXSW simulations. In the simulations the marker layer is empty of N, F, and B. However, the marker layer does contain some carbon from CHCl_3 , the density of atomic carbon in the marker layer from CHCl_3 being $0.27\times$ the atomic density of carbon in the ionic liquid spacer layer (calculated using the molar volumes of the materials). The carbon atomic density within the marker layer will be lower still due to the presence of water in the marker layer as well. So the marker layer has been considered empty of carbon for the VPXSW simulations. Figure A3 A shows a fixed marker layer, empty of carbon, 12 \AA thick on an ionic liquid spacer layer of thickness that varies from 201 - 241 \AA . The dip at 0.6° and the peak at 0.7° in the experimental data are less pronounced than the simulations as the simulations have no disorder included. The best fit is $223 \pm 15 \text{ \AA}$. Figure A3 B shows a fixed total thickness of

223 Å with a marker layer thickness that varies from 2 to 42 Å. The best fit thickness is 12 ± 10 Å. Also shown in B is the boron 1s data which simulates a boron empty marker layer of thickness 42 ± 10 Å and matches the experimental boron data well.

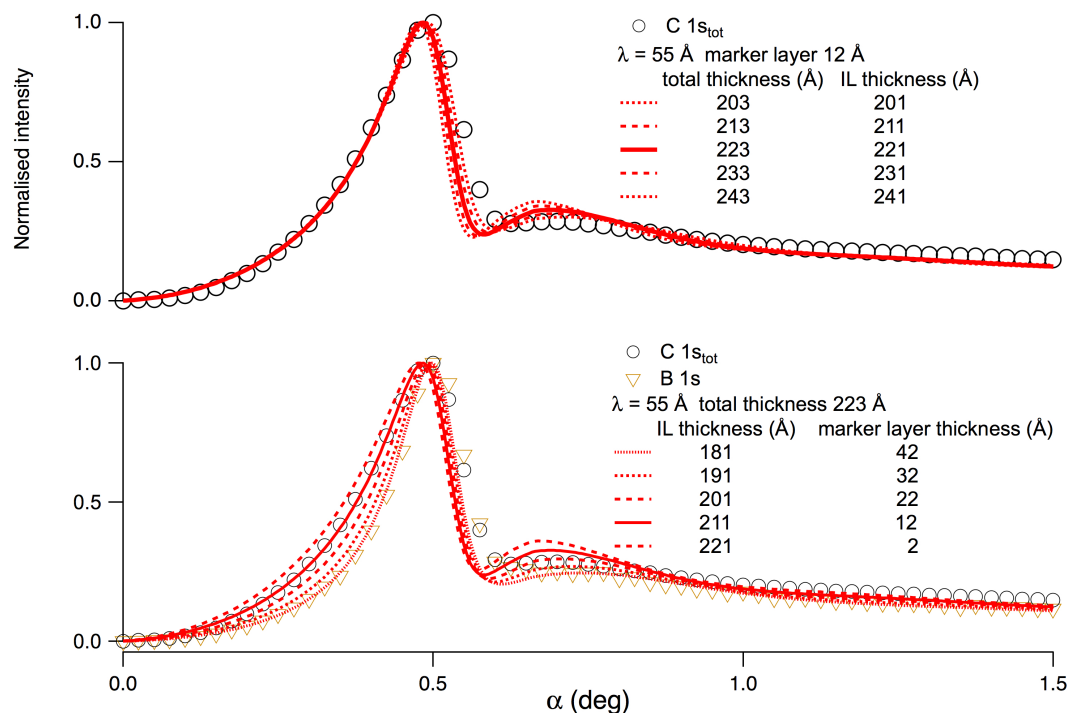


Figure A3. A, C 1s_{tot} VPXSW data with simulations using a 12 Å thick marker layer and ionic layer thicknesses of 201 to 241 Å. B, C 1s_{tot} and B 1s VPXSW data with simulations using a total thickness of 223 Å and spacer layer thicknesses of 181-221 Å. All simulations (footprint and path length corrected and shifted by 0.025°) used $\lambda = 55$ Å.

References

- 1 B. L. Henke, E. M. Gullikson, and J. C. Davis, in *Atom. Data Nucl. Data Tables*, 1993), Vol. 54, p. 181.
- 2 I. A. Shkrob, T. W. Marin, S. D. Chemerisov, and J. F. Wishart, *J. Phys. Chem. B* **115**, 3872 (2011).
- 3 NIST, in <https://webbook.nist.gov/chemistry/>, Standard Reference Database Number 69

