ATOMIC RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPY OF INTERFACES

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The ability of high resolution STEM instruments to provide EELS data at the ultimate atomic resolution offers significant new insights into interfacial phenomena. Not only can composition profiles now be collected plane-by-plane across an interface¹, but in addition, the EELS near edge fine structure can be analysed to determine the valence states of atoms at the interface, and hence the nature of the bonding across the interface plane. By applying the spatial difference technique², these effects can be studied quantitatively with high sensitivity.

Atomic resolution EELS played a critical role in explaining a completely unexpected interfacial structure found recently at CdTe/Si interfaces grown by a particular molecular beam epitaxy growth procedure³. The high resolution Z-contrast image in Fig. 1 shows the CdTe film to be terminated by Te, but in addition, for several monolayers into the Si substrate, occasional columns show brighter than the surrounding Si, although remaining in the correct position. To determine the origin of the bright columns, EELS spectra were collected plane by plane across the interface, as shown in Fig. 2. The Cd M_{45} edge decreased to zero by the second Si plane, whereas the Te M_{45} edge continued to be detected to a depth of 4 or 5 Si {200} layers. The Te arose from flooding the Si wafer with Te after cleaning, while still at high temperature. The temperature was then reduced significantly for growth, explaining the lack of Cd diffusion. Thus we can identify each bright spot in the image with a few (or possibly single) atoms of Te located substitutionally in that particular Si column. Careful observation of the relative positions of the Te and Si columns across the interface in Fig. 1 shows no sign whatsoever of localized interface dislocations, leading to the surprising conclusion that the interface is incommensurate. This conclusion is backed up by a maximum entropy measurement of a large 3.2 Å separation between film and substrate. This spacing is too high for strong covalent bonds to form, consistent with the incommensurate interface deduced from the image. The Te detected in the substrate by EELS passivates the Si surface, allowing only a Van der Waals interaction.

The remarkable sensitivity available from spatial difference analysis is shown by a study of a Ni-ZrO₂(cubic) interface, formed by the reduction of a NiO-ZrO₂(cubic) directionally solidified eutectic⁴. Accurate measurement of the interplanar spacing across the interface, from maximum entropy analysis of Z-contrast images, indicated the interface structure to be Ni-ZrO₂, rather than NiO-ZrO₂. A more sensitive and quantitative measurement of the charge state of the Ni at the interface was obtained through EELS. Ni $L_{2,3}$ spectra from bulk NiO, bulk Ni, and the Ni-ZrO₂ interface are shown in Fig. 4, after normalization for the contribution from the continuum. No edge is seen in the difference spectrum obtained by subtracting the metal Ni spectrum from the interface spectrum. A quantitative estimate of the detection limit for Ni²⁺ present in the interface plane is shown in Fig. 5. By mixing the (normalised) spectra for Ni metal and NiO in the proportions indicated, and subtracting the Ni spectrum, difference spectra could be simulated for a range of Ni²⁺ concentrations in the interface plane. It is clear that less than 4% of the Ni at the interface shows fine structure indicative of the 2+ oxidation state.

Quantitative studies of this nature will be further enhanced when EELS becomes available on higher voltage STEMs. Although inelastic excitations are less localised than the elastic scattering used to form a Z-contrast image, for all inner shell excitations, the width of the real-space cross section is less than 1 Å,

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and does not increase with increasing accelerating voltage². The reduced probe sizes available with higher voltage instruments will significantly improve the sensitivity of studies such as these.

References

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FIG. 1.--Z-contrast image of CdTe/Si interface showing large film/substrate separation.
 FIG. 2.--EELS spectra obtained plane by plane across the interface in Fig. 1.
 FIG. 3.--EELS spectra from NiO/ZrO₂ interface compared to bulk Ni and NiO.
 FIG. 4.--Simulated difference spectra showing sensitivity to Ni²⁺ concentration in the interface plane.

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