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Electron Probe Micro-Analysis at Low Accelerating Voltages: The Impacts of Surface Coatings and Oxide Layers on Quantification

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Under the low accelerating voltage conditions commonly required for high resolution electron probe micro-analysis (EPMA) even thin surface layers become significant components of the analysis volume. In a previous study the authors presented the results of modelling a mono-elemental coating on a homogenous substrate at low accelerating voltages [1]. However, for air sensitive materials it cannot be assumed that the substrate surface is pristine prior to application of a conductive coating. For example, Uranium is known to oxidize readily in air, to the extent that it cannot be considered to be oxide free unless prepared and analyzed under ultra-high vacuum conditions [2]. Here we present the results of modelling a more complex three-layer system, of an oxidized surface on a bulk homogeneous substrate, on which a conducting coating has been applied. The results are compared against experimental measurements on electro-polished depleted uranium (DU) coated with silver.

Models were calculated using GMRFilm [3] and PENEPMA [4], at accelerating voltages of 5, 7, 10 and 15kV, for a pure U substrate, with a UO_2 layer of varying thickness (5-20nm) and a Ag coat of varying thickness (5-20nm). Over the range of conditions modelled, the k-ratio can be approximated using bi-planar functions of the coating thickness, t_c, and oxide thickness, t_o: k-ratio = $at_c + bt_o + ct_ct_o + d$, where a, b, c and d are the bi-planar parameters. The coating k-ratio was found to be essentially independent of the oxide thickness so can be reduced to a simple linear relationship: Ag k-ratio = $at_c + d$.

The U Mα emitted from the oxide layer is strongly dependent on the oxide layer thickness, and weakly on the coating thickness, whilst that from the substrate is influenced by both. Conversely, the total U k-ratio is strongly dependent on the coating thickness but only weakly on the oxide thickness. Thus, whilst the substrate k-ratio, and therefore its quantification, is significantly influenced by the oxide thickness, the presence of an oxide layer is not obviously indicated from measurement of the Ag or U k-ratios.

A DU tile was electro-polished in ethanol, osphoric acid, and ethylene glycol, in the ratio 5:3:3, at 0.5nA and 19V for 5min, then transferred under Ar to a sputter coater. The tile was sequentially masked to provide an uncoated strip and three coated strips of 4.9nm, 9.9nm and 19.7nm thicknesses of Ag, as measured with an in-coater Film Thickness Monitor (FTM). The tile was analyzed at 5, 7, 10 and 15kV in a JEOL JXA-8530F FEG-EPMA, calibrated using uncoated Ag and Fe_2O_3 for Ag and O respectively, and the uncoated strip of the DU tile for U.

The Ag coating thicknesses calculated from EPMA measurements were in good agreement with each other (Figure 1a), but were ~25% higher than the FTM values. Direct measurements taken from a Focused Ion Beam (FIB) cross-section of the 19.7nm sample agree more closely with the EPMA calculated thicknesses. Measured O Kα k-ratios reveal an oxide layer of 15 – 25nm (Figure 1b), confirming the propensity of U to oxidize, even after only short exposures to air.

Calculated Bi Mα k-ratios were compared against measured k-ratios. The effect of an oxide layer on the

U standard (the uncoated DU strip) for measured k-ratios was examined and corrected for.. The results for the 4.9 and 19.7nm Ag coated strips are shown in Figure 2. For the 4.9nm strip the oxide 'corrected' k-ratios reduce the analysis error from ~10% to ~1% at low voltages. For the 19.7nm strip the 'corrected' results are less accurate than the uncorrected values, but both sets are significantly better than the FTM derived results, which show an error of ~50% at 5kV.

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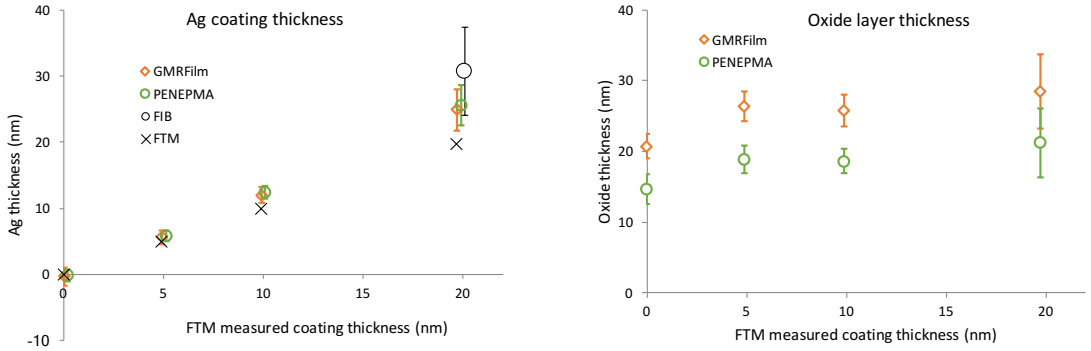

Figure 1 Coating (a) and oxide layer (b) thicknesses calculated using GMRFilm and PENEPMA from measured Ag Lα and O Kα k-ratios respectively.

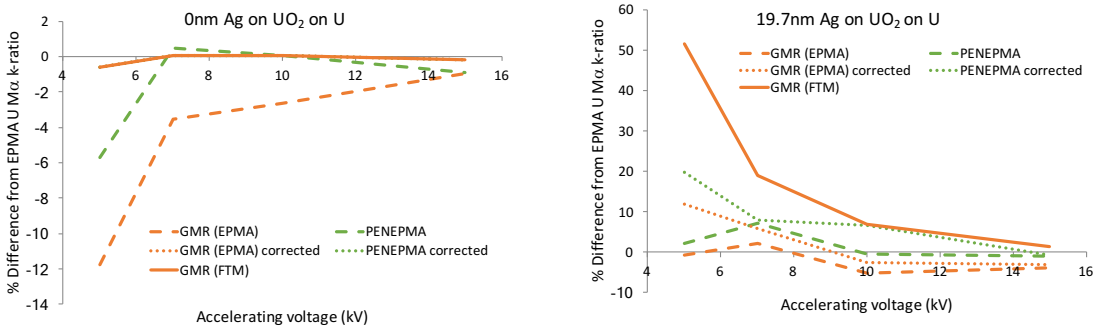

Figure 2 Percent differences between calculated and EPMA measured U Mα k-ratios for the 4.9nm and 19.7nm Ag coated sections of the DU tile.

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