ESRF EXPERIMENTAL REPORT

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PROPOSAL TITLE: Non-destructive depth profile of mixed Cr/Si oxides by Hard X-Ray Photoelectron Spectroscopy

MAIN PROPOSER: R. ESCOBAR GALINDO

CO-PROPOSERS: G.R. CASTRO, J. RUBIO-ZUAZO, C. PALACIO, N. BENITO

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Mixed Cr-Al(Si) oxides are very interesting materials because they are suitable for being used, among others, as optical coatings with an adjustable refractive index. In most cases the synthesis of these coatings is completed by chemical vapour deposition (CVD) techniques although undesirable incorporation of chlorine, hydrogen or carboxyl groups to the films is frequently reported. We are currently investigating the formation of chromium and aluminium (silicon) mixed oxides using a DC magnetron sputtering as well as reactive ion beam mixing using O_2^+ on Cr/Al(Si) interfaces. The concentration depth profiles of the above mentioned films were obtained either by means of Rutherford backscattering spectrometry (RBS) with He ions at 3.035 MeV to make use of the resonance of alpha particles with oxygen at this specific energy or by XPS with simultaneous ion milling using Ar^+. However the first of these techniques lacks of chemical sensitivity and the second one is destructive therefore we pretend to look for a complementary analytical tool to obtain in a non-destructive way the compositional depth profile of thin films and buried interfaces in the tens of nanometer scale. To fulfil this purpose we have chosen to use a synchrotron X-ray source of variable photon energies (from 7.5-16.6 keV) to vary the probed depth by changing the kinetic energy of the photoelectrons leaving the analyzed samples. That range of energies allows the analysis of thin films and buried interfaces from thicknesses of few nanometers to several tens of nanometers. A comparative analysis of very thin Cr, Al and Si oxides and a buried interface Cr-O-Al/Si interface using ARXPS, XPS with ion milling and HAXPES techniques was carried out in order to obtain a complete chemical and compositional characterization. The main aim of the proposal is to assess how chemical and compositional changes are related to the optical properties of the coatings (mainly refractive index) as measured by spectroscopic ellipsometry.

In order to test the validity of HAXPES to solve the above mentioned problems the Al, Cr, and Si natural oxides belonging to reference Al, Cr and Si substrata were analyzed using both HAXPES (Fig. 1a) and ARXPS (Fig. 1b) techniques. HAXPES analysis was carried out in the Spanish CRG Spline beamline (Branch B) at the ESRF, Grenoble, France. The photon energy was varied in the range (7.5-16.5 keV) and a CMA (HV-CSA300) was used as electron energy analyser. Further experimental details can be seen in J. Rubio et al. J. Electron Spectrosc. & Rel. Phen., 184 (2011) 440, and J. Rubio et al. NIMB 547 (2005) 64. ARXPS spectra were measured in an ultrahigh vacuum system at a base pressure below 8×10^{-8} Pa using a hemispherical analyzer (SPECS Phoibos 100 MCD-5). The pass energy was 9 eV giving a constant resolution of 0.9 eV. The Au $4f_{7/2}$, Ag $3d_{5/2}$ and Cu $2p_{3/2}$ lines of reference samples at 84.0, 368.3 and 932.7 eV, respectively, were used to calibrate binding energies. A twin anode (Mg and Al) X-ray source was operated at a constant power of 300 W using Mg Kα radiation. For ARXPS measurements, the sample was placed in a sample stage with four degrees of freedom in such a way that the take-off angle can be varied between 0º and 70º (see N. Benito et al., Surf. & Coat. Technol.206 (2011) 1484). Fig. 1b indicates that the intensity ratios metal/oxide in the natural oxides can be modelled using step-like depth profiles where thicknesses can be calculated fitting the model (continuous lines) to the experimental results. Therefore we have used the same model to reproduce the HAXPES experimental results of Fig. 1a (continuous lines). The best fit parameters for the film thickness are: d = 40.7 Å for the Al oxide, d = 19.5 Å for the Cr oxide and d = 4.7 Å for the Si oxide. As can be observed in both figures the agreement between experimental results and the model is very good and the agreement between both techniques is very good indeed.

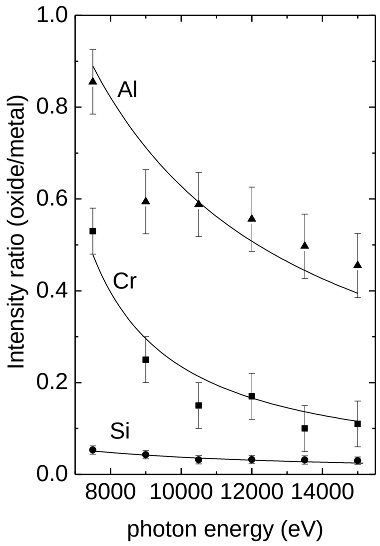

Fig.1a

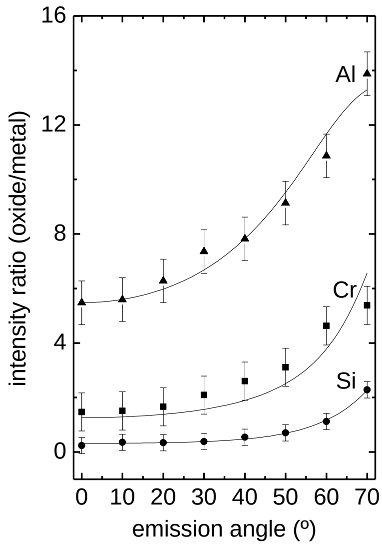

Fig.1b

Fig. 2 shows the inelastic mean free path of the emitted photoelectrons as a function of their kinetic energy calculated using a modified form of the Bethe equation for inelastic scattering of electrons in matter (Tanuma, Powell and Penn SIA 43 (2011) 689). Since the used photon energies for HAXPES are in the range 7.5-16.5 keV the IMFP for Si 1s electrons (which were used in Fig. 1a) are in the range 102-231 Å and therefore deep interfaces buried at depths in the above mentioned range should be resolved using HAXPES.

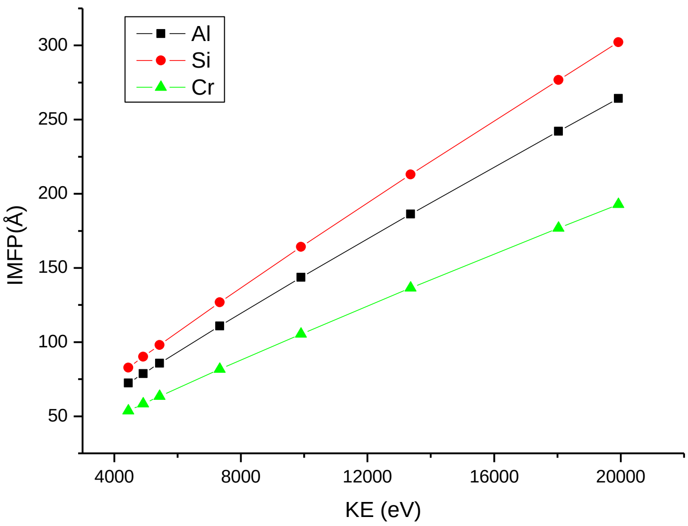

Fig.2

Figure 3 shows the intensity ratios I_{Al}/I_{Si} and I_{SiO}/I_{Si} using the Al 1s and Si 1s bands measured by HAXPES, full squares and full circles, respectively measured on a Cr-O-Al mixed oxide grown by DC magnetron sputtering. Concentration depth profiles (CDP) of those mixed oxides (N. Benito et al., Surf. & Coat. Technol. 206 (2011) 1484) show a rather uniform film of a substitutional mixed oxide Me_2O_3 (Me = Cr+Al) with and Si oxide interface above the Si substrate. Therefore it seems plausible to use a box-like model for the CDP of such interfacial oxide. This model has two parameters d_2 and d_3, being d_2 the interface depth and $d_3 - d_2$ the thickness of the interfacial oxide layer. As can be observed from Fig 3 the fitting between the experimental data (full circles) and the model is very good leading to an interfacial oxide 4.9 Å thick in good agreement with the thickness for the natural oxide measured using data of Fig. 1a. An important point is that the above model provides directly the thickness of the mixed oxide layer without any fitting as can be observed in Fig. 3 from the I_{Al}/I_{Si} ratio (full squares). In this case, continuous line do not represents a fit but the theoretical model of a uniform layer of Cr-O-Al mixed oxide with a step-like CDP of thickness d_1 = 129 Å which is exactly the depth of the interfacial Si oxide.

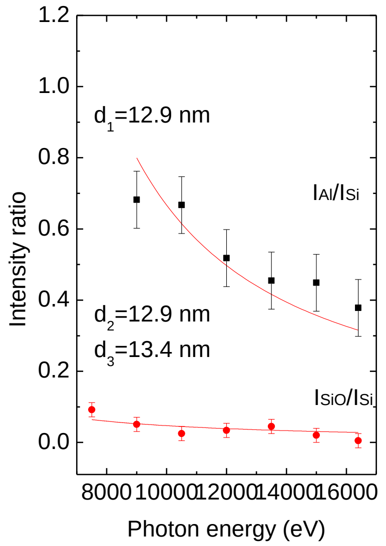

Fig.3

To summarize, it has been shown that HAXPES is a useful tool to characterize non-destructively very thin films and buried interfaces. However additional experiments are necessary in order to resolve chemical effects, as well as to determine experimentally the effective attenuation lengths, its dependence with the energy and the possible influence of the chemical element.