Electronic Supplementary Information: Core level shifts as indicators of Cr chemistry on hydroxylated α-Al_2O_3(0001): a combined photoemission and first-principles study

Maya Messaykeh,[1] Stéphane Chenot,[1] Pascal David,[1] Gregory Cabailh,[1] Jacques Jupille,[1] Alexey Koltsov,[2] Pierre Lagarde,[3] Nicolas Trcera,[3] Jacek Goniakowski,[1] and Rémi Lazzari[1,*]

[1] *CNRS/Sorbonne Université, Institut des NanoSciences de Paris, UMR 7588, 4 Place Jussieu, F-75005 Paris, France*

[2] *ArcelorMittal Maizières Research, voie Romaine, F-57280 Maizières-lès-Metz, France*

[3] *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette, France*

(Dated: September 20, 2021)

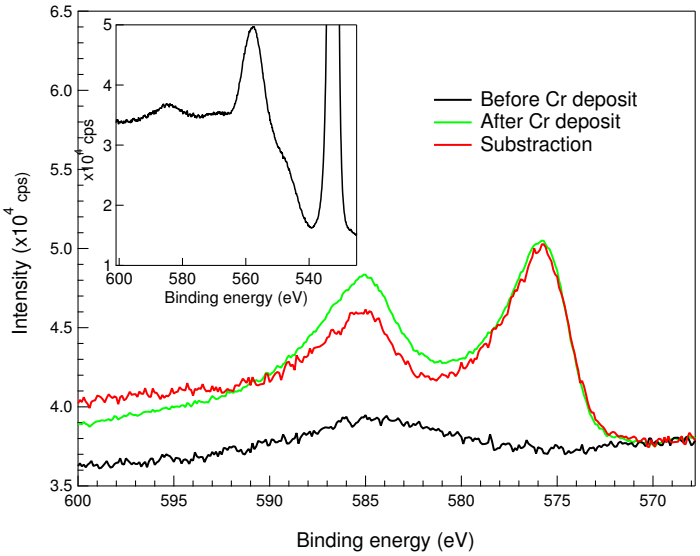

FIG. S1. Binding energy region of the Cr 2p core level before (black line) and after a 0.34 Å Cr/Al_2O_3 deposit (green line). The wide range scan of the O 1s core level of the bare surface (inset) shows the presence of the O 1s plasmon replica below the Cr 2p line. Their removal performed by substraction after a proper rescaling allows to recover the right 2p branching ratio between 1/2 and 3/2 components (red line).

* remi.lazzari@insp.jussieu.fr

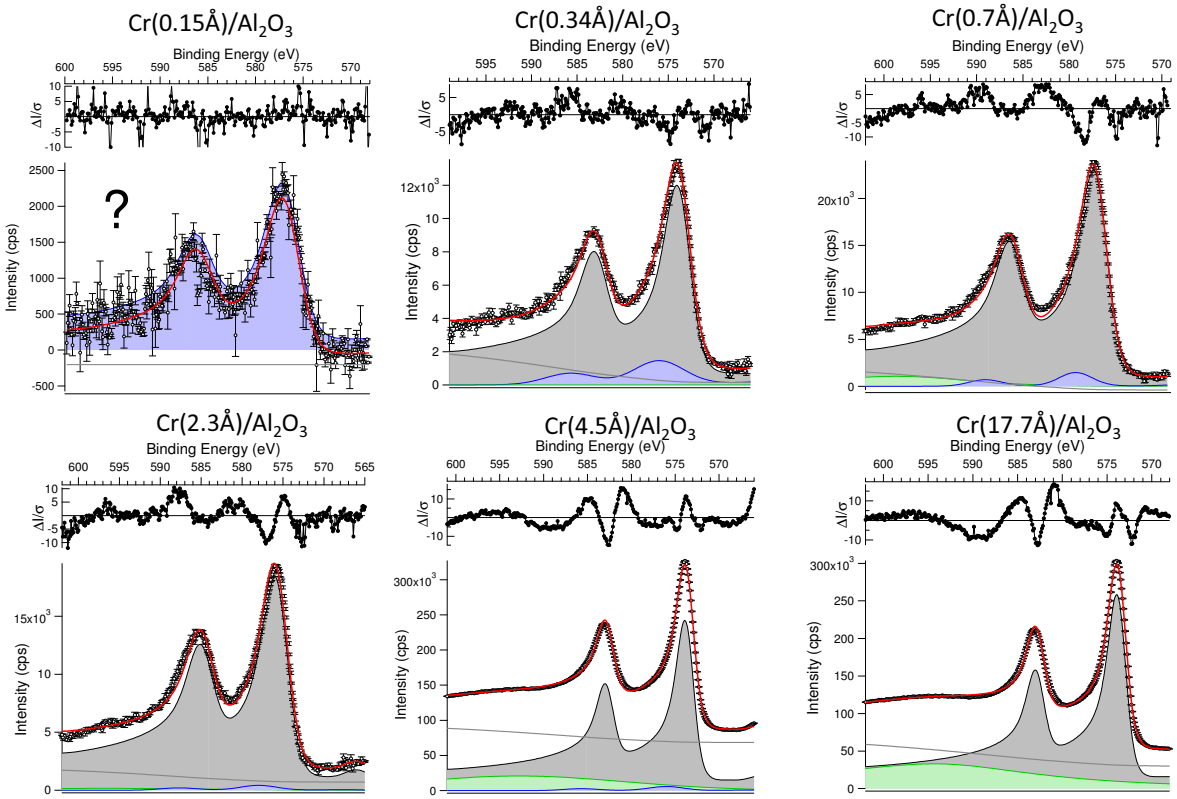

FIG. S2. Fits (red line) of the evolution of the Cr 2p core level (points) as function of Cr/alumina film thickness. The metallic component is accounted for via a Doniach-Sunjic profile (grey curve) coupled with a broad plasmon (green curve), the parameters of which are fixed with respect to the thickest deposit (see Figure 3-a of the article). Similarly the oxidized Voigt profile is obtained from a fit of a thick CrO_x film (see Figure 3-b of the article); its shake-up satellites do not clearly appear in the data and are not accounted for (see article for explanation). The background (grey line) is of Tougaard type. Although the spectrum of the 0.15 Å deposit can be reasonable fitted with only one component, the concomitant existence of metallic and oxidized Cr can not be ruled out. O 1s plasmon satellites have been systematically removed prior to fit (see Fig. S1).

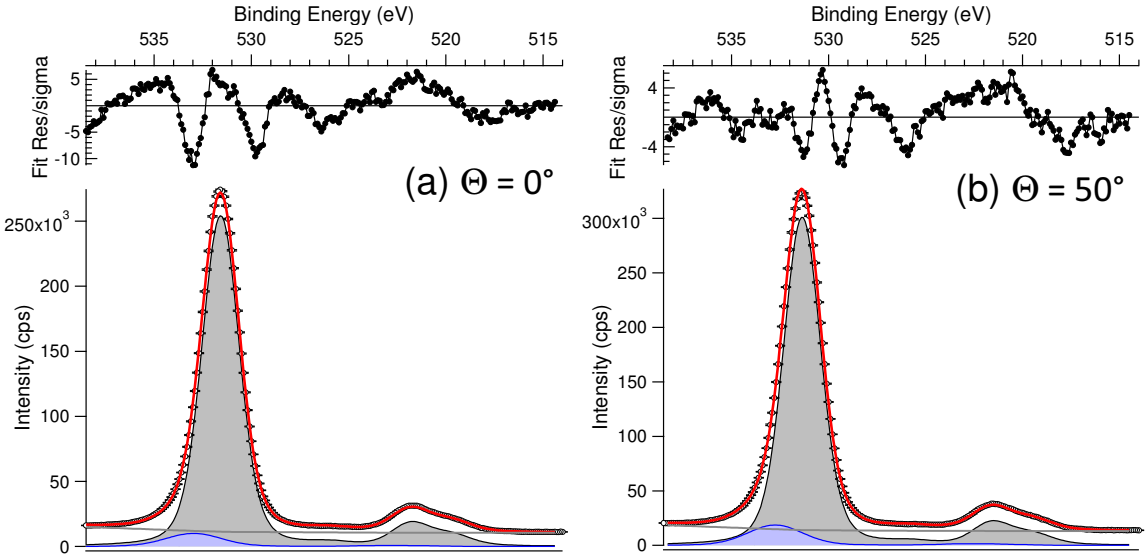

FIG. S3. Fit of the O 1s core level of a vacuum annealed $Al_2O_3(0001)$ surface at (a) normal $\Theta = 0°$ and (b) grazing $\Theta = 50°$ emissions. The observed systematic asymmetry on the high energy side of O 1s is accounted for by a component shifted by 1.4 eV wit an intensity increasing at grazing emission. Assuming an effective attenuation length of 24.3 Å in Al_2O_3, the corresponding 4 % of the bulk peak area ($\Theta = 0°$) amounts to ~ 0.5 O-monolayer in the corundum structure *i.e.* 4.8 O.nm^{-2}.