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$3p \rightarrow 3d$ resonant photoemission spectroscopy of a TiO_2 sub-monolayer grown on Al_2O_3

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Abstract

The valence band resonant photoemission spectra of a TiO_2 sub-monolayer grown on an Al_2O_3 substrate have been measured throughout the Ti 3p absorption edge, i.e. at photon energies between 40 and 60 eV. The resonance process has been analysed in terms of constant initial state (CIS) curves, showing a peak at 49.5 eV photon energy, corresponding to a Fano-like resonant process. The Ti 3d contribution to the valence band shows a significant energy shift with respect to bulk TiO_2. These results are compared to cluster model calculations for a TiO_6 cluster.

Keywords: Synchrotron radiation photoelectron spectroscopy; Aluminum oxide; Titanium oxide; Interface states

1. Introduction

The main purpose of this paper is to study the electronic structure of the TiO_2–Al_2O_3 interface by means of $3p \rightarrow 3d$ resonant photoemission. The analysis of the first TiO_2 monolayer grown on the Al_2O_3 substrate gives information on the electronic structure at the interface. In a previous work [1], we have already studied the electronic structure of this system by means of X-ray absorption spectroscopy (XAS). The Ti 2p XAS spectra allowed us to observe strong overlayer–substrate interaction, as reflected by the unoccupied Ti 3d electronic states. This interaction should also be reflected by the occupied Ti 3d electronic states. We also studied the TiO_2–Al_2O_3 interface by means of $2p \rightarrow 3d$ resonant photoemission [2,3]. Indeed, in those studies we found that the occupied Ti 3d states at the valence band of the TiO_2 sub-monolayer deposited on Al_2O_3 move towards lower binding energies with respect to bulk TiO_2 or, in other words, the occupied electronic states of the overlayer are affected by the presence of the substrate. In this work, we present the $3p \rightarrow 3d$ valence band resonant photoemission spectra of a TiO_2 sub-monolayer grown on Al_2O_3. Although the occupied states of the overlayer have already been studied in our previous work on the $2p \rightarrow 3d$ resonance, two reasons support the investigation

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of the 3p → 3d resonant photoemission. First, the 3p → 3d resonance deals with in-shell transitions as compared to those produced in the 2p → 3d resonance. So that it seems interesting to compare the resonance process at both edges. Besides, such comparison is very scarce in the literature. Secondly, the photoelectrons involved in the valence band spectra obtained in the 2p → 3d resonance have much larger kinetic energy (about 450 eV), so that the information of the spectra is strongly influenced by the substrate. However, for the 3p → 3d resonance the kinetic energy of the photoelectrons is about 50 eV. This means that the photoelectrons come from a nearer surface region and the spectra are more surface sensitive.

In this work we first present the valence band photoemission spectra as a function of the photon energy taken through the Ti 3p absorption edge. Then the spectra are analysed in terms of the constant initial state (CIS) curves. The Ti 3d electronic states of the TiO_2 overlayer obtained from the 3p → 3d resonance are compared to those obtained by the resonance at the 2p → 3d absorption edge of the same system. Finally, a cluster model calculation is presented for the interpretation of the above results.

2. Experimental details

Titanium oxide has been grown by reactive thermal evaporation of pure Ti in an oxygen atmosphere (5×10^{-6} Torr). The evaporation rate was so low to allow coverages under the monolayer regime. The Al_2O_3 substrate was previously prepared in situ by thermal oxidation of a high purity (99.999%) Aluminium foil at 350 °C for 30 min in an oxygen atmosphere (1×10^{-5} Torr). The TiO_2 stoichiometry and coverage has been estimated by quantitative analysis of the intensities of the Al 2p and Ti 3p photoemission peaks. Besides, other Ti oxidation states (i.e. Ti^{3+} and Ti^{2+}) would produce occupied Ti states at lower binding energies as it can be seen in the literature [2,4]. Although there is no evidence of the layer by layer growth of the TiO_2 overlayer on the Al_2O_3 substrate, the coverage has been obtained in equivalent TiO_2 monolayers.

The photoemission measurements were performed at the beamline 41 of the MAX-1 storage ring at MAX-Lab in Lund, Sweden. This beamline is equipped with a TGM monochromator working in the 15–200 eV energy range [5]. The overall resolution (monochromator + analyser) has been estimated as better than 200 meV. The spectra have been normalized with the I_0 intensity in order to correct the beam losses during measurements.

3. Results and discussion

Valence band photoemission spectra taken through the Ti 3p absorption edge, corresponding to 0.5 ML of TiO_2 grown on Al_2O_3 are shown in Fig. 1. Taking into account that the electron mean free path at these kinetic energies (30–50 eV) is only a few monolayers, these spectra correspond to the superposition of the valence bands of some monolayers of the Al_2O_3 substrate and the TiO_2 sub-monolayer. In general, the spectra show two

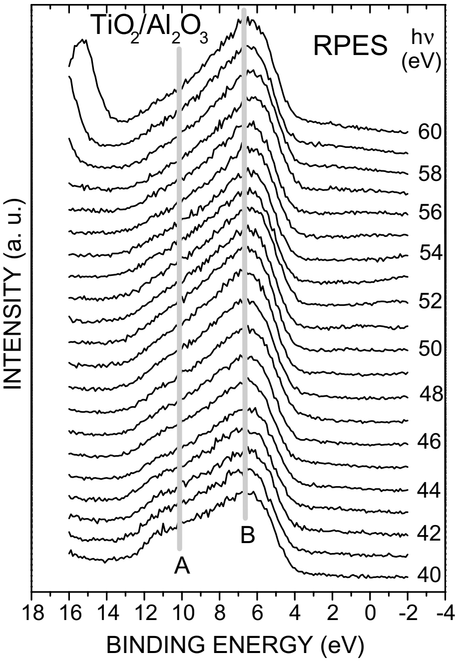

Fig. 1. Valence band resonant photoemission spectra of 0.5 ML of TiO_2 grown on Al_2O_3 as a function of the photon energy through the Ti 3p → 3d absorption edge.

main features located about 7 and 10 eV binding energy and labelled as B and A respectively. It can be seen that the intensities of these two bands in the series of spectra are continuously varying due to photoemission cross-sections effects and the possible resonance effect. For higher photon energy spectra, i.e. 57–60 eV, a new peak appears at about 15 eV binding energy. However, this peak moves in energy in steps of 2 eV as the photon energy changes in 1 eV. We have assigned this moving peak as a photoemission peak of the Al 2p states excited by the second order light from the monochromator. Fortunately this peak does not affect the valence band structure in the energy region of interest (4–12 eV) at the photon energies used in this work so that no second order light suppression had to be handled.

We have performed the classical constant initial state (CIS) analysis of the resonance process by plotting the intensities of these two features as a function of the photon energy. The CIS curves for the TiO_2 sub-monolayer on Al_2O_3 are shown at the bottom of Fig. 2. Similar curves obtained from the spectra (not shown) of the clean Al_2O_3 substrate have been depicted at the top of Fig. 2 for comparison. It is clearly seen that there is an increase of the intensities with a maximum at 49.5 eV. This curve is clearly indicating a Fano like resonance process. By comparing these curves with those of the Al_2O_3 substrate (top Fig. 2) it seems to be clear that this effect is due to the presence of the TiO_2 sub-monolayer. Another important aspect is that the increase of intensity of the feature at 7 eV is larger than that of the feature at 10 eV, indicating that the spectral weight of the Ti 3d states present in the valence band is mainly located at lower energies.

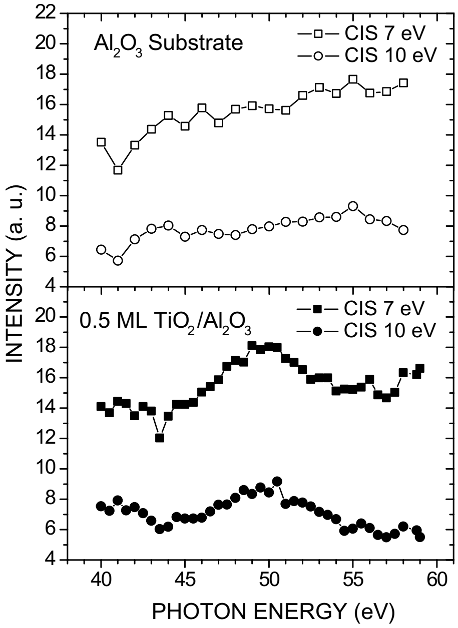

Fig. 2. Constant initial state (CIS) curves for the 7 eV (B) and 10 eV (A) features of the valence band of the Al_2O_3 substrate (top) and of 0.5 ML TiO_2 on Al_2O_3 (bottom).

To obtain the partial density of Ti 3d states we have performed the common method of subtracting the spectrum off resonance (45.0 eV) from the spectrum on resonance (49.5 eV). The results obtained are shown at the bottom of Fig. 3. It can be seen that the resonant part of the valence band is a weak bump centred at about 7.0 eV. We have also included on-resonance and off-resonance spectra for the $2p \rightarrow 3d$ absorption edge of 0.5 ML TiO_2–Al_2O_3 (Fig. 3, center) and a TiO_2 thin film (Fig. 3, top) as well as their corresponding difference spectra, taken from Ref. [6]. It is seen that the Ti 3d states of the TiO_2 sub-monolayer as obtained from the $3p \rightarrow 3d$ resonance agree with those obtained from the $2p \rightarrow 3d$ resonance. In both cases the Ti 3d states are symmetrically distributed and centred at about 7.0 eV. However, in the case of the $3p \rightarrow 3d$ resonance, the bump is slightly broader than for the $2p \rightarrow 3d$ resonance, probably due to differences in lifetime broadening of the Ti 3p and Ti 2p core levels, involved in the corresponding transitions. On the other hand, the resonance effect is about four times stronger for the $2p \rightarrow 3d$ transitions than for the $3p \rightarrow 3d$. In order to compare the results obtained by these two processes, many factors have to be taken into account, such as changes in the photoionization cross-sections of the metal Ti 3d states, probability of decay of the intermediate state in the de-excitation process and also the error in the estimation of the TiO_2 coverage in both experiments. However, in our opinion, the main differences are due to the larger intermediate state decay probability of the 2p core–hole as compared with that of the 3p core–hole.

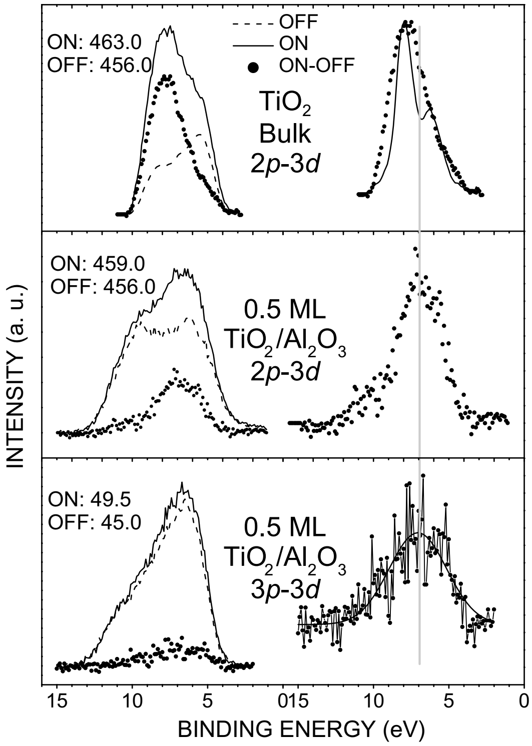

Fig. 3. Bottom left: valence band photoemission spectra of 0.5 ML TiO_2 on Al_2O_3 at the $3p \to 3d$ resonance: on resonance (49.5 eV) (solid line), off resonance (45.0 eV) (dashed line) and difference spectrum (dots); bottom right: normalized difference spectrum; center left: valence band photoemission spectra of 0.5 ML TiO_2 on Al_2O_3 at the $2p \to 3d$ resonance taken from Ref. [2]: on resonance (459.0 eV) (solid line), off resonance (456.0 eV) (dashed line) and difference spectrum (dots); center right: normalized difference spectrum; top left: valence band photoemission spectra of bulk TiO_2 at the $2p \to 3d$ resonance taken from Ref. [6]: on resonance (463.0 eV) (solid line), off resonance (456.0 eV) (dashed line) and difference spectrum (dots); top right: normalized difference spectrum (dots); Ti 3d partial density of states from Ref. [7] (solid line).

The Ti 3d states participating in the valence band of a TiO_2 thin film as obtained from the $2p \to 3d$ resonance are shown at the top-right of Fig. 3 (dots). Also the Ti 3d states as calculated by Munnix and Schmeits [7] are shown for comparison. Whereas the spectral weight of the Ti 3d states in bulk TiO_2 is asymmetrical showing a maximum at about 8 eV, the Ti 3d states of the TiO_2 sub-monolayer on Al_2O_3 are both symmetric and shifted to lower energies. This results indicate that the electronic structure of the TiO_2 sub-monolayer is strongly affected by the presence of the substrate.

To understand the effect of the substrate on the Ti 3d states of the TiO_2 sub-monolayer we show in Fig. 4 the cluster model calculation of the occupied and unoccupied electronic states of a TiO_6 cluster (Fig. 4, bottom) taken from Ref. [2]. To simulate a decrease of covalence, the calculations have been repeated by introducing a reduction factor affecting the O $2p \to$ Ti 3d interaction in the Hamiltonian. The results of such calculations for a reduction factor of 25% and 50% are shown in Fig. 4, centre and Fig. 4, top, respectively. The results show that when covalency is reduced in TiO_2 the splitting of the two bumps in the valence band corresponding to the σ and π hybrid sub-bands is reduced and the total spectral weight is shifted towards lower energies. So that, our results on the Ti 3d states in the valence band of the TiO_2 sub-monolayer on Al_2O_3 are consistent with a decrease of the covalency, which, on the other hand, has to be assigned as due to the presence of the substrate. Although from this experiment there is no information of the

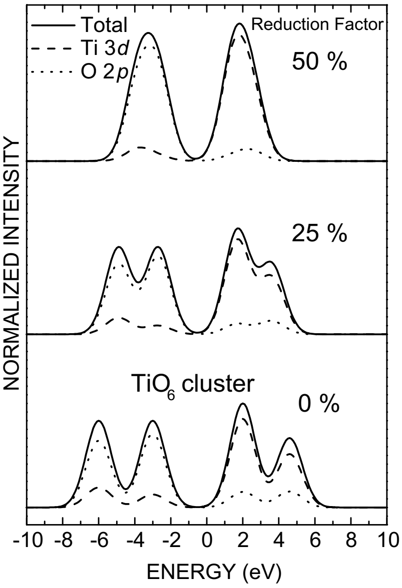

Fig. 4. Single cluster model TiO_2 calculation taken from Ref. [2] as a function of the covalent bonding reduction factor (%). The curves represent the total density of states (solid line); partial Ti 3d density of states (dots) and partial O 2p density of states (open dots).

way of growth of the TiO_2 overlayer on Al_2O_3, we suggest that at least the first monolayer is homogeneously formed. This is supported by our previous XAS study [1] in which the Ti 2p XAS spectra for coverages below 1 ML are identical and different from bulk TiO_2. Only when the formation of the first monolayer is complete the spectra approach that of bulk TiO_2. So that the reduction of covalence of the TiO_2 sub-monolayer observed in this work is consistent with the formation of Al–O–Ti bonds observed in the XAS experiments.

4. Conclusions

We have studied the Ti 3p → 3d resonant photoemission of a TiO_2 sub-monolayer grown on Al_2O_3. The constant initial states curves show a maximum at 49.5 eV indicating a Fano-like resonant process. The partial Ti 3d density of states of the TiO_2 sub-monolayer as obtained by the on resonance minus off resonance difference spectra shows a shift to lower binding energies as compared to bulk TiO_2. The Ti 3p → 3d resonance has been compared with the same process through the Ti 2p → 3d absorption edge. Both resonances gave similar results on the Ti 3d distribution, although the last one gives a better description of the Ti 3d states due to enhancement of the resonant effect. The results reported in this work are consistent with a reduction of the covalence of the first TiO_2 monolayer as shown by cluster model calculations.

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