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# Electronic structure of TiO<sub>2</sub> monolayers grown on Al<sub>2</sub>O<sub>3</sub> and MgO studied by resonant photoemission spectroscopy

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#### Abstract

The electronic structure of the  $TiO_2-Al_2O_3$  and  $TiO_2-MgO$  interfaces have been studied using resonant photoemission spectroscopy. To this end, respective  $TiO_2$  monolayers have been grown on both substrates. Valence band photoemission spectra through the Ti  $2p \rightarrow 3d$  absorption edge, i.e. 455-470 eV, have been measured. The results have been analysed in terms of the constant initial state curves. On-resonance minus off-resonance difference spectra have been used to separate the contribution to the valence band of the Ti 3d states for both monolayers. From the comparison of the results obtained for each interface it is inferred that the covalent-ionic character of the substrate affects the Ti–O bonding at the interface and the Ti 3d states' contribution to the valence band. © 2002 Elsevier Science B.V. All rights reserved.

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#### 1. Introduction

During the last few years a big effort has been made in order to investigate the oxide–oxide interfaces. Previously, we have published the study of the  $TiO_2$ –SiO<sub>2</sub> interface [1] by means of X-ray absorption spectroscopy (XAS). It was shown that strong overlayer–support interaction exists at the interface. Similar effects were observed in the study of the  $TiO_2$ –Al<sub>2</sub>O<sub>3</sub> interface [2], although in this

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case the effect was slightly weaker, suggesting that the covalence of the substrate was a key parameter to understand the mechanism of such interaction. In fact, in the case of the  $Al_2O_3$  substrate, we have shown that the strong covalent character of the Al–O bonding leads to a decrease of the covalence of the Ti–O bonding at the interface [3]. Therefore, the study of the growth of TiO<sub>2</sub> on a more ionic oxide like MgO seems well justified. In this work we present a comparative study of respective TiO<sub>2</sub> monolayers grown on two substrates such as  $Al_2O_3$ and MgO, which clearly differ in ionicity.

Similar effects to those observed in the unoccupied electronic states, as shown by the XAS spectra, should also be reflected in the occupied

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states in the valence band. To investigate this, we have used resonant photoemission spectroscopy (RPES), which has already proved its potential in the analysis of interfaces [3]. RPES has been widely used in the analysis of the electronic structure of bulk compounds. In particular, RPES has been used to isolate the cationic contribution to the valence band in transition metal compounds. More details can be found in the review by Davis [4]. TiO<sub>2</sub> has been previously characterised by resonant photoemission at the  $3p \rightarrow 3d$  edge [5–7] and at the  $2p \rightarrow 3d$  edge [8].

In this work we present and discuss the Ti 2p XAS spectra for respective  $TiO_2$  monolayers on  $Al_2O_3$  and MgO. They are compared to the spectra of a bulk  $TiO_2$  thin film. Then, we present the experimental valence band RPES through the Ti  $2p \rightarrow 3d$  absorption edge of the respective  $TiO_2$  monolayers on  $Al_2O_3$  and MgO. The RPES spectra are analysed in terms of constant initial state curves and on-resonance minus off-resonance difference spectra.

#### 2. Experimental

The Al<sub>2</sub>O<sub>3</sub> substrate was prepared by thermal oxidation of a high purity (99.999%) aluminium foil at 350 °C for 30 min in an oxygen atmosphere ( $1 \times 10^{-5}$  Torr). The MgO substrate was prepared by reactive evaporation of Mg in an oxygen atmosphere ( $1 \times 10^{-5}$  Torr) at room temperature. TiO<sub>2</sub> was grown by reactive evaporation of Ti in an oxygen atmosphere ( $5 \times 10^{-6}$  Torr) at room temperature. The deposition rate was low enough to allow a good control of the coverage. For long evaporation time, a 200 Å thick TiO<sub>2</sub> film was grown. Then, it was submitted to thermal annealing at 300 °C in an oxygen atmosphere ( $5 \times 10^{-6}$  Torr) for 30 min.

The photoemission measurements were performed at the SU8 beam-line of the SuperAco storage ring at LURE. This beam-line is equipped with a plane grating-spherical mirror monochromator (PGM-SM). The electron analyser was an angle resolved analyser from VSW working at constant pass energy. The exit slits were adjusted in order to obtain an acceptable count rate and resolution. The spectra were normalised to the incident  $I_0$  current as measured from a gold grid located at the entrance of the chamber to correct the beam intensity loss. The absolute energy scale was calibrated according to the Fermi level of a Cu sample.

## 3. Results and discussion

#### 3.1. The Ti 2p XAS spectra

The Ti 2p XAS spectra are usually interpreted in terms of atomic multiplets projected in a crystal field with the corresponding symmetry. These spectra are site and symmetry selective and very sensitive to the local environment of the atoms. According to this, the Ti 2p XAS spectra of a monolayer should reflect the local environment of the Ti atoms located at the interface and consequently the possible electronic interaction between overlayer and substrate. This is clearly illustrated in Fig. 1, where the spectra of the reference  $TiO_2$ thin film grown at room temperature (b) and after heating at 300 °C (a) are shown in comparison with those of the respective TiO<sub>2</sub> monolayers grown on MgO (c) and  $Al_2O_3$  (d). The spectra have been normalised to their maximum intensity for comparison purposes.

The spectrum of the TiO<sub>2</sub> thin film after annealing at 300 °C (Fig. 1a) agrees well with other published spectra for TiO<sub>2</sub> [9,10]. This spectrum has already been interpreted in the literature and has been theoretically simulated in terms of multiplets using a crystal field (10 Dq) of 1.8 eV [10]. The spectrum corresponding to the TiO<sub>2</sub> thin film grown at room temperature (Fig. 1b) shows significant differences with respect to the previous one. These differences can be explained in terms of disorder of the TiO<sub>2</sub> thin film grown at room temperature [2].

On the other hand, the spectra of the respective  $TiO_2$  monolayers grown on MgO and  $Al_2O_3$  clearly differ from each other. Whereas the spectrum of the  $TiO_2$  monolayer on MgO (Fig. 1c) resembles that of the as-grown  $TiO_2$  thin film, the spectrum of the  $TiO_2$  monolayer on  $Al_2O_3$  (Fig. 1d) differs significantly from the others showing



Fig. 1. The Ti 2p XAS spectra of: (a) TiO<sub>2</sub> thin film grown at room temperature and annealed at 300 °C in an oxygen atmosphere (see text); (b) TiO<sub>2</sub> thin film grown at room temperature; (c) TiO<sub>2</sub> monolayer grown on MgO; solid line represents the  $2p \rightarrow 3d$  atomic multiplet calculation for Ti<sup>4+</sup> in octahedral symmetry with a crystal field 10 Dq = 1.3 eV; (d) TiO<sub>2</sub> monolayer grown on Al<sub>2</sub>O<sub>3</sub>.

only two main peaks with weaker structures at the low energy side of the main peaks. This spectrum has already been explained in terms of Ti<sup>4+</sup> species with an important reduction of the crystal field of the Ti atoms located at the Al<sub>2</sub>O<sub>3</sub> surface (10 Dq  $\sim$  1.0 eV) with respect to bulk TiO<sub>2</sub> (10  $Dq \sim 1.8 \text{ eV}$  [2]. In the case of the TiO<sub>2</sub> monolayer on MgO the crystal field of the Ti atoms at the interface, as inferred from the comparison of the Ti 2p XAS spectrum with atomic multiplet calculations [10], is 1.3 eV (Fig. 1c). This value is in between those of bulk TiO<sub>2</sub> and the TiO<sub>2</sub> monolayer on  $Al_2O_3$ . It is important to note here that these spectra cannot be interpreted in terms of other oxidation states, i.e.  $Ti^{3\hat{+}}$  and  $Ti^{2+},$  as they have no resemblance at all with experimental XAS spectra for Ti<sub>2</sub>O<sub>3</sub> and TiO [11] and existing multiplet calculation for Ti atoms in  $d^1$  and  $d^2$  symmetries [12]. The presence of metallic Ti can also be discarded as otherwise the spectra should be broader and shifted in energy as it is shown by experimental data for metallic Ti [13]. Therefore, the Ti 2p XAS spectra reveal that the more covalent  $Al_2O_3$  substrate strongly affects the Ti atoms of the TiO<sub>2</sub> monolayer by reducing significantly the crystal field whereas the effect of the more ionic MgO substrate is weaker.

## 3.2. The valence band resonant photoemission spectra

Fig. 2 shows the valence band resonant photoemission spectra through the Ti  $2p \rightarrow 3d$  thresh-



Fig. 2. The valence band resonant photoemission spectra as a function of the photon energy for a  $TiO_2$  monolayer grown on MgO (bottom) and a  $TiO_2$  monolayer grown on  $Al_2O_3$  (top).

old, i.e. 456-467 eV energy range for the respective  $TiO_2$  monolayer on  $Al_2O_3$  (top) and on MgO (bottom). Both valence bands are different because their shapes are nearly those of the substrates, i.e.  $Al_2O_3$  and MgO, respectively. In both cases, the valence band is formed by two main structures labelled as A and B. These bands come from the hybridisation of the O 2p states with Al 2p and Mg 2p states, respectively, forming the  $\sigma$  (A) and  $\pi$  (B) bands in the valence band. Also the O 2p and Ti 3d states of the  $TiO_2$  monolayer are present in these spectra. For the  $TiO_2$  monolayer on  $Al_2O_3$  we can observe important changes in intensity of the structures of the valence band, specially that labelled as B ( $\pi$  band). For the TiO<sub>2</sub> monolayer on MgO the changes in intensity of these structures seem to be weaker than those for  $TiO_2-Al_2O_3$ . In both cases, these changes in intensity correspond to a resonant photoemission process from the  $TiO_2$  monolayer. This is an example of a Fano type resonance mechanism involving the Ti  $2p^63d^0 \rightarrow$ 2p<sup>5</sup>3d<sup>1\*</sup> excited state which occurs when the incident photon energy varies through the Ti  $2p \rightarrow$ 3d threshold. We have also performed resonant photoemission measurements of the substrates confirming that no resonance phenomena take place in this energy range for Al<sub>2</sub>O<sub>3</sub> or MgO.

Fig. 3 shows the constant initial states (CIS) curves for the respective TiO<sub>2</sub> monolayers and for the TiO<sub>2</sub> thin film annealed at 300 °C for comparison. The CIS curves have been generated by plotting the intensities of the main features A and B of the valence band as a function of the photon energy. The values of the two, A and B, features taken for each sample are: 8.5 and 5.2 eV for the Al<sub>2</sub>O<sub>3</sub> substrate, 8.6 and 6.0 for the MgO substrate and 8.0 and 5.7 eV for the TiO<sub>2</sub> thin film, respectively. In the case of the  $TiO_2$  thin film, the two main structures of the valence band present the same resonant behaviour. This is due to the fact that Ti 3d states are distributed throughout the whole valence band in agreement with the density of states (DOS) calculated by Munnix and Schmeits [14] for bulk TiO<sub>2</sub>. Our CIS curves coincide with those reported by Prince et al. [8] for a TiO<sub>2</sub> single crystal which is a good indication of the quality of our  $TiO_2$  thin film. The CIS curves for the TiO<sub>2</sub> monolayer on MgO in Fig. 3 also

text.

show that both structures A and B have the same resonant behaviour, i.e. both structures resonate at the same energies. However, for the TiO<sub>2</sub> monolayer on Al<sub>2</sub>O<sub>3</sub> only the lower binding energy feature (B) of the valence band, i.e. the  $\pi$  band, resonates. This clearly indicates that the Ti 3d states in the valence band for the TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> monolayer are distributed in a narrower energy region. This is consistent with a reduction of the covalence of the Ti-O bonding in the monolayer due to the more covalent character of the  $Al_2O_3$ substrate [3]. In general, and as expected, there is a good agreement between XAS spectra in Fig. 1 and CIS curves in Fig. 3 for the corresponding monolayer.

PHOTON ENERGY (eV) Fig. 3. CIS curves for a TiO<sub>2</sub> thin film annealed at 300 °C (top); TiO<sub>2</sub> monolayer grown on MgO (middle); and TiO<sub>2</sub> monolayer grown on Al<sub>2</sub>O<sub>3</sub> (bottom). Open circles (A) indicate the intensity of the high binding energy structure of the valence band and solid circles (B) indicate the intensity of the low binding energy side of the valence band. For explanation see



In order to separate the Ti 3d contribution to the valence band, the spectra have been analysed in terms of on-resonance minus off-resonance difference spectra. This method has been commonly used in the literature for transition metal compounds [4]. Fig. 4 shows the on-resonance minus off-resonance difference spectra of the TiO<sub>2</sub> thin film after annealing at 300 °C as well as those of the monolayers of TiO<sub>2</sub> grown on both substrates. In the case of the TiO<sub>2</sub> thin film we have depicted the Ti 3d DOS (solid line) calculated in [14]. As mentioned above, it is seen that the Ti 3d states are



Fig. 4. On-resonance (solid circles) minus off-resonance (open circles) difference spectra (crossed circles) for a  $TiO_2$  thin film annealed at 300 °C (top);  $TiO_2$  monolayer grown on MgO (middle); and  $TiO_2$  monolayer grown on Al<sub>2</sub>O<sub>3</sub> (bottom). Solid line shows the occupied Ti 3d states as calculated in [14] for bulk  $TiO_2$ . Dotted lines are plotted as an eye guide.

distributed through the whole valence band with a higher weight of the high binding energy side ( $\sigma$  band) in agreement with the difference spectrum (crossed circles).

In the case of the  $TiO_2$  monolayer on MgO, the difference spectrum is also distributed throughout the whole valence band. This spectrum roughly reproduces that of the TiO<sub>2</sub> thin film, although the structures are broader and the spectral weight is slightly shifted at lower binding energies with respect to that of the thin film. This is consistent with the small decrease of the crystal field for this monolayer (1.3 eV) with respect to bulk  $TiO_2$  (1.8 eV) observed in the XAS spectra. However, for the TiO<sub>2</sub> monolayer on Al<sub>2</sub>O<sub>3</sub> the Ti 3d states are mainly distributed at the lower binding energy feature of the valence band (6.0 eV). This significant change in the distribution of the Ti 3d states is also consistent with the lowering of the crystal field (down to 1.0 eV) observed in the Ti 2p XAS spectrum of this monolayer.

These results confirm that not only the unoccupied electronic states of the  $TiO_2$  monolayer, as observed by XAS, are affected by the presence of the substrate but also the occupied states in the valence band as observed by RPES. It is clear that whereas in the case of more ionic MgO substrate the results obtained are closer to those obtained in bulk  $TiO_2$ , in the case of the more covalent substrate, i.e.  $Al_2O_3$ , the electronic structure of the  $TiO_2$  monolayer is strongly affected by the substrate.

### 4. Conclusions

We have made a comparative study of the electronic structure of the  $TiO_2-Al_2O_3$  and TiO-MgO interfaces by means of the Ti 2p XAS and the valence band resonant photoemission spectra. From the comparison of the results obtained for the respective  $TiO_2$  monolayers on  $Al_2O_3$  and MgO it is inferred that the more covalent  $Al_2O_3$  substrate leads to a reduction of the covalence in the bonding of the  $TiO_2$  overlayer. This covalence reduction of the crystal field on the  $Ti^{4+}$  ions and a different distribution of the Ti 3d states in the

valence band. However, when the substrate is a more ionic oxide like MgO, the results are closer to those obtained for a  $TiO_2$  thin film.

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