TiO₂(100) structure–reactivity relationship

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Abstract. The influence of point defects (oxygen vacancies) and steps on the reactivity of TiO₂(100) has been studied with LEED and soft x-ray photo-emission, using H₂O as a model adsorbate. An O termination of the TiO₂(100)1 × 1 surface is deduced by comparison of surface core-level shift data for this surface and TiO₂(001); ordering of O vacancies produced in the surface layer by annealing gives rise to a TiO₂(100)1 × 5 reconstruction. The interaction of H₂O with 1 × 1 and 1 × 5 TiO₂(100) surfaces in the range 120 to 450 K is almost identical, indicating that the ordered oxygen vacancies of the 1 × 5 surface do not play a major role in the surface chemistry. A comparison of planar and 3° vicinal TiO₂(100)1 × 1 reactivity shows that steps also play a spectator role. Although unreactive at room temperature, H₂O adsorbs molecularly at 120 K. Thermally induced dissociation occurs on annealing, to form Ti–O–H species with a bond angle of ~90°.

1. Introduction

The use of TiO₂ as a model photocatalyst for the dissociation of water has led the interaction of H₂O with TiO₂(001) (100) and (110) surfaces to be studied by a number of groups. This work has principally involved the use of x-ray and untraviolet photo-electron spectroscopies (XPS, UPS). Henrich *et al* (1977) evidenced a small degree of dissociative H₂O adsorption on both the argon ion (Ar⁺) bombarded and annealed TiO₂(110) surface at low exposure (<30 L (1 L = 1.32 × 10⁻⁶ mbar s)). At higher exposure (>10⁴ L) a significant degree of molecular adsorption is suggested, with the 3a₁ molecular orbital exhibiting a bonding shift of 0.5–1.0 eV to higher binding energy. Lo *et al* (1978) conclude that at 10⁵ L a small degree of molecular H₂O adsorption occurs at room temperature on the oxygen-rich TiO₂(100)1 × 3 surface, while H₂O dissociates on the Ti³⁺ rich (1 × 7) surface. Smith and Bernasek (1987) found that H₂O dissociatively adsorbs on well annealed and Ar⁺-bombarded TiO₂(001) surfaces. Finally, a recent study by Eriksen *et al* (1987) suggests that dissociative adsorption occurs at room temperature on TiO₂(110) surfaces which contain defects introduced either by electron or Ar⁺ bombardment.

In this work we have studied the H₂O–TiO₂(100) interaction at low H₂O exposure using soft x-ray photo-emission spectroscopy. Our specific aim was to determine the effect on the reactivity of reasonably well characterised oxygen vacancies and steps. To this end, we have characterised both the surface termination of TiO₂(100)1 × 1 using

surface core-level shift data, and the step structure of a 3° vicinal surface. We find that neither the step structure studied nor oxygen vacancies notably change the reactivity.

2. Experimental

The photo-emission measurements were performed using the grazing incidence mono-chromator ($30 \leqslant h\nu \leqslant 200$ eV) and cylindrical mirror analyser (CMA) on station 6.1, and the toroidal grating monochromator ($18 \leqslant h\nu \leqslant 120$ eV) and Vacuum Generators ADES 400 system on station 6.2 at the SRS, Daresbury Laboratory. The photon energy used for the surface core-level shift work was 110 eV, while the valence band photo-emission experiments were carried out at 33 eV, the combined resolution (mono-chromator + analyser) being $\simeq 0.4$ eV and 0.15 eV (FWHM) at 110 eV and 33 eV respect-ively.

Most of the data presented here were recorded from a TiO_2 surface which was cut and polished 3° off the (100) plane towards [010]. Analysis of the spot splitting observed in low-energy electron spectroscopy (LEED) indicates that the surface has terraces of length ~12 unit cells connected by (110)-plane steps with a displacement of $a/2$ along [100]. The sample was cleaned *in situ* by 500–1000 eV Ar^+ bombardment and subsequent annealing in O_2 at 870 K; the latter procedure restores the surface stoichiometry, as determined by the lack of band-gap emission in UPS (Lo *et al* 1978). In our work we found that a stoichiometric surface corresponds to $TiO_2(100)1 \times 1$. The ordered-defect $TiO_2(100)1 \times 5$ surface was prepared by annealing the crystal in vacuum to 1100 K for 1–2 h. Surface contamination was monitored with Auger electron spectroscopy, with LEED used to monitor the transition of the surface from 1×1 to 1×5 on annealing. Exposure to H_2O was carried out using the vapour of double distilled water which was thoroughly degassed before use. With the exception of the planar (100) surface, which has not been studied in detail at room temperature, we found the $TiO_2(100)$ surfaces studied to be unreactive at room temperature up to the maximum exposure employed (10 L), at least on the basis of photo-emission spectra. The adsorption data presented here resulted from exposure at ~120 K, where a typical dose of 2 L resulted in approxi-mately a monolayer coverage.

$TiO_2(001)$ surface core-level shift measurements were obtained from a sample frac-tured *in situ* to yield a clean and well ordered 1×1 surface, as determined by Auger and LEED.

3. Results and discussion

3.1. Substrate characterisation

The Ti 3s core-level photo-emission spectra of the clean $TiO_2(001)$ and $(100)1 \times 1$ surfaces are displayed in figure 1, along with the spectrum recorded after H_2O adsoprtion on the (001) surface. The photon energies used yielded Ti 3s photo-electron energies of ~40 eV, which is close to the electron mean free path minimum, thus enhancing surface-related features. The Ti 3s spectra of the (001) surface have been fitted with three overlapping symmetric Gaussian peaks. Attempts to fit with one bulk and one surface peak were not satisfactory. The experimental surface core-level shifts for the (001) surface (i.e. binding energy shifts relative to the bulk peak position) of 0.79 and -0.80 eV
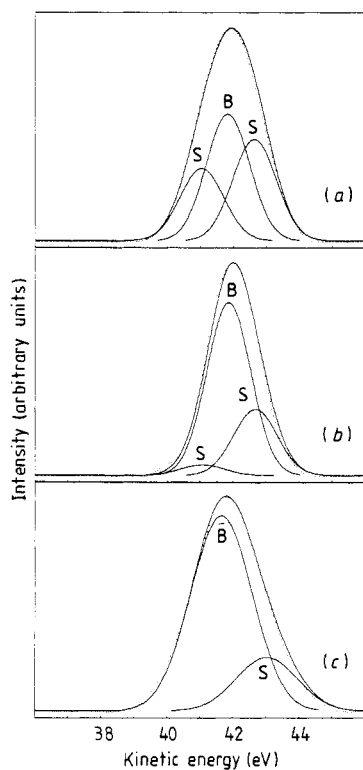
Figure 1. Ti 3s photo-emission spectra at 140 K of: (*a*) clean TiO$_2$(001): (*b*) 10 L H$_2$O-dosed TiO$_2$(001); and (*c*) clean TiO$_2$(100)1 × 1, recorded at hν = 110 eV. TiO$_2$(001) spectra are aligned with the TiO$_2$(100) spectrum at the bulk peak position. The spectra have been background subtracted and fitted to symmetric Gaussian peaks. Dotted curves, experimental; full curves, sum of the Gaussian components. S(B) indicates a surface (bulk) origin.

compare with values calculated on the basis of bulk termination, 0.75 and −0.2 eV for the first and second layer Ti atoms respectively (Kasowski and Tait 1979). Hence, the most obvious assignment would be the low (high) kinetic energy component to surface (2nd layer) Ti atoms. This is supported by the reaction of the features of H$_2$O adsorption, where the amplitude of the low kinetic energy component is much more strongly attenuated relative to the bulk feature.

While only one termination of the TiO$_2$(001) surface is possible, having four-fold coordinated Ti, in principle three terminations are possible for TiO$_2$(100)1 × 1 (Munnix and Schmeits 1984). Since only one surface core-level shifted feature is resolved in the TiO$_2$(100)1 × 1 data, which is unaffected by H$_2$O adsorption, it seems reasonable to suppose that, as in the case of TiO$_2$(001), this high kinetic energy feature arises from second-layer Ti. In turn this tends to rule out a four-fold coordinate Ti termination of the (100)1 × 1 surface which would be expected to give a well separated low kinetic energy core-level shift. Furthermore, surface dipole considerations, based on Tasker's rule (Tasker 1983), would also argue against the 'O$_2$ termination', which contains six-fold coordinate Ti, leaving as a working model the 'O termination' containing five-fold coordinate Ti. On this basis we suppose that the 1 × 5 surface is formed by removing some O atoms from the surface layer to yield four-fold coordinate Ti.

3.2. Reactivity

A comparison of valence band photo-emission spectra obtained from TiO$_2$(100)1 × 5 before and after exposure to H$_2$O at ~120 K is shown, along with the difference spectrum
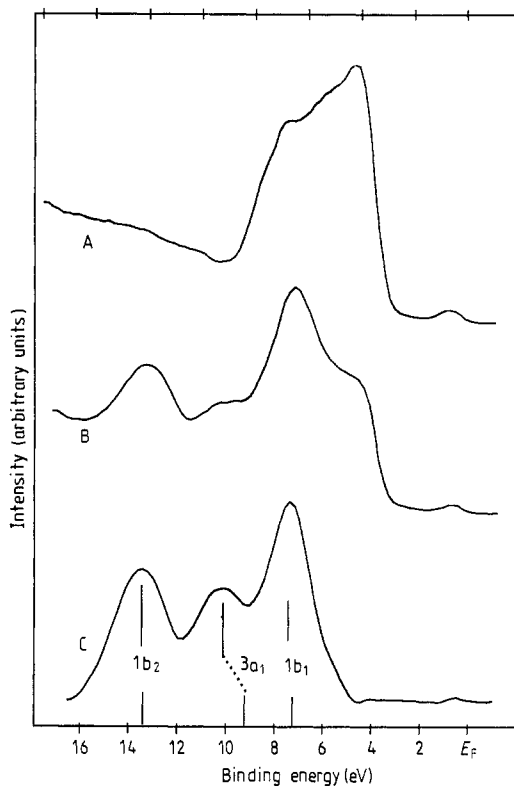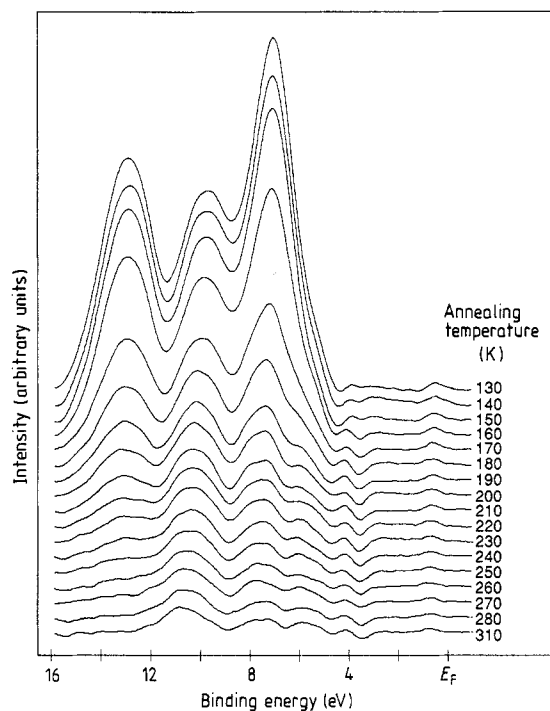
Figure 2. $TiO_2(100)1 \times 5$ normal emission photo-electron spectra ($h\nu = 33$ eV) obtained from: A, a clean surface at 120 K; B, after dosing with 2 L H_2O at 120 K; and C the difference of the spectra B − A. The lower ticks show the position of the molecular orbitals of gas phase H_2O.

in figure 2. The three features observed in the difference spectrum can be attributed to the $1b_2$, $3a_1$ and $1b_1$ molecular orbitals of H_2O. When aligned at the $1b_2$ energy a $3a_1$ bonding shift of 0.9 eV is observed in the difference spectrum, similar to that observed by Brookes *et al* (1988) for $SrTiO_3(100)$.

Figure 3 shows the difference spectra obtained by annealing the sample incrementally. It is apparent that between the temperatures of 130 K and 150 K little loss in the H_2O-induced peak intensities is observed; however between 150 K and 170 K the peak intensities fall by ∼50%. At temperatures above 170 K we see a gradual decrease in peak intensities with the peak at ≈13 eV disappearing at 280–290 K, while the other features are still present after annealing to 450 K. These remaining features, '$3a_1$' and '$1b_1$', are however shifted to higher binding energy by 1.23 and 0.4 eV respectively. An additional peak appears at ≈6 eV at temperatures higher than 170 K; at lower temperatures the $1b_1$ peak masks its presence and it can only be seen as a small shoulder. This additional peak follows the same pattern of intensity loss with temperature as the '$3a_1$' and '$1b_1$' features.

Our interpretation of the above data involves the thermally activated dissociation of H_2O, being evidenced by the disappearance of the $1b_2$ peak and the apparent shift of the $3a_1$ and $1b_1$ orbitals at positions characteristic of OH_σ and OH_π (Brookes *et al* 1988) (note however that in this paper the σ–π separation was erroneously compared with final state splitting in the gas phase OH_π spectrum). The 6 eV peak has been observed previously in He–I ($h\nu = 21.2$ eV) UPS work (Lo *et al* 1978, Henrich *et al* 1977), where it was interpreted as the $1b_1$ orbital of H_2O. The data shown in figure 3, which benefit

Figure 3. Normal emission photoelectron difference spectra ($h\nu = 33$ eV) obtained by sequentially annealing the surface represented in figure 2 curve B incrementally to the temperature indicated.

from the use of a higher photon energy and hence a lower inelastic background, indicate a different origin. We attribute this peak to a surface hydroxyl group in which the Ti–O–H bond angle is around 90°, which removes the degeneracy of the OH_π orbitals. A similar feature in the spectrum of H_2O dosed Si(111) has been assigned in a similar manner by comparison with electronic structure calculations (Fives *et al* 1989); the low binding energy shoulder of the OH_π spectrum shown by Brookes *et al* (1988) probably has the same origin.

Comparison of the data obtained from the 1×1 and 1×5 surfaces shows no significant differences, which would seem to indicate that the presence of surface defects does not play a major role in the dissociation of H_2O. In addition, data obtained from planar $TiO_2(100)$ compared to those obtained from the stepped surface produced by cutting a crystal 3° off the (100) plane show no significant difference.

4. Summary

In this paper we have investigated the effect of oxygen vacancies and steps on the reactivity of $TiO_2(100)$ with H_2O and found that oxygen vacancies do not play a prominent role. Although this might appear contrary to the accepted view regarding minority site domination of oxide surface reactivity, we note that oxygen vacancies were found to be equally unimportant in the reactivity of $SrTiO_3(100)$ (Brookes *et al* 1988). As for step site reactivity, it is perhaps not surprising that the (110) steps do not enhance the reactivity since the Ti coordination number on these steps is 5, the same as on the terraces. This is in contrast with $SrTiO_3(100)$ step sites, which were found to be reactive (Brookes *et al* 1988), where four-fold coordinate Ti edge sites are present.

Acknowledgment

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