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Changes to the occupied and unoccupied electronic structure of $\text{TiO}_2(100)$ upon alkali metal reduction

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Abstract: Direct and inverse ultraviolet photoemission spectroscopy (UPS and IPS) are used to measure the occupied and unoccupied electronic structure of $\text{TiO}_2(100)1 \times 1$ and $\text{TiO}_2(100)c(2 \times 2)K$. UPS results from stoichiometric $\text{TiO}_2(100)1 \times 1$ are in good agreement with earlier studies. IPS data recorded from $\text{TiO}_2(100)1 \times 1$ show two distinct features with energy positions 1.7 eV and 5.3 eV above the Fermi level (E_F). These features are associated with the Ti 3d derived t_{2g} and e_g levels. Upon formation of $\text{TiO}_2(100)c(2 \times 2)K$, achieved by annealing K treated $\text{TiO}_2(100)1 \times 1$, several changes are observed to occur to the surface electronic structure. Population of a band gap state pins E_F and removes band bending at the surface. The valence band of $\text{TiO}_2(100)c(2 \times 2)K$ is noted to be substantially narrower (of the order of 0.5 eV) than that of $\text{TiO}_2(100)1 \times 1$. In addition to this, a sharp feature lying to the high binding energy side of the valence band is populated. Concurrently, intensity in the Ti t_{2g} derived conduction band level is lost. This redistribution of spectral intensity observed between $\text{TiO}_2(100)1 \times 1$ and $\text{TiO}_2(100)c(2 \times 2)K$ is interpreted in terms of a K induced redistribution of charge at the surface. We use resonant photoemission to test the idea that this charge redistribution involves mainly the Ti d levels.

1. INTRODUCTION

The wide variety of physical and chemical properties possessed by transition metal (TM) oxides provides the basis for their technological importance as well as their fundamental scientific interest. Their broad technological relevance is reflected in their use as catalysts and catalytic support materials, as gas sensor devices and as support structures for a variety of applications, including the high temperature superconductors. Scientifically, interest in these materials has recently been increasing, with established techniques, both theoretical and experimental, being extended to tackle these challenging systems.

In this paper we examine the occupied and unoccupied electronic structure in the region of the Fermi level of a prototype TM oxide, rutile $\text{TiO}_2(100)$ [1], and the modification to this caused by alkali metal surface reduction. Similarities have previously been noted between O deficient rutile surfaces and those which have been exposed to alkali metals [2, 3]. We principally address the ordered form of the K treated surface, $\text{TiO}_2(100)c(2 \times 2)K$. This system also serves as a model for the technologically important metal to metal oxide interface.

2. EXPERIMENTAL

Direct and inverse photoemission spectra were recorded using the IBM Rüsclikon spectrometer [4]. IPS were performed in the isochromat mode, with photons of 9.5 eV being collected by a Geiger-Müller type detector. UPS measurements employed He I radiation (21.2 eV) and a hemispherical angle resolving analyser. Complimentary resonant photoemission data were recorded utilising the grazing incidence monochromator of station 6.1 at the Synchrotron Radiation Source, Daresbury Laboratory.

The rutile $\text{TiO}_2(100)$ sample was prepared by standard methods [5]. Charging problems were obviated by working with a sample that has been rendered oxygen deficient in the bulk. Annealing the sample to 850 K in a partial pressure of O_2 (1×10^{-6} mbar), results in the formation of a stoichiometric surface which displays a clear 1×1 LEED pattern. K was provided by a well outgassed getter source. Ordering of the adsorbate could only be achieved by post annealing the K dosed surface to ~ 1000 K. This results in a clear $c(2 \times 2)$ LEED pattern.

3. RESULTS AND DISCUSSION

Figure 1 displays inverse and direct photoemission from $\text{TiO}_2(100)1 \times 1$ and $\text{TiO}_2(100)c(2 \times 2)K$ covering the range -9 to $+9$ eV. The energy scales of these spectra are referenced to the Fermi level of the spectrometer. Data from $\text{TiO}_2(100)1 \times 1$ have been adjusted to account for band bending, mentioned further below. These spectra were recorded in a geometry where the component of electron momentum parallel to the surface (k_{\parallel}) is zero (or near zero in the case of the inverse photoemission spectrum from $\text{TiO}_2(100)1 \times 1$). The IPS spectra do not show a strong k_{\parallel} dependence. The photoemission spectra do show a strong dependence on k_{\parallel} , and this is discussed below.

Firstly, we note that the UPS data from $\text{TiO}_2(100)1 \times 1$ are in line with previous studies [6]. The valence band (VB) of rutile TiO_2 , represented by the UPS data, is derived predominantly from O $2p$ levels. The conduction band (CB), on the other hand, is principally Ti $3d$ derived. In rutile TiO_2 , Ti sits in a distorted octahedral co-ordination. In a molecular orbital picture, this type of co-ordination for a TM leads to a crystal field splitting of the d levels into t_{2g} and e_g levels. Two prominent features in the CB density of states of rutile are generally described within this picture [7] and we associate the two

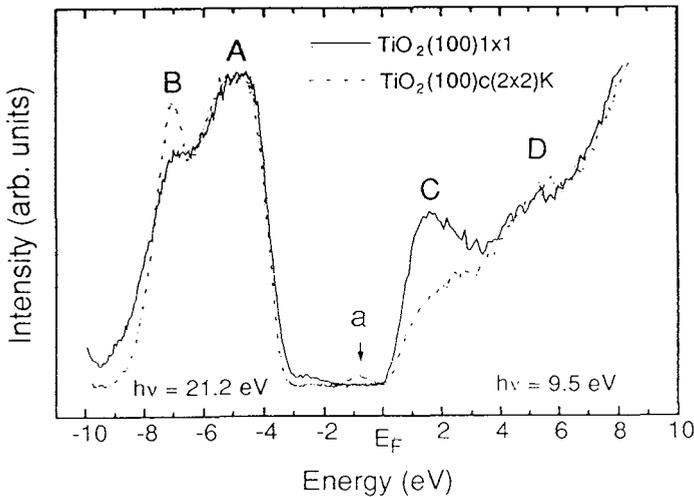


Figure 1. Valence band and conduction band spectra of $\text{TiO}_2(100)1 \times 1$ and $\text{TiO}_2(100)c(2 \times 2)K$. The arrow marks the band gap state mentioned in the text. Spectra are recorded at (or close to, in the case of the $\text{TiO}_2(100)1 \times 1$ IPS data) normal electron incidence/emission. The data sets from $\text{TiO}_2(100)1 \times 1$ have been corrected for band bending, as described in the text. Relative normalisation of the UPS and IPS spectra has been performed only with presentation in mind. Linear backgrounds have been subtracted from all spectra.

peaks observed at 1.7 (C) and 5.3 eV (D) in the IPS data from $\text{TiO}_2(100)1 \times 1$ with the t_{2g} and e_g levels, respectively.

Band bending at the $\text{TiO}_2(100)1 \times 1$ surface arises due to the difference in stoichiometry between the surface and the oxygen deficient bulk. As previously noted [2], adsorption of K onto $\text{TiO}_2(100)1 \times 1$ results in the population of a state in the band gap (a in figure 1). Similar to the effect when the surface is made O deficient [5], this state serves to pin E_F . The effect of band bending on both occupied and unoccupied states can most clearly be seen in a comparison between $\text{TiO}_2(100)1 \times 1$ and the O deficient $\text{TiO}_2(100)1 \times 3$ surface phase [8]. Apart from pinning E_F , we observe that the VB of $\text{TiO}_2(100)c(2 \times 2)K$ is substantially narrowed in comparison to that of $\text{TiO}_2(100)1 \times 1$. Both the VB onset and the high binding energy edge of the VB are brought towards the centre of the band, and the band width is reduced by ~ 0.5 eV. One consequence of this is that the position of the VB onset cannot be taken as a measure of band bending, as was previously thought [2]. The IPS data show that the conduction band onset above E_F does not experience a similar K induced shift.

The most striking difference between the electronic structure of $\text{TiO}_2(100)c(2 \times 2)K$ and $\text{TiO}_2(100)1 \times 1$ is a dramatic reduction in intensity of the t_{2g} peak in the CB for $\text{TiO}_2(100)c(2 \times 2)K$, together with a similarly dramatic appearance of a prominent peak at the high binding energy side of the VB. The prominence of this feature is even more apparent in angle integrated UPS data [8]. Apart from the drawing in of the upper VB edge, the main VB structure above ~ -6 eV is little changed between $\text{TiO}_2(100)1 \times 1$ and $\text{TiO}_2(100)c(2 \times 2)K$. Similarly, there is little difference in the CB structure between the two surfaces above ~ -4 eV (in the range measured). The data are interpreted in a direct manner, where unoccupied Ti levels are being occupied with charge injected into the surface by the adsorbate. The spectral contribution of K 4s states is taken to be zero: the K 3p core levels lie at around -18 eV, and we believe that the cross sections relevant to our spectrometer of higher lying levels is too small for us to observe them. It has already been demonstrated that the band gap state populated when K is adsorbed onto $\text{TiO}_2(100)1 \times 1$ has Ti d character [10]. Based partly on a comparison with band structure calculations [11] which show that the dominant Ti 3d contribution to the VB lies to the high binding energy side, we surmise that the prominent peak which appears upon formation of $\text{TiO}_2(100)c(2 \times 2)K$ can also be associated with the Ti d levels. We make an initial test of this hypothesis using resonant photoemission, below. This is an extension of the model for $\text{TiO}_2(100)c(2 \times 2)K$ prior to this work, where K bonds to surface O on an unrelaxed surface and is responsible for an injection of charge into the substrate [10]. D^+ scattering experiments support a model where an alkali metal adsorbate bonds to rutile with complete loss of its outer electron [12]. Furthermore, the lowering of the work function from $\text{TiO}_2(100)1 \times 1$ by ~ 2 eV upon formation of $\text{TiO}_2(100)c(2 \times 2)K$ is consistent with a formation of a surface dipole. Given that the annealing conditions required to achieve the ordered form of the K treated surface are high enough to remove surface O from $\text{TiO}_2(100)1 \times 1$ [5], it seems likely that further modification to the model for $\text{TiO}_2(100)c(2 \times 2)K$ will be necessary. We remain confident, however, that K bonds to surface O [10].

Finally, we present in table 1 results from photoemission data recorded from $\text{TiO}_2(100)c(2 \times 2)K$ at two different photon energies, 47 eV and 110 eV. Due to a coupling of 3p-3d excitations in Ti, the cross section for photoemission from Ti 3d levels goes through a resonance at 47 eV [10]. Resonant photoemission in principle allows one to disentangle element specific partial density of states of the VB. The data in table 1 represent relative peak intensities at two points in the valence band: one at high binding energy (-7.5 eV), corresponding to the position of the K derived feature; and one at relatively low binding energy (-5.5 eV), corresponding to part of the valence band insensitive to the formation of the $c(2 \times 2)K$ overlayer system. The ratio of the high binding energy to low binding energy peak intensities on (47 eV) and off (110 eV) the Ti 3d resonance energy is given. These figures show that the enhancement of the high binding energy side of the valence band at resonance is greater than that at the low binding energy side. This relative enhancement is further pronounced for $\text{TiO}_2(100)c(2 \times 2)K$, thus supporting the idea of increased Ti d character in the VB causing the peak at -7 eV. The wide energy distribution of Ti 3d levels, both theoretically calculated and experimentally observed, leads one to terms such as covalent solid, to describe this material. The evidence from this and other [12] studies points to K sitting on the surface in an ionic configuration. Nevertheless, it seems that the nature of

bonding in the substrate in the $\text{TiO}_2(100)c(2 \times 2)K$ system is more covalent than the stoichiometric rutile surface, in the sense that the Ti 3d partial density of states is less heavily weighted in the CB. In this interpretation of enhanced covalency, one might expect to see peaks dispersing with k_{\parallel} . In particular one might expect to see the VB peak at -7 eV disperse. This has not been observed. What is observed as electrons are collected with finite k_{\parallel} , however, is a strong dependence in the magnitude of this feature, although this could be an escape depth phenomenon [8].

We conclude that the adsorption of K onto $\text{TiO}_2(100)1 \times 1$ and subsequent ordering to $\text{TiO}_2(100)c(2 \times 2)K$ results in a major redistribution of charge in the surface region. We further note that this could have important implications for alkali metal promotion of catalytic activity.

Table 1. A comparison of the relative intensity of the high and low binding energy (b.e.) sides of the valence bands (VB) of the two surfaces studied on (47 eV) and off (110 eV) the Ti 3d photoemission resonance. For both $\text{TiO}_2(100)1 \times 1$ and $\text{TiO}_2(100)c(2 \times 2)K$, the high b.e. side of the VB is enhanced over the low b.e. side at 47 eV. This enhancement is greater for $\text{TiO}_2(100)c(2 \times 2)K$, suggesting that there is a greater degree of Ti 3d weight in this region of the VB compared to $\text{TiO}_2(100)1 \times 1$. See the text for further details

photon energy	$\text{TiO}_2(100)1 \times 1$		
	intensity at A (I_A)	intensity at B (I_B)	I_B/I_A
47 eV	1.3	1.5	1.1
110 eV	1.2	1	0.90
$\text{TiO}_2(100)c(2 \times 2)K$			
47 eV	1.4	1.9	1.3
110 eV	1.1	1	0.90

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