

## Potassium adsorption on $\text{TiO}_2(100)$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 S91

(<http://iopscience.iop.org/0953-8984/3/S/014>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:23

Please note that [terms and conditions apply](#).

## Potassium adsorption on $\text{TiO}_2(100)$

R Casanova†, K Prabhakaran and G Thornton

Interdisciplinary Research Centre in Surface Science and Chemistry Department,  
Manchester University, Manchester M13 9PL, UK

Received 25 April 1991

**Abstract.** Potassium adsorption on  $\text{TiO}_2(100)$  has been studied with low energy electron diffraction, Auger electron spectroscopy and photoemission. Potassium progressively lowers the work-function of  $\text{TiO}_2(100)$  with increasing coverage to a limit of  $2.2 \pm 0.1$  eV. A clear work-function minimum is not observed, as found for other semiconductor surfaces. The work-function decrease is accompanied by a downward band-bending, limiting at  $0.75 \pm 0.05$  eV. This arises from the population of band-gap states following charge transfer from K to the substrate. At half-monolayer coverage an ordered  $c(2 \times 2)$  overlayer is formed.

### 1. Introduction

Alkali metal adsorption on the surfaces of metal and semiconductor surfaces continues to be a subject of extensive study [1,2]. This work is motivated by interest in the alkali metal to substrate charge-transfer process, and its relation to promotion of catalytic reactions. Relatively little work has so far addressed the interactions of alkali metals with oxide surfaces, despite the known catalytic promotion effects [3].

Here we report a study which serves to characterize the adsorption of potassium on rutile  $\text{TiO}_2(100)$ .  $\text{TiO}_2$  surfaces have been the subject of a number of studies related to their photocatalytic properties [4]. More recently, charge transfer from sodium to  $\text{TiO}_2(110)$  has been claimed [5] and associated with the enhanced reactivity to  $\text{CO}_2$  and NO [6]. The  $\text{TiO}_2(100)/\text{K}$  system offers a number of advantages as a model with which to investigate structural and electronic properties of the alkali metal-oxide interface. In particular, we have previously characterized the stoichiometric  $(1 \times 1)$  and ordered oxygen vacancy  $(1 \times 3)$  surfaces of the substrate in a low energy electron diffraction (LEED) and photoemission study [7]. In addition, the potassium adsorption site is amenable to study by surface extended x-ray absorption fine structure (SEXAFS). Moreover, because  $\text{TiO}_2$  is a reducible oxide, charge transfer from K is clearly evidenced by changes to the valence electronic structure.

In this work we find that K progressively lowers the work-function of  $\text{TiO}_2(100)$  with increasing coverage, accompanied by a downward band bending which arises from the population of band-gap states. At half-monolayer coverage an ordered  $c(2 \times 2)$  overlayer is formed.

† Permanent Address: Universidad de los Andes, Facultad de Ciencias, Departamento de Física, Laboratorio de Física de Superficies, Mérida-Estado, Mérida, Venezuela.

## 2. Experimental details

LEED, Auger electron spectroscopy (AES) and He I ( $h\nu = 21.22\text{ eV}$ ) photoemission experiments were performed using an instrument described elsewhere [8]. In this work we employed a photoemission energy resolution of  $0.1\text{ eV}$  (FWHM), and an angular resolution of  $\pm 2^\circ$ . Photoemission spectra are referenced to the Fermi level,  $E_F$ , recorded from the Ta sample holder. AES measurements employed Varian LEED optics as a retarding field analyser with a primary beam energy of  $3\text{ keV}$ . The base pressure of the instrument during measurements was  $5 \times 10^{-11}\text{ mbar}$ .

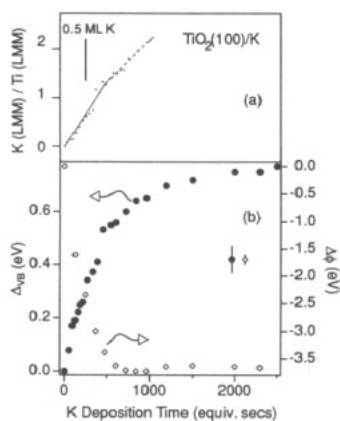
The  $\text{TiO}_2$  sample was cut from a boule of rutile  $\text{TiO}_2$  (Commercial Crystals Inc.) and polished ( $0.25\ \mu\text{m}$ ) to within  $0.25^\circ$  of the (100) plane as determined by Laue diffraction. Vacuum reduction was used to introduce n-type conductivity (ca.  $10^{18}\text{ cm}^{-3}$ ). The sample was cleaned *in situ* by  $500\text{ eV Ar}^+$  bombardment (5 minutes) resulting in a sample drain current of  $10\text{--}15\ \mu\text{A}$ , and subsequent annealing at  $870\text{ K}$ . This cycle was repeated until surface contamination was below the level of detection of AES. The  $1 \times 1$  stoichiometric surface was formed by annealing the clean sample in  $1 \times 10^{-6}\text{ mbar O}_2$  (99.985%; BOC Research Grade) at  $870\text{ K}$  for 15 minutes. This yielded a well-ordered surface as judged by LEED, the presence of a stoichiometric surface being confirmed by the absence of band-gap states in the He I photoemission spectrum [7]. Potassium was deposited using a well-degassed SAES getter source located at about  $3\text{ cm}$  from the room temperature sample. The pressure in the instrument increased to  $2 \times 10^{-10}\text{ mbar}$  during the initial stages of K deposition.

## 3. Results and discussion

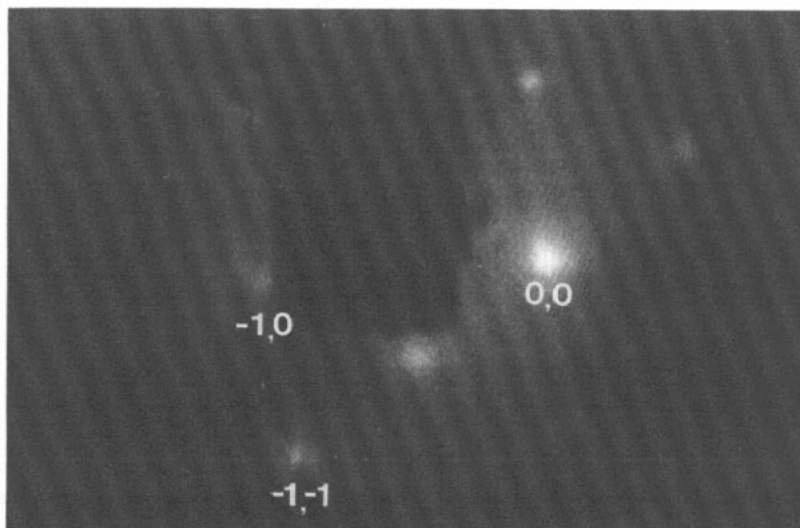
We firstly consider the growth of potassium on  $\text{TiO}_2(100)1 \times 1$  as viewed by AES. To do so we monitor the ratio of the K LMM/Ti LMM Auger peak heights. These features arise at kinetic energies of  $251\text{ eV}$  (K LMM) and  $381\text{ eV}$  (Ti LMM). Figure 1(a) depicts the Auger ratio as a function of deposition time. The latter is given in equivalent seconds to account for different conditions of the getter source during Auger and work-function and band-bending measurements. The behaviour observed in figure 1 was reproduced several times. A clear change in slope of the Auger ratio is apparent at  $\sim 500$  seconds, which we take to indicate formation of the first atomic layer of K. The Auger ratio at  $\sim 250$  seconds is  $0.68 \pm 0.02$ , which is consistent with half-monolayer coverage on the basis of standard sensitivity factors [9] and the transmission of the retarding field analyser [10]. No further breaks in the slope of the K-uptake curve were observed up to a total deposition period of 35 minutes. This is typical of Stranski-Krastranov behaviour, with first layer formation followed by island growth [11].

At a half-monolayer coverage of K a  $c(2 \times 2)$  LEED pattern is observed, which is reproduced in figure 2. A  $c(2 \times 2)$  LEED pattern was observed in the Auger ratio range of  $0.65\text{--}0.75$ , indicating the absence of island formation. The half-order beams are lost at higher coverages, the substrate beams becoming more diffuse and the background increasing. A model of a possible structure of the  $c(2 \times 2)$  overlayer is shown in figure 3. This model assumes that the substrate is terminated with oxygen atoms, with Ti in the second layer [12]. In figure 3, K atoms are shown to be bound to two O atoms in a symmetric bridge site, the geometry favoured by recent SEXAFS measurements [13].

The changes in the work-function,  $\Delta\phi$ , and band-bending,  $\Delta V_B$ , accompanying K adsorption are displayed in figure 1(b). Work-function measurements employed the



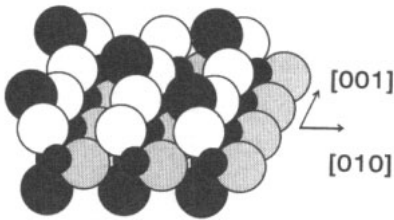
**Figure 1.** Variation with the period of K deposition on  $\text{TiO}_2(100)1 \times 1$  of : (a) the ratio of K LMM/Ti LMM Auger peak intensities; and (b) the change in work-function ( $\Delta\phi$ ) and downward band-bending ( $\Delta_{VB}$ ). The error bar on the Auger ratio is  $\pm 0.02$ . The time scale is that of the work-function and band-bending measurements. Work-function measurements carried out when measuring the Auger ratio were used to normalize the time scale.



**Figure 2.** The  $c(2 \times 2)$  LEED pattern observed at half-monolayer coverage of K, recorded at an electron energy of 47 eV. The position vector of the 0, -1 beam is parallel to [001].

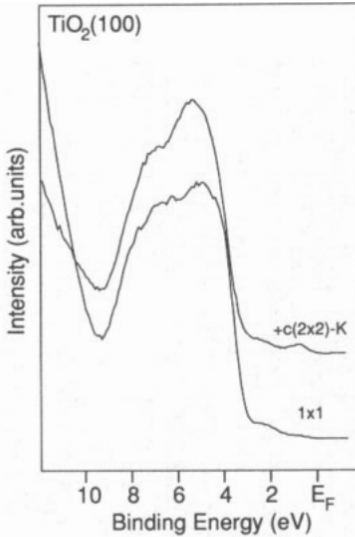
width of the photoemission spectrum while applying a sample bias of 9 V [14]. Band bending was obtained from the shift of the valence band edge with respect to  $E_F$ .

The work-function decreases from the clean surface value of  $5.9 \pm 0.1$  eV to  $3.5 \pm 0.1$  eV at half-monolayer K coverage with a limit of  $2.2 \pm 0.1$  eV, the work-function of metallic K [15]. Within experimental error, no minimum is observed in the variation of  $\Delta\phi$  with coverage, typical of alkali metal adsorption on semiconductors [16]. For metals, the work-function decrease is linear with coverage initially, as in the case of semiconductors. However, at higher coverage the unoccupied levels of the alkali metals



**Figure 3.** Proposed structural model of  $\text{TiO}_2(100)c(2 \times 2)\text{-K}$ . Atom types are approximately scaled to their ionic radii. Empty and shaded large circles represent the first- and lower-layer atoms, respectively. Small circles are Ti and filled circles are K.

drop in energy and cross  $E_F$ . This causes an electron flow from the substrate to the positive ions resulting in an increase in work-function. In the case of semiconductors the presence of band-gap states prevents this re-neutralization. The detailed origin of the surface dipole which gives rise to the decrease in work-function on semiconductors is still the subject of debate. This is focussed on the extent of charge transfer from the alkali metal to the semiconductor [16].



**Figure 4.** Unpolarized He I ( $h\nu = 21.22 \text{ eV}$ ) photoemission spectra of  $\text{TiO}_2(100)1 \times 1$  and  $\text{TiO}_2(100)c(2 \times 2)\text{-K}$  recorded at room temperature, normal emission and an angle of incidence of  $45^\circ$  in the  $[001]$  azimuth. Spectra have not been corrected for band-bending.

A downward band-bending towards the surface is observed, with a change of gradient at monolayer coverage, and a saturation limit of  $0.75 \pm 0.05 \text{ eV}$ . The origin of the band-bending for  $\text{TiO}_2(100)c(2 \times 2)\text{-K}$  can be seen in figure 4, which compares the photoemission spectra of  $\text{TiO}_2(100)1 \times 1$  and  $\text{TiO}_2(100)c(2 \times 2)\text{-K}$ . As well as changes to the valence band structure on K adsorption, band-gap state emission is seen at  $\sim 1 \text{ eV}$  binding energy. These states, which are very sensitive to contamination, pin  $E_F$  at the surface. While the spectrum of  $\text{TiO}_2(100)1 \times 1$  does not contain band-gap states, the creation of surface oxygen vacancies gives rise to a characteristic feature at  $0.9 \pm 0.1 \text{ eV}$  binding energy [7]. This corresponds to reduction of surface Ti atoms to

$\text{Ti}^{3+}$ , with the band-gap feature representing Ti 3d ionization. The implication that K-adsorption results in K 4s to Ti 3d charge transfer is clear. This is borne out by resonance photoemission measurements at the Ti  $M_{2,3}$  absorption edge [13].

#### 4. Summary

In this work we have investigated the adsorption properties of potassium on  $\text{TiO}_2(100)1 \times 1$ . We find that adsorption follows Stranski-Krastranov growth behaviour, with a  $c(2 \times 2)$  ordered overlayer formed at half-monolayer coverage. The model proposed for the  $c(2 \times 2)$ -K overlayer has K bonded to two top-layer oxygen atoms in a symmetric bridge site. The lowering of the work-function by K adsorption is accompanied by a downward band-bending towards the surface. We conclude that the origin of the band-bending and the decrease of the work-function is due to K 4s  $\rightarrow$  Ti 3d charge transfer.

#### Acknowledgment

The work was funded by the Science and Engineering Research Council, including the award of a Visiting Fellowship to RC.

#### References

- [1] Persson B N J and Ishida H 1990 *Phys. Rev. B* **42** 3171 and references therein
- [2] Wu R-Q and Wang D S 1990 *Phys. Rev. B* **41** 12541
- [3] Driscoll D J, Martir W, Wang J X and Lunsford J H 1985 *J. Am. Chem. Soc.* **107** 58
- [4] Izumi I, Fan F R F and Band A J 1981 *J. Phys. Chem.* **85** 218
- [5] Onishi H, Aruga T, Egawa C and Iwasawa Y 1988 *Surf. Sci.* **199** 54
- [6] Onishi H, Aruga T, Egawa C and Iwasawa Y 1989 *J. Chem. Soc.; Faraday Trans. I* **85** 2597
- [7] Muryn C A, Hardman P J, Crouch J J, Raiker G N, Thornton G and Law D S-L 1991 *Surf. Sci.* **251/252** 747
- [8] Wincott P L, Brookes N B, Law D S-L, Thornton G and King G C 1989 *J. Phys. E: Sci. Instrum.* **22** 42
- [9] Davis L E, MacDonald N C, Palmberg P W, Riach G E and Weber R E 1976 *Handbook of Auger Electron Spectroscopy* 2nd edn (Minnesota: Physical Electronics Industries)
- [10] Wincott P L 1986 *PhD Thesis* Manchester University
- [11] Zangwill A 1988 *Physics at Surfaces* (Cambridge: Cambridge University Press)
- [12] Munnix S and Schmeits M 1984 *Phys. Rev. B* **30** 2202
- [13] Prabhakaran K, Purdie D, Casanova R, Muryn C A, Hardman P J, Lindsay R, Wincott P L and Thornton G 1991 *Phys. Rev. B* submitted
- [14] Derry G N 1986 *J. Phys. Chem. Solids* **47** 237
- [15] Cardona M and Ley L 1978 *Photoemission in Solids I (Topics in Applied Physics 26)* (Berlin: Springer)
- [16] Mönch W 1984 *Chemistry and Physics of Solid Surfaces V (Series in Chemical Physics 35)* (Berlin: Springer)