



A surface X-ray diffraction study of $\text{TiO}_2(1\ 1\ 0)(3 \times 1)\text{-S}$

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ARTICLE INFO

Article history:

Received 24 October 2008

Accepted for publication 18 March 2009

Available online 31 March 2009

Keywords:

X-ray scattering, diffraction, and reflection

Chemisorption

Surface relaxation and reconstruction

Titanium oxide

Sulphur

Low index single crystal surfaces

ABSTRACT

Surface X-ray diffraction has been used to investigate the structure of $\text{TiO}_2(1\ 1\ 0)(3 \times 1)\text{-S}$. In concert with existing STM and photoemission data it is shown that on formation of a $(3 \times 1)\text{-S}$ overlayer, sulphur adsorbs in a position bridging 6-fold titanium atoms, and all bridging oxygens are lost. Sulphur adsorption gives rise to significant restructuring of the substrate, detected as deep as the fourth layer of the selvedge. The replacement of a bridging oxygen atom with sulphur gives rise to a significant motion of 6-fold co-ordinated titanium atoms away from the adsorbate, along with a concomitant rumpling of the second substrate layer.

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1. Introduction

The adsorption of elemental sulphur and sulphur-containing molecules on metal and metal oxide surfaces has been extensively studied; reviews of previous work can be found in Ref. [1,2]. Major motivators for such work include the study of catalyst poisoning and the development of novel desulphurisation catalysts. The study of sulphur adsorption on metal oxides is of particular interest; they are widely used as catalysts and catalyst supports [3] and offer both metal and oxygen sites, allowing the formation of surface species with considerably different electronic properties. Titanium dioxide, which is the subject of the present work, is employed as a commercial desulphurisation catalyst [3], and recent work suggests that the study of sulphur adsorption on TiO_2 surfaces will be relevant in the design of novel dye molecules for use in low-cost dye sensitised solar cells [4].

Previous investigations have concentrated on the adsorption of sulphur-containing molecules on TiO_2 surfaces (see [5] and references therein) with fewer studies investigating the adsorption of elemental sulphur. Diebold and co-workers have identified a variety of surface phases arising from sulphur deposition with scanning tunnelling microscopy (STM), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) [6,7]. They have also explored the effect of the substrate reduction state on sulphur adsorption [8]. Other studies have employed photoemission [8–10], thermal desorption mass spectroscopy,

and first principles density functional theory calculations [10]. First principles molecular dynamics simulations have been undertaken by Langel to elucidate the mechanisms by which sulphur adsorbs [11].

Adsorption of elemental sulphur on a substrate heated to between 470 and 570 K gives rise to a $(3 \times 1)\text{-S}$ structure [6,7], which is the subject of the present work. STM images of this phase recorded at low coverage indicate adsorption of sulphur in the position of the bridging oxygen rows. The binding energy of the S 2p photoemission peak (162.4 eV) indicates the formation of S–Ti rather than S–O species. In addition, the appearance of a Ti^{3+} shoulder to the Ti 2p_{3/2} XPS peak suggests the formation of under-coordinated titanium atoms due to the loss of surface oxygen. On the basis of this evidence, it is concluded that the (3×1) structure is formed by the complete removal of bridging oxygens, every third of which is replaced by a sulphur atom [6]. This model is illustrated in Fig. 1.

While the model in Fig. 1 is intuitively reasonable, neither the adsorption site nor bridging oxygen occupancy have been rigorously determined. On the basis of the STM data, it is reasonable to place sulphur on the rows of 6-fold co-ordinated titaniums, but STM provides no evidence for the registry of sulphur atoms in the [0 0 1] direction. The Ti^{3+} peak is attributed to under-coordinated titaniums arising from missing oxygen atoms, but it is not possible to quantitatively determine the occupancy of bridging oxygens from this observation. Moreover, Langel has demonstrated the stability of models where one or no bridging oxygen per unit cell are present [11]. Clearly a quantitative structural probe, such as surface X-ray diffraction (SXRD), is necessary to resolve these

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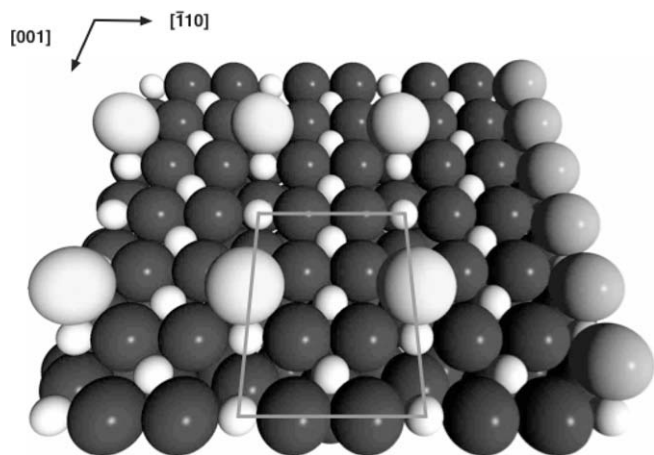


Fig. 1. Space filling model of the $\text{TiO}_2(1\ 1\ 0)(3 \times 1)\text{-S}$ structure proposed by Diebold et al. [6]. Sulphur adsorbs bridging 6-fold co-ordinated titanium atoms, displacing all bridging oxygens. Sulphur is represented by large white spheres, oxygen by black spheres and titanium by small white spheres. At the right of the figure a row of bridging oxygen atoms represented by grey spheres, is retained for comparison. A (3×1) unit cell is outlined.

questions. Such a study can be expected to yield precise values for any adsorbate-induced restructuring of the substrate.

2. Experimental

Surface X-ray diffraction measurements were undertaken at beamline 9.4 [12] of the Synchrotron Radiation Source (SRS), Daresbury (UK), employing the ultra-high vacuum endstation IN-GRID (INstrument for GRazing Incidence Diffraction). A $\text{TiO}_2(1\ 1\ 0)$ single crystal was prepared by cycles of bombardment with 1 keV Ar^+ ions and annealing to approximately 1000 K in UHV until partial reduction of the bulk was detectable by a change in sample colour from yellow to dark blue. The presence of a clean, well-ordered (1×1) surface was confirmed with LEED and Auger electron spectroscopy (AES). Sulphur was generated *in situ* by electrochemical decomposition of silver sulphide in a solid state electrochemical cell consisting of a silver iodide electrolyte, silver sulphide anode and silver cathode [13]. The clean surface, heated to approximately 570 K, was exposed to a beam of sulphur after which the presence of a well-ordered (3×1) surface was confirmed with LEED. The resulting pattern was comparable with those obtained *ex situ* from surfaces with saturation coverage, characterised with STM and XPS.

For the SXRD measurements, the INGRID chamber was coupled to a five-circle diffractometer, equipped with an additional manual sixth circle, which almost doubles the amount of accessible reciprocal space in the out-of-plane direction [14]. An X-ray wavelength of 0.9 Å was selected to maximise the available reciprocal space, whilst maintaining a usable photon flux. Data were accumulated using rocking scans, in which the sample was rotated about its surface normal while the scattered X-ray intensity was recorded with a cryogenically cooled, single element germanium detector. The data are indexed with reference to the (1×1) unit cell, with lattice vectors \mathbf{a}_1 and \mathbf{a}_2 being orthogonal in the plane of the $(1\ 1\ 0)$ surface in the $[\bar{1}\ 1\ 0]$ and $[0\ 0\ 1]$ directions respectively, with \mathbf{a}_3 perpendicular to the surface in the $[1\ 1\ 0]$ direction. The magnitudes of the unit cell vectors are $a_1 = a_3 = 6.495$ Å and $a_2 = 2.958$ Å. Reciprocal space axes h , k and l are parallel to \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 , respectively.

Rocking scans were performed at integer values of (h, k) as a function of (l) , providing profiles of scattered intensity versus perpendicular momentum transfer – crystal truncation rods (CTRs).

In-plane rocking scans were also acquired, at both integer and appropriate fractional (h, k) points, using small incidence and exit angles for the X-rays to give small values of perpendicular momentum transfer ($l = 0.3$). All data were recorded with the substrate at room temperature. During X-ray measurements, surface integrity was monitored by repeatedly measuring the $(h, k, l) = (3, 1, 0.3)$ and $(0, 1, 1.8)$ reflections. After completion of X-ray measurements, the integrity of the surface was confirmed with LEED and AES, a clear (3×1) LEED pattern being observed.

The rocking scans were integrated and corrected for effective sample area, X-ray beam polarisation and Lorentz factor to give structure factor amplitudes. Wherever possible, one or more symmetry-equivalent reflections were recorded and equivalent structure factors were averaged together to give the final data set. The variation between equivalent data points was used to estimate the systematic error, which at $\pm 9\%$ is the dominant error in the data set.

3. Results

The data consists of 168 symmetry inequivalent reflections including three CTRs $(h, k) = (0, 1)(0, 2)(1, 1)$ and an in-plane data

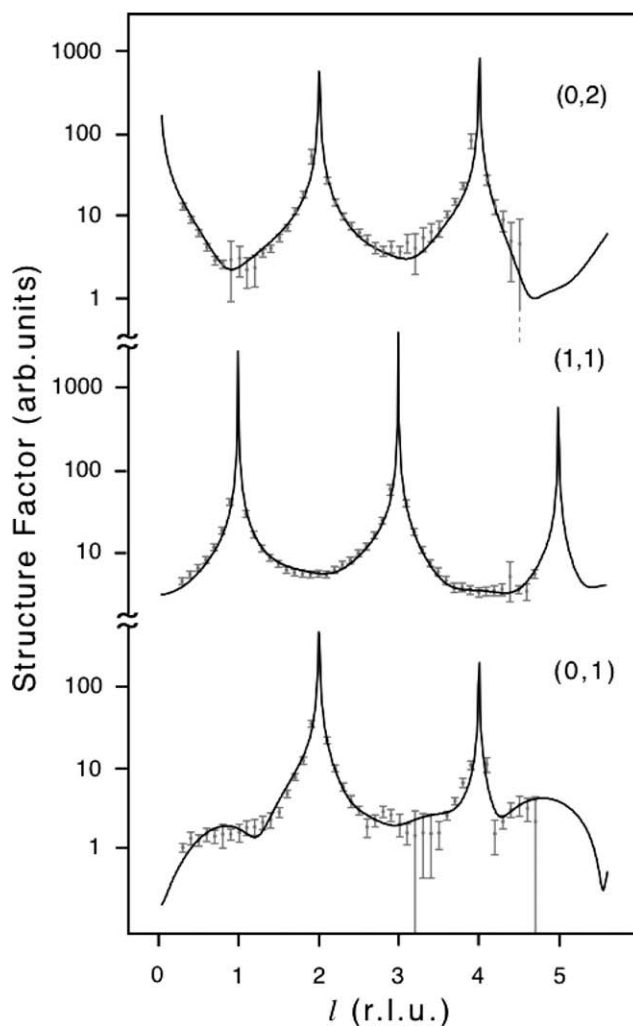


Fig. 2. Comparison of crystal truncation rod data and calculated best fit model data. Structure factors (F) are given in arbitrary units, out-of-plane momentum transfer (l) is given in reciprocal lattice units. Experimental data is plotted in grey with error bars, calculated data is shown as a continuous black line. The truncated error bars at $(0, 2, 4.5)$, $(0, 1, 3.2)$ and $(0, 1, 4.7)$ indicate a lower limit that extends to zero.

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