Reactive re-oxidation of reduced TiO$_2$(110) surfaces demonstrated by high temperature STM movies

P Stone, R A Bennett and M Bowker†
Catalysis Research Centre, Department of Chemistry, University of Reading, Reading, RG6 6AD, UK
E-mail: M.Bowker@Reading.ac.uk

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Abstract. The re-oxidation of slightly reduced TiO$_2$(110) surfaces by exposure to an oxygen pressure of $\sim 2 \times 10^{-7}$ mbar in the temperature range 473–1000 K occurs by re-growth of TiO$_2$ overlayers by diffusion of Ti$^{n+}$ interstitials from the bulk. Starting with a (1 × 2) reconstructed surface, scanning tunnelling microscope images of the surface reacting under these conditions show that the (1 × 1) islands nucleate within the (1 × 2) layer and grow laterally. As the islands reach a critical size, which is temperature dependent, a new (1 × 2) layer begins to nucleate and grow. At both extremes of the temperature range nucleation of the second layer occurs before coalescence of the (1 × 1) islands, however, at temperatures between 673 and 773 K large areas of (1 × 1) surface form before growth of the second layer. The reaction is cyclic and several layers of TiO$_2$ can be grown in this way.

1. Introduction

The surface structure of TiO$_2$(110) has recently been the subject of much interest partly due to the wide use of titania industrially as a white pigment in paint and cosmetics, as a support for catalysts and photocatalysts and as a biocompatible interface for medical implants. The behaviour of these disparate functions are critically determined by the surface properties of the oxide. The ability to prepare conducting TiO$_2$ samples in UHV has lead to a wealth of studies on its surface structure and chemistry [1]–[14]. Investigating the mechanisms of oxidation and reduction of oxide surfaces is crucial to understanding the behaviour of supported catalysts and greatly influences the development and design of new catalysts. For example, reducible oxide catalysts and supports commonly lose oxygen from the lattice during reaction which is replenished either
from the gas phase or diffusion from the bulk (the Mars–van Krevelen mechanism). By mixing oxides with different properties it is possible to gain enhanced reactivity by spilling oxygen over from one phase of the catalyst to the other such that a synergy is built up in the catalytic system as a whole [15]. The re-oxidation step is fundamental to the steady state reaction proceeding. Similarly, the mechanisms of re-oxidation are important to the fields of gas sensors and materials oxidation.

(110) oriented TiO$_2$ crystals show three different surface terminations; the bulk ($1 \times 1$) truncation, added rows of stoichiometry Ti$_2$O$_3$ to produce a ($1 \times 2$) reconstruction, or added rows of TiO$_2$ to form a different type of ($1 \times 2$) with cross-links. We have recently shown that the ($1 \times 2$) reconstructions show different reactivity toward oxygen at elevated temperature and have proposed a model for the structure of the rows and cross-links [14]. For large departures from stoichiometry, defects can cluster and form crystallographic shear (CS) planes within the crystal [16]–[18] in which adjacent regions of the crystal are displaced half a lattice unit in the $\langle 011 \rangle$ direction with respect to each other. On TiO$_2$(110) such shear planes have recently been shown to terminate at the surface in a well ordered array of half height steps [1], [19]–[22]. These CS planes are common in reducible d$^0$ metal oxides (TiO$_2$, V$_2$O$_5$, MoO$_3$ and WO$_3$) and have been seen in powdered catalysts in which TiO$_2$ is the support for metal particles [23].

Early scanning tunnelling microscopy (STM) studies of TiO$_2$ initially showed some variation in the interpretation of images but more recently the dominant contributions to the tunnelling have been established [7]. For reduced samples, which become n-type semiconducting, the Fermi level is pinned at the conduction band minimum which primarily has states composed of Ti 3d character. Valence band states have O 2p character and are approximately 3 eV below the Fermi level (i.e. the bandgap). The high biases required to reach these states preclude stable tunnelling. Consequently the empty states of the Ti ions are imaged for positive sample biases (as used here and in other studies of TiO$_2$) whereas the bridging O atoms, which are geometrically closer to the tip, appear dark.

Two approaches have commonly been employed to systematically investigate the re-oxidation of TiO$_2$ surfaces. The first involves the formation of a reduced surface layer by sputtering, which selectively removes oxygen from the surface, and re-oxidation by increasing the temperature until ion mobility restores near stoichiometry in the surface region. The second involves direct adsorption of oxygen on the surface at various temperatures and the effect of annealing cycles on the overlayers produced. Most work on TiO$_2$ in vacuum involves a combination of these techniques to prepare a conductive sample with a ($1 \times 1$) surface termination. Recently Henderson [11] has shown that re-oxidation of a sputtered surface occurs by incorporation of the excess Ti ions produced at the surface into the bulk. This is a thermally activated process which has an appreciable rate at 700 K and relies on the diffusion of Ti to form interstitial Ti$^{n+}$ ions in the bulk. In this way the surface region is re-oxidized at the expense of a slight bulk reduction. Recently STM has been employed to probe the interaction of oxygen gas with the TiO$_2$(110) surface. The first study by Onishi et al [2, 3] with adsorption at 800 K showed the formation of one-dimensional strings on the surface which were ascribed to Ti$_2$O$_3$ like added rows, which then formed a ($1 \times 2$) overlayer. The mechanism by which the added rows formed was tentatively suggested to be from re-oxidation of Ti$^{n+}$ interstitials diffusing from the bulk. Later investigations of oxygen exposure at elevated temperature with room temperature imaging show the formation of a cross-linked ($1 \times 2$) phase in which the cross-links were produced by adsorption above 950 K and increased in number with oxygen exposure [5, 6]. More recently the influence of oxygen on intrinsic defects on the ($1 \times 1$) surface was investigated at room...
Oxygen was seen to reduce the density of defects which appeared as bright features on the dark rows of the \((1 \times 1)\) and the defects were thus interpreted as oxygen vacancies. Oxygen exposure also gave rise to bright round points on the terrace, which the authors report degraded the stability of the tip causing frequent tip changes. These bright features were denoted ‘type C’ defects and were ultimately ascribed to hydroxyl groups generated from water impurity in the oxygen gas as they could be reduced in number by annealing to 500 K, which would desorb hydroxyl groups.

The effect of oxygen adsorption and annealing temperature was investigated in some detail by Li et al. [13] in the temperatures regime from 300–710 K, with all images being recorded at room temperature. The authors noted that adsorption between 470 and 670 K formed small \((1 \times 1)\) terraces of monatomic height with the region between these islands (and on top of some islands) forming an irregular network of rosettes with pseudohexagonal symmetry. Exposure of the surface to oxygen below 420 K produced white dots on the bright rows of the \((1 \times 1)\) which were again assumed to be hydroxyls from spurious water in the oxygen gas. The origin of the terraces and rosette structure was again proposed to be due to segregation of Ti interstitials to the surface.

In this paper we report the restructuring of the \((110)\) surface and growth of \(\text{TiO}_2\) in an oxygen ambient imaged at high temperature (up to 1000 K). Varying the adsorption temperature shows a change in reactivity pattern from the formation of small \((1 \times 1)\) islands that rapidly nucleate a second layer of growth at 573 K to the formation of large terraces of \((1 \times 1)\) before growth of the next layer between 673 and 773 K. Adsorption at the higher temperatures shows more step movement across the surface. At 1000 K island growth still occurs but the islands that are formed have a \((1 \times 2)\) termination. Patches of the \((1 \times 1)\) termination forming prior to the growth of the new layer are not readily observed at this temperature.

### 2. Experimental

The experiments were performed with an Oxford Instruments variable temperature STM additionally fitted with facilities for \(\text{Ar}^+\) ion sputtering, LEED/RFA Auger (VG Scientific), temperature programmed desorption and gas dosing. Tips were prepared by electrochemical etching of W(97%)Re(3%) alloy wire of 0.2 mm diameter. A more detailed description of the apparatus may be found elsewhere [25]. The \(\text{TiO}_2(110)\) single crystal (PI KEM, UK) was prepared by repeated sputter (600 eV, 1000 K) and anneal (1200 K) cycles to produce a dark blue/black crystal. During the initial preparation stages a \((1 \times 1)\) surface could be prepared by annealing at 1200 K, however, with time this procedure produced predominantly the \(\text{Ti}_2\text{O}_3\) type \((1 \times 2)\) termination. After even more cycles of sputter/anneal treatments only the cross-linked \((1 \times 2)\) surface could be prepared. Ca was seen to be the main impurity removed during cleaning (it produces a sharp \(c(2 \times 6)\) LEED pattern [26]). While it is difficult to assess the level of reduction of the crystal we have observed some small features which we assign to CS plane formation (see the 1000 K images which follow for instance). This indicates that the crystal has a stoichiometry of approximately \(\text{TiO}_{2-x}, \ x < 10^{-3}\) [16]. Images take around 60 s to acquire and save and so the movies represent time lapse images of the surface. A linear background subtraction is employed which removes thermally induced vertical drift from the images. There is no compensation for lateral drift other than moving the tip slightly between images to maintain imaging of the same area. All images are taken with a positive sample bias, i.e. empty states of the surface are probed. Bias voltages given in the figure captions correspond to sample biases.
Figure 1. (a) STM image (600 mV, 3 nA) taken at 573 K of the \((1 \times 2)\) reconstructed surface exhibiting a range of cross-linked structures. These aggregate into linked chains in the \(\langle 1\bar{1}0 \rangle\) direction with either a single link or double links in the form of cross shapes. Combination of cross and single links gives rise to ‘rosette’ features. The \((1 \times 2)\) reconstruction, single and cross links are shown schematically in (b).

3. Results

Figure 1(a) shows the cross-linked \((1 \times 2)\) surface, which is the starting point for the reaction sequences discussed below, imaged at 573 K. The surface is characterized by rows of \((1 \times 2)\) reconstruction, with an internal double row structure, which are predominantly cross-linked approximately every 12 lattice spacings in the \(\langle 001 \rangle\) direction. These crosses are composed of two halves, a shallow V and inverted V shape brought together, and these can commonly be observed as chains of V shapes extended in the \(\langle 1\bar{1}0 \rangle\) direction. The cross-linked structures can interact strongly and for well annealed surfaces generate 12th-order spots in LEED [14]. Typically the cross-links are well ordered and form extended chains, see movies 2, 3, 4, 5; figure 1(a) shows a variety of the structures that can form including single links, cross shaped links, chains off cross-links and staggered chains of cross-links. These latter features appear similar to the rosette structure of Li et al [13] except on a larger scale than they propose. Figure 1(b) shows a schematic representation of the surface structure of the \((1 \times 2)\).

The reactivity of the surface at 1000 K to \(2.1 \times 10^{-7}\) mbar \(O_2\) is shown in movie 1 where each frame is 100 nm square. Step edges are seen to be highly mobile and grow rapidly, flowing across the surface. Two small islands oriented diagonally in the centre of the early frames show the characteristic half height step edges of a CS plane. We shall focus here on the ‘normal’ surface; we will discuss the creation and reactivity of CS planes in a forthcoming paper [27].
Islands nucleate and grow rapidly on the larger terraces with further layers growing on top, preferentially in the ⟨001⟩ direction. The surface remains in the (1 × 2) reconstruction on both terraces and on top of the growing islands. The cross-links are not clearly visible, presumably because they become mobile at high temperature (the dark rows in the (1 × 2) appear flecked). This effect is shown more clearly in figure 2 which shows a typical area of the surface maintained at 1000 K. In comparison to images taken at lower temperature, see the early frames of movie 4 for example, the cross-links are not discernible. This commonly happens when diffusion events occur on the time-scale of scanning and suggests that the cross-links are mobile.

At 873 K and in 1.4 × 10⁻⁷ mbar O₂, movie 2 (50 nm square frames), the reaction sequence follows a similar pattern except islands of (1 × 1) can be seen nucleating within the (1 × 2) overlayer prior to growth of the higher (1 × 2) layers. These islands are rapidly covered with a second layer of the cross-linked (1 × 2) reconstruction which occupy approximately > 70% of the total island area. Islands with less than ~ 4 nm radius do not seem to start the second layer of growth, but once above this size the new layer nucleates and grows rapidly over the island.

At 773 K and in 1.1 × 10⁻⁷ mbar oxygen the surface shows different reactive trends as can be seen in movie 3 (50 nm square). The surface starts with the cross-linked (1 × 2) reconstruction which progressively develops both wider (in the ⟨001⟩ direction) and more numerous (single) links. The widening of the cross-linked areas seems to occur by bunching together of single or cross-shaped links. The step edges appear to be immobile. Small islands of (1 × 1) termination nucleate from the widened cross-links and begin to grow within the (1 × 2) terrace. These small islands grow rapidly and coalesce to form relatively large terraces of (1 × 1) with small strings growing out of the descending step edges onto the lower terrace. Small bright points begin to form on the terrace, with apparently low mobility, which act as nucleation centres for the growth of the new layer. The bright points initially grow in the ⟨001⟩ direction as a narrow row. However, this quickly converts to a wider row which we denote as a string as it has a double row internal structure [14]. The strings grow rapidly in the ⟨001⟩ direction and they aggregate and...
form cross-linked \((1 \times 2)\) islands raised above the \((1 \times 1)\) terrace. The step edges tend to grow across the resulting \((1 \times 1)\) terraces in contrast to their relative immobility for movement across the \((1 \times 2)\) terraces which were initially present at the start of the reaction.

Reducing the adsorption temperature still further to 673 K begins to reduce the reactivity of the surface and so movie 4 (50 nm square) shows several oxygen overpressure changes. Specifically these occur at frame 21 where the pressure is increased from 2 to \(3.8 \times 10^{-7}\) mbar, in frame 32 a further increase to \(5.8 \times 10^{-7}\) mbar and a final increase at frame 101 to \(1.1 \times 10^{-6}\) mbar. The slight jump at frame 81 is due to taking extra images of the metastable structures which grow in the \((1 \times 2)\) rows during the re-oxidation and are discussed below. As can be seen from this sequence the \((1 \times 1)\) islands again nucleate from the regions where the cross-links in the \((1 \times 2)\) surface have become wider. These \((1 \times 1)\) islands spread to cover the terraces. The largest islands produce bright points on the \((1 \times 1)\) terraces and these points then nucleate the growth of the strings which make up a new layer of \((1 \times 2)\). The overall reactive trends are similar to those at 773 K but a higher pressure of oxygen is required to reach a reasonable rate of growth.

In the low temperature regime, 573 K movie 5 (50 nm square), a different reaction regime is reached. The reactivity is again low and only appreciable changes in the images occur after frame 19 at which point the pressure has been increased from \(1.0 \times 10^{-7}\) mbar to \(5.4 \times 10^{-7}\) mbar. The changes which are apparent do not follow the same mechanism as shown previously for higher temperatures. Firstly the cross-links do not appear to be affected by the oxygen overpressure, they remain with essentially the same width and in the same relative positions during the early stages of reaction. However, the bright \((1 \times 2)\) rows are strongly influenced and appear to gain bright flecks along their length. These bright flecks increase in number and gradually fill in the dark rows of the \((1 \times 2)\). In many regions that have reacted in this way the \((1 \times 2)\) converts to form small \((1 \times 1)\) islands. The overall morphology of the terrace looks rather disordered with a mainly sponge-like film dotted with small islands of \((1 \times 1)\). The \((1 \times 1)\) islands grow slowly and tend to acquire bright points and strings on top after reaching only a relatively small size. These features on the islands spread with a slight preference for lateral growth in the \(\langle 1\bar{1}0\rangle\) direction, ultimately collapsing to form a new \((1 \times 1)\) layer. The final state of the surface can be seen in the larger scale image figure 3 which shows an area far removed from the region scanned in the sequence. The growth has produced a percolation network with a preference for the step edges of the resultant small raised islands to be aligned roughly in the \(\langle 1\bar{1}0\rangle\) direction. Similar trends in reactivity are seen at 473 K.

4. Discussion

There are several important clues to the mechanism for the re-oxidation of sub- stoichiometric TiO\(_2\) that can be discerned from the images presented here. The first is that the surface grows outwards, steps advance across terraces, islands form and grow laterally and vertically. This suggests that oxygen is being incorporated into new layers of TiO\(_2\) and not just filling oxygen vacancies in the surface or bulk. Secondly, the images generally do not show significant streaking. This implies that the rates of surface diffusion are not comparable to the scan time, i.e. diffusion is either slow in which case stable features appear in the images (bright points, rows and strings) or is very fast and cannot be imaged. Due to the similar quality (non- streakiness) of images acquired for all temperatures measured we suggest that there is little surface diffusion (other than cross-links moving up and down the \((1 \times 2)\) rows at 1000 K). The repeated growth of new layers of TiO\(_2\) on the original substrate in an oxygen ambient requires the supply of Ti, which
Figure 3. STM image (1200 mV, 0.1 nA) taken at 573 K of the final state of the surface after oxygen exposure. A percolation network of raised islands can be seen to spread across the terraces preferentially in the \( \langle 110 \rangle \) direction.

we believe diffuses from interstitial sites in the bulk of the crystal. The Ti ions are captured at the surface to form TiO\(_2\) with the oxygen. This mechanism would produce a growing layer with little surface diffusion as the Ti\(^{n+}\) interstitials are free to diffuse in the subsurface region which results in the ability to observe high quality images. Diffusion of interstitial Ti\(^{n+}\) ions in reduced bulk TiO\(_2\), and the formation of extended defect structures such as CS planes to accommodate the non-stoichiometry, is complex [28, 29]. For example, extended defects (CS planes) show stoichiometry dependence in their dissolution temperatures (the temperature at which a homogenous distribution of interstitial defects is preferred over extended defects) TiO\(_{1.9985}\) dissolves defects at 830 K while in TiO\(_{1.9966}\) they dissolve at 1000 K [30].

From the results presented above it is clear that non-stoichiometric TiO\(_2\)(110) surfaces show considerable activity for the adsorption of oxygen and the re-growth of the crystal. There is a trend for increasing areas of \((1 \times 1)\) surface to be formed as the temperature of the reaction is reduced from 1000 K towards 673 K, although at 573 K a slightly different mechanism takes over. We will therefore first concentrate on the higher temperature results.

As mentioned above the growth mechanism results from diffusion and capture of interstitial Ti\(^{n+}\) ions present in the bulk and near surface region by the oxygen ambient at the surface. Initially this mechanism drives the increase in the number and thickness of cross-links observed at 873, 773 and 673 K. These cross-links are themselves mobile at 1000 K and are able to rapidly diffuse to step edges where they add to the end of the rows. This effect manifests itself in the preferential growth of islands in the \( \langle 001 \rangle \) direction. Many authors including ourselves have reported that the cross-links form ordered arrays which suggest long range interaction and mobility at elevated temperature [5, 6, 8]. For these reasons step edge mobility also tends to be high at the highest temperatures. However, at the lower temperatures the cross-links are less mobile (we observe little movement at 873 K without oxygen for instance) and so when the density of links rises they begin to aggregate and form the \((1 \times 1)\) termination.

Figure 4 shows a metastable structure resulting from the widening of the cross-links in the \((1 \times 2)\), taken from between frames 81 and 82 of movie 4, as the \((1 \times 1)\) terraces encroach from both sides. The smaller cross-links close packed between the rows probably arise from the filling
of the deep troughs with TiO in their normal crystallographic positions. However, these cross shaped features have not yet acquired the bridging oxygen that completes the (1 × 1). The final conversion to (1 × 1) occurs at the edge of the cross shapes which meets the (1 × 1) suggesting the possibility that the oxygen spills over from the (1 × 1).

The (1 × 1) islands grow within the (1 × 2) layer with a slight preference for growth along the cross-links in the ⟨110⟩ direction. Interestingly, these islands then show a temperature dependence in their ability to grow an overlayer, higher temperatures produce more rapid formation of the new features on the (1 × 1) terraces. We ascribe this effect principally to the activation energy for a Ti\(^{n+}\) interstitial to promote itself into or onto the surface layer. From here the ion may be captured by an incoming oxygen molecule and form a metastable surface unit before the Ti can return to a subsurface state. The result of this conjunction is to form the stable bright points seen on the (1 × 1) surface in the images which act as nucleation centres for more Ti\(^{n+}\) and oxygen leading to the formation of the bright rows and the (1 × 2). Figure 5(a) shows a collection of features that grow on the (1 × 1) surface during reaction. Firstly there are the bright points that nucleate the growth which form on the bright rows of the (1 × 1). These bright points are probably the same as the type C defects seen at room temperature in previous studies and ascribed to hydroxyl species [24]. The surface temperature here is far too high to stabilize the hydroxyl species (imaged here at 830 K) and we believe that these bright points are undercoordinated Ti starting to grow the next layer, i.e. bridging Ti. Also apparent in the image are bright rows which appear similar to the bright points except they are elongated in the ⟨110⟩ direction, and strings which have a double row internal structure. Our assignment of these features is shown schematically in figure 5(b).

A schematic model showing the adsorption of oxygen and growth of TiO\(_2\) at high temperatures is shown in figure 6. O\(_2\) molecules dissociatively adsorb extracting Ti to increase the density and width of the cross-links. These aggregate and form a (1 × 1) layer through which Ti\(^{n+}\) interstitials migrate and react with ambient O\(_2\) to form the bright points on the terrace. These points then act as nuclei for growth in the ⟨110⟩ direction, and for aggregation of the (1 × 2) rows, and the cycle then repeats.
Figure 5. (a) STM image (1000 mV, 1 nA) taken at 830 K showing the principal stable features imaged during the oxygen induced re-growth of the TiO$_2$ surface. Where bright strings grow close together they tend to cross-link. (b) Shows a schematic overview of the proposed structures for these features.

Figure 6. Schematic representation of the re-oxidation process. Incoming O$_2$ molecules dissociatively adsorb, and extract Ti, which has the effect of initially widening the cross-links and then forming a (1 × 1) surface. Interstitial Ti$^{n+}$ ions migrate through this layer and are captured at the surface resulting in a bright point/row. These then grow as bright strings and eventually form the (1 × 2) terminated surface. The reaction is cyclic and can be followed over many layers of growth. (See movie 6.)

One further interesting observation is that in most cases the formation of a bright point on a (1 × 1) terrace occurs in the centre of that terrace. This may be due to depletion of subsurface Ti interstitials at island edges. Such a depletion may result from competitive capture by the surrounding (1 × 2) or by an increased barrier height for diffusion into the reactive state. In support of the former case the (1 × 1) islands initially grow laterally within the (1 × 2) overlayer and one would intuitively expect the interfacial region between these structures to have a lower
density of Ti$^{n+}$ interstitials. Furthermore, the interstitial Ti ions reside and preferentially diffuse along the $\langle 001 \rangle$ channels in the crystal [28] and these channels will be significantly different under the $(1 \times 1)$ terminated surface in comparison to the $(1 \times 2)$ surface, see figure 1(b) for instance. In the latter case it is likely that the channels in the uppermost (reconstructed) layer are energetically unfavourable whereas in the former they are accessible. As vertical transport in the $\langle 110 \rangle$ and diffusion in $\langle 1\bar{1}0 \rangle$ directions is slow in comparison to diffusion in the $\langle 001 \rangle$ we may expect interstitials to be trapped under the surface of the $(1 \times 1)$ islands embedded in the $(1 \times 2)$ terrace. Removal of these ions occurs at the edges as the $(1 \times 1)$ island spreads until the centre of the island is further from the edges than the diffusion length of the Ti$^{n+}$ in the subsurface state. Thus the density of interstitials increases at the centre of relatively large islands and a second layer can begin to nucleate on the terrace.

Once the $(1 \times 2)$ overlayer has formed the adsorption process repeats. However, depending on oxygen pressure and temperature, it is possible to roughen the surface as the islands may grow without significant merging. The growth of the overlayer is limited by supply of both Ti and oxygen to the surface and the rates of reaction increase with temperature and pressure.

At the lowest temperature, 573 K, there appears to be a slightly different mechanism operating. At this temperature diffusion of Ti$^{n+}$ in the bulk (and hence to the surface) would be expected to be suppressed, however, we still see considerable reactivity and growth. In the initial stages of adsorption the oxygen does not interact strongly with the cross-links but instead forms bright spots on the $(1 \times 2)$ rows. Bright spots are generally associated with under-coordinated Ti [7, 31] and so we tentatively suggest that oxygen dissociatively adsorbs in the troughs of the surface and disrupts the $(1 \times 2)$ reconstruction. This leaves some Ti undercoordinated which appears bright. The presence of excess oxygen on the surface allows its oxidizing potential to be felt and as such the Ti$^{n+}$ in the near surface region feels an additional chemical driving force to diffuse to the surface. The concentration gradient that develops between re-oxidized surface region and reduced bulk may also introduce space charge segregation of the Ti$^{n+}$ interstitials [32]. Once at the surface the interstitial may react with the oxygen but because of the low temperature it is not free to diffuse far. Thus a rather disordered looking film is produced. The small $(1 \times 1)$ islands grow where the local density of disordered TiO$_2$ units is high. Further growth of the bright points and $(1 \times 2)$ rows on these islands occurs in much the same manner as before, i.e. with a chemical driving force assisted diffusion to the surface. However, the islands which nucleate the second layer of growth are much smaller than those at the other temperatures as would be in accord with the limited lateral diffusion length of Ti interstitials below a $(1 \times 1)$ layer as discussed above.

These results demonstrate that this particular oxide surface is not a passive spectator but actively changes as a function of environment, even at low temperature and with a low pressure of oxidant. The mechanisms demonstrated and discussed here have wide implications for the understanding of the nature of catalysis, gas sensors, semiconductivity in oxides, and sample preparation. The re-oxidation mechanism may be general as TiO$_2$ is a model system for many reducible $d^0$ metal oxides, V$_2$O$_5$, MoO$_3$ and WO$_3$, which all show the formation of CS planes in the bulk and therefore may be expected to form interstitials in a similar manner. Surface re-oxidation steps are crucial to many catalytic processes and the demonstration of substantial surface rearrangement at a low pressure and in a catalytically realistic temperature regime is significant. Furthermore the bulk of the crystal also changes in response to the surface, which makes its use as a gas sensor promising in thin and thick film devices [33, 34]. Currently accepted mechanisms for sensing ability concentrate on oxygen vacancy formation/annihilation in reduced
TiO$_{2-x}$ and their effect on electrical conductivity [34]. We have shown that re-growth at the surface removes Ti$^{n+}$ from the bulk which in turn will lower the conductivity of the crystal. Clearly we have demonstrated that Ti$^{n+}$ interstitials are the active species in oxidation and therefore that their creation or incorporation as TiO$_2$ may drive the sensing mechanism. TiO$_2$ is also used as a support for metal particles which can enable photocatalytic water splitting [35], and titania supported catalysts are classic systems for showing so called strong metal support interaction (SMSI) [36]. We shall report on the influence of re-oxidation of a model supported metal catalyst with reference to SMSI in the near future [37].

5. Conclusions

We have employed high temperature scanning tunnelling microscopy in a low pressure oxygen atmosphere to probe the fundamental steps of surface and bulk re-oxidation of non-stoichiometric TiO$_2$. At high temperature, 1000–873 K, oxygen adsorption and reaction with the surface is rapid which produces island growth and mobility of step edges. As the surface temperature is reduced, 773–673 K, there is an increasing tendency to form unreconstructed (1 × 1) islands and terraces rather than with the original (1 × 2) termination. At low temperature, 573–473 K, small multilayered islands dominate the surface with little or no step movement. The resulting island system forms a percolation network.

Common to all temperature regimes investigated here is the growth of the surface; step edges flow across terraces, islands form and spread. This is proof that the surface re-oxidizes by extracting interstitial Ti$^{n+}$ ions from the bulk crystal lattice which then reacts with the oxygen ambient to reform a stoichiometric layer at the surface. Thermally driven interstitial diffusion to the surface region maintains the growth at elevated temperatures. At low temperature such bulk diffusion is hindered but the adsorption of oxygen at the surface sufficiently raises the chemical potential to produce a driving force for interstitials to diffuse to the surface. Thus the surface can slowly re-oxidize even at low temperature and pressure.

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