STM and LEED observations of the surface structure of TiO$_2$(110) following crystallographic shear plane formation

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(Received 5 June 1998; revised manuscript received 7 December 1998)

Extended vacuum annealing of rutile TiO$_2$(110) produces macroscopic and nanoscopic changes in the surface morphology. These result from the ordering of oxygen vacancies/Ti^{n+} interstitials in bulk TiO$_2$ into crystallographic shear (CS) planes. We have employed low-energy electron diffraction (LEED) and scanning tunnelling microscopy (STM) to identify the surface termination of CS planes produced in the bulk. The directions of the planar defects along the surface indicate the {132} series of shear planes dominate the STM images, which is also supported by the LEED results. The spacing between planes gradually varies across the surface suggesting that a series of Magnéli phases are formed. LEED patterns confirm the coexistence of both relatively large areas of a single phase and a continuum of separations between planes. Formation of CS planes also leads to extensive facetting of the crystal, which is visible to the naked eye as a rippled surface finish. Some Ca segregation is observed during CS plane formation; however, when removed the CS planes remain, indicating they are not significantly stabilized by the Ca. [S0163-1829(99)02215-8]

I. INTRODUCTION

Vacuum annealing of rutile TiO$_2$ produces reduced oxide phases with compositions of TiO$_{2-x}$ due to formation of oxygen vacancies and Ti^{n+} interstitials. At low concentration ($x < 10^{-4}$) the vacancies are accommodated as point defects while for higher degrees of reduction interstitials are produced along with the oxygen deficient point defects. These defects are eliminated at elevated temperature by formation of crystallographic shear (CS) planes.[1] CS planes, in which certain lattice planes move relative to each other leading to the collapse of the lattice, are a form of planar defect clustering common to reduced d^0 oxides of Ti, V, Mo, and W. For the case of TiO$_2$, CS plane formation can be visualized as a change from the normally edge-shearing octahedra (Ti at the center, oxygen atoms at the apices) in stoichiometric rutile to a face sharing arrangement at the CS planes, see Ref. 1 for detailed structure. As the concentration of CS planes increases, they can order into regular arrays and so produce new crystallographic phases known as Magnéli phases. These phases can be thought of as consisting of small volumes of the original, unmodified rutile structure joined together along CS planes. Depending on the CS plane concentration two homologous series of Magnéli phases are known to exist for rutile TiO$_2$ each of which has a different family of shear planes as shown in the Table I.[2]

Although CS planes and Magnéli phases are well characterized by bulk structural techniques, in particular transmission electron microscopy and electron diffraction,[1,3] there are very few surface science studies of reduced TiO$_2$ containing these phases. Rohrer, Henrich, and Bonnell[4–5] used scanning tunnelling microscopy (STM) to observe a range of periodic structures on TiO$_2$(110), attributed to steps resulting from CS plane displacements, with repeat distances ranging from 3.2 to 30 Å and domain sizes of <1000 Å. The CS displacement is always $\frac{1}{2}\langle 0\bar{1}1 \rangle$ leading to adjacent sections of the crystal being displaced by 1.6 Å with respect to one another along the $\langle 110 \rangle$ direction. The actual values measured by Rohrer were, however, ~ 1 Å. Low-energy electron diffraction (LEED) patterns were reported to be similar to the nonreduced TiO$_2$(110) surface. Again using STM, Murray, Condon, and Thornton[6] report facetting of TiO$_2$(110) subjected to repeated sputter/anneal cycles; however, they concluded that the structures with steps running along the $\langle 1\bar{1}1 \rangle$ direction were due to facetting and not shear plane formation. Nörenberg *et al.*[7] also report periodic steps attributed to shear plane formation on heating TiO$_2$(110) to 1133 K for 12 h. The direction of the steps was reported as being consistent with the formation of a {112} family of shear planes, which have not previously been reported as a CS plane series. Considerable Ca segregation to the surface region (1–2 ML, where 1 ML is the number density of atoms in the surface plane) was also observed by Auger electron spectroscopy (AES) and was, according to Nörenberg *et al.*, a possible cause of the shear plane formation. Reflection high-energy electron diffraction patterns were shown for this surface along with some discussion of LEED results (not shown), which suggested the surface could be considered ".... a disordered (1×3) reconstruction." The presence of surface Ca clearly complicates the observations made in this study as this adsorbate forms well ordered structures and a

TABLE I. Characteristics of shear planes in TiO$_2$.

Shear plane series	Formula	Approx. composition
{121}	Ti$_n$O$_{2n-1}$ ($4 < n < 10$)	TiO$_{1.75}$–TiO$_{1.90}$
{132}	Ti$_n$O$_{2n-1}$ ($16 < n < \sim 37$)	TiO$_{1.90}$–TiO$_{1.9375}$

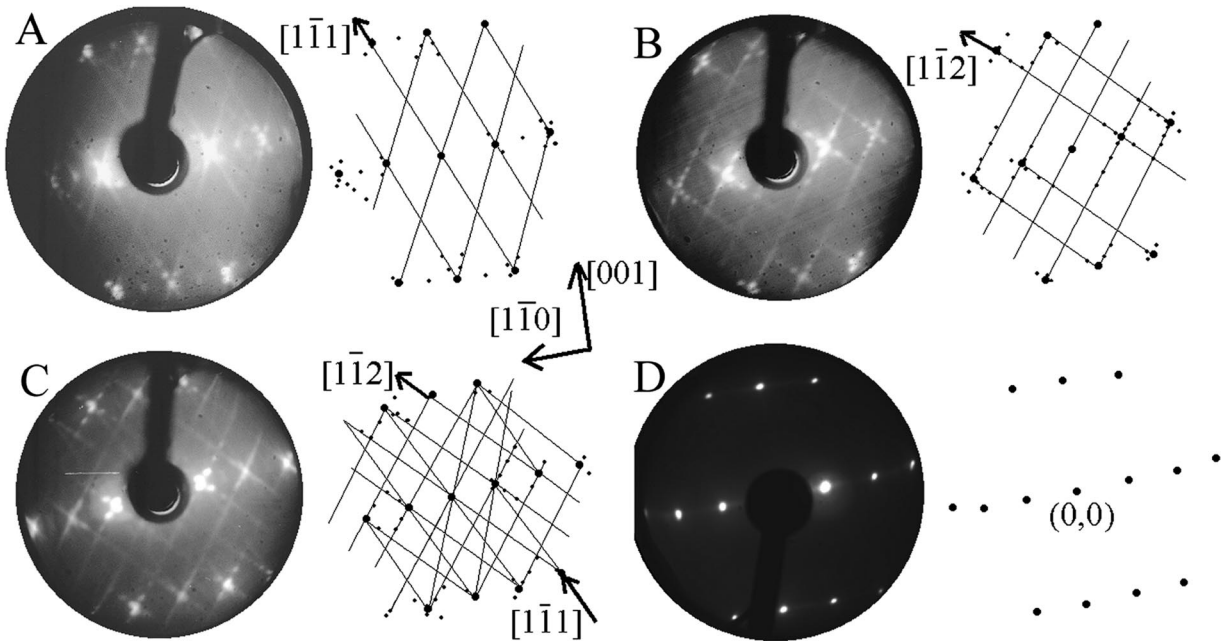FIG. 1. (a)–(c) LEED patterns formed after vacuum annealing the $TiO_2(110)$ sample to 1223 K for 6 h. (d) LEED pattern for the (1×1) terminated $TiO_2(110)$ surface formed by vacuum annealing at 973 K and heating in 1×10^{-6} mbar O_2 at 973 K for 15 min then flashed to 1173 K *in vacuo*. (a) 37 eV, (b) 38 eV, (c) 49 eV, (d) 58 eV. Also shown alongside each image are schematics drawn to scale in which integral order spots are indicated by larger dots while superstructure spots are represented by smaller dots. The lines indicate the principal directions of the streaking in the LEED.

$c(2 \times 6)$ LEED pattern.[8] Very recently Nörenberg and Briggs have reported on the surface structure of the most oxygen deficient Magnéli phase, Ti_4O_7.[9]

From the small number of reports in this area and the variation between them it is clear that considerable scope remains for further investigation into the surface structure of TiO_2 containing CS planes. In particular a combination of the microstructure given by LEED and nanostructure by STM would help to clarify the disparate reports in this area. Here, we present STM and LEED data of a reduced $TiO_2(110)$ single crystal and discuss the observed surface structure in terms of the surface truncation of CS planes. We also relate the formation of CS planes to a macroscopic facetting of the surface to such an extent that the roughening is clearly visible to the naked eye.

II. EXPERIMENT

STM experiments were performed using an Oxford Instruments variable temperature STM. The STM (described in detail elsewhere[10]) was contained within a UHV chamber equipped with additional facilities for Ar^+ ion sputtering, a Vacuum Generators 3 grid retarding-field-analyser for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), and a quadrupole mass spectrometer. The $TiO_2(110)$ sample (PI-KEM, UK) was cleaned using cycles or Ar^+-ion bombardment and vacuum annealing. Auger spectra were recorded in $dN(E)/dE$ mode with a primary energy of ~ 1 keV. Peak intensities were measured peak to peak. All STM images shown have a planar background subtracted, which tends to make terraces look flat. Additionally the tilting coarse approach mechanism of the STM makes it difficult to accurately assess tilt planes of terraces and so the

$3-7°$ slope expected for ordered arrays of shear planes becomes hidden in the images.

III. RESULTS

The $TiO_2(110)$ sample was annealed in vacuum at ~ 1223 K for 6 h. Following this, a substantial Ca signal was observed in AES indicating considerable surface segregation as the bulk Ca concentration is quoted at <10 ppm (suppliers value). Repeated cycles of Ar^+ bombardment and vacuum annealing at 1223 K resulted in the almost complete elimination of the Ca signal Ca(297 eV)/Ti(390 eV) ratio of <0.02, indicating that the amount of Ca in the surface region had fallen to <0.05 ML.

The annealing process also produced a change in the appearance of the crystal from almost transparent off white to a dark blue-black color. The surface of the crystal then showed a rippled texture that was visible to the naked eye. Prior to vacuum annealing the crystal had a flat polished surface with no apparent defects.

The surface structure was observed following this reduction procedure using LEED and STM. The LEED patterns showing CS plane formation and a reference (1×1) surface are shown in Figs. 1(a)–1(c), and 1(d), respectively. The schematics shown alongside each LEED pattern are drawn to scale from the images. The larger dots indicate the integral order spots while smaller dots represent those due to the surface superstructure. Lines on the schematics show the principle streaking directions in the LEED. In Fig. 1(a), bright streaks can be observed in the $\langle 1\bar{1}1 \rangle$ and symmetrically equivalent directions. Also apparent are half order spots in the $\langle 1\bar{1}0 \rangle$ direction between integral order spots. These may be due to areas of the surface that have reconstructed to
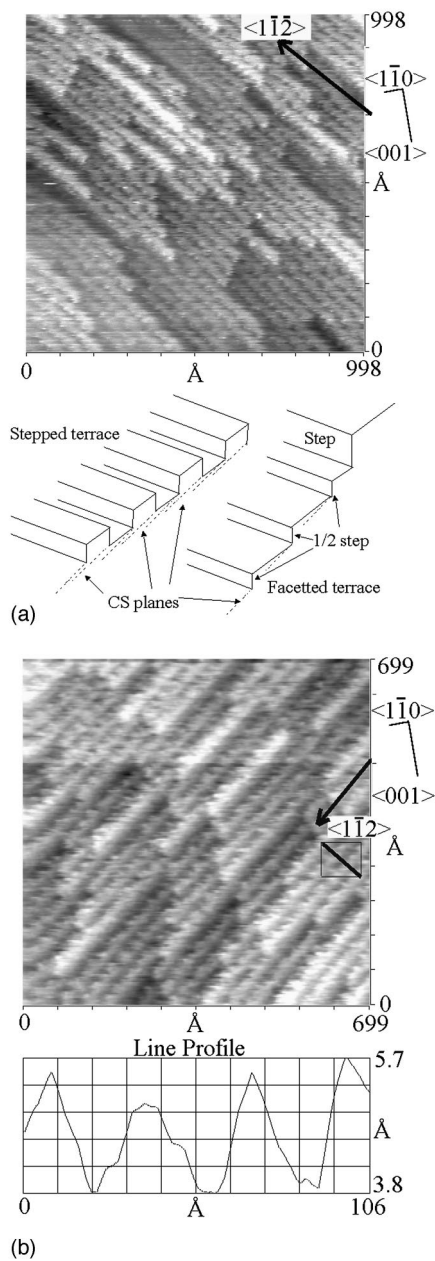
FIG. 2. (a)–(b) STM images of the $TiO_2(110)$ sample vacuum annealed to 1223 K for 6 h. (a) shows the shear planes terminating at the surface and intersecting the bulk TiO_2 step edges that run approximately bottom left to top right (1 nA, 1.5 V). The schematic indicates how the shear planes may be visualized terminating at the surface as a terrace or a sequence of steps. The image (b) (1 nA, 1 V) and associated line profile indicate the apparent height (~ 1.6 Å) of the CS planes that form half-height steps on the surface.

FIG. 3. STM images of (a) (1×1) terminated $TiO_2(110)$ (1 nA, 1 V) and (b) (1×2) terminated $TiO_2(110)$ (1 nA, 0.5 V). The (1×2) structure contains small regions of the original (1×1) surface.

(1×2) on reduction. On moving to a different part of the crystal Fig. 1(b), streaks in the $\langle 1\bar{1}2 \rangle$ direction can be resolved, which are decorated with diffraction spots with approximately 1/16th order in this direction. Figure 1(c) shows a LEED pattern in which both streak directions can be resolved with the $\langle 1\bar{1}2 \rangle$ streaks being brighter and resolved into individual spots in places. This pattern appears to be a superposition of the two patterns shown in Figs. 1(a) and 1(b) and may arise from grain boundaries between regions of different shear planes or from CS planes of the same type but
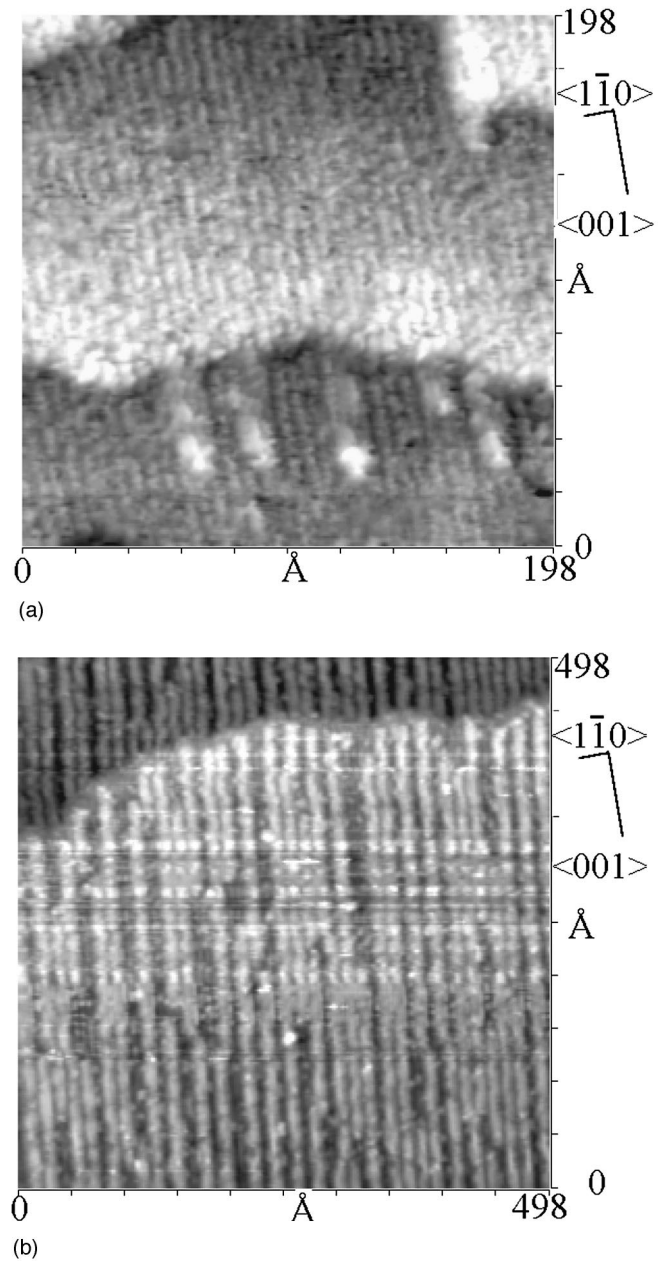
differing orientation. For comparison Fig. 1(d) shows the LEED pattern obtained from the clean (1×1) terminated $TiO_2(110)$ surface prepared by subjecting a second, less reduced, sample to cycles of Ar^+ bombardment and annealing to 973 K followed by heating the sample in 1×10^{-6} mbar of O_2 at 973 K for 15 min, flashing to 1173 K and cooling in vacuo to room temperature. In the absence of the oxygen treatment, annealing the sample to 973 K for 30 min resulted in the formation of a streaky (1×2) LEED pattern. The observation of the (1×2) reconstruction is well documented in the literature[11–15] and may be associated with the formation of Ti_2O_3 strings along the surface although recently other terminations have been proposed.[16,17] Note that both the (1×1) and (1×2) terminations of the TiO_2 are aligned

with the $\langle 1\bar{1}0 \rangle$ direction. The Ti(390 eV)/O(510 eV) AES ratio of the (1×1) surface was 1.14 compared with 1.22 for the heavily reduced surface formed by vacuum annealing at 1223 K.

STM images of the heavily reduced TiO_2 sample, which gave the LEED patterns of Figs. 1(a)–(c) are shown in Figs. 2(a) and (b). Several important features can be observed. The surface contains a large concentration of steps observed as dark lines running across the images. These steps were observed aligned with the $\langle \bar{1}12 \rangle$ and $\langle 1\bar{1}2 \rangle$ crystallographic directions, as indicated in the images. The distance between these steps also varied, ranging from 20–80 Å. Line profiles across the steps [Fig. 2(b)] revealed that the step height was 1.6 ± 0.1 Å, that is half the normal step height of $TiO_2(110)$ and indicates that these steps are due to CS planes. For comparison Figs. 3(a) and (b) show STM images of the surface of a second $TiO_2(110)$ sample that was prepared as described above to produce a (1×1) and a (1×2) LEED pattern, respectively. For the surface exhibiting the (1×2) LEED pattern areas of both (1×1) and (1×2) periodicity were observed with STM showing that the surface was not completely reconstructed to (1×2).

Considerable variation in the mesoscopic morphology of the surface was observed using STM. In some areas there were relatively large terraces ($>500 \times 500$ Å), Fig. 4(a) which displayed the expected (for normal crystallographic steps) height of 3.2 Å between terraces which were themselves covered with evenly spaced CS planes, Fig. 4(b). However, on moving laterally across the surface the normal steps occurred with greater frequency, Fig. 4(c), and eventually resulted in areas exhibiting large scale facetting, Fig. 4(d). In this image it is apparent that the step edges have aligned with the CS planes. Stabilization of step edges aligned with the CS plane may be expected as the natural 3.2 Å steps can be reduced in height by incorporation of a CS plane step thus reducing the free energy of the step edge. Some evidence for this may also be seen in Fig. 4(c), where steps preferentially align in the $\langle 1\bar{1}2 \rangle$ direction. The extent of the facetting induced by this alignment can be gauged from the line profile taken across Fig. 4(d) as indicated in the figure. The extensive microscopic facetting demonstrated by the STM images may be the cause of the macroscopic rippling evident with the naked eye. In support of this a second crystal was mounted orthogonal to the first and CS planes were generated by the above procedures. Such a preparation produced ripples running orthogonal to the first crystal indicating that crystallographic structure is the cause of the ripples rather than the incidence angle of the sputtering ions or other artefacts introduced by the preparation procedure. $TiO_2(110)$ crystals cleaned so as to form (1×1) and (1×2) surfaces for imaging maintain their highly polished front face and display no rippling despite acquiring the dark blue color. Rippling appears to be solely due to the restructuring of the crystal bulk in forming the CS planes.

IV. DISCUSSION

From the LEED and STM data it is clear that substantial changes in the surface structure and morphology of the $TiO_2(110)$ sample occur on prolonged annealing to 1223 K.

The formation of a high concentration of steps with height 1.6 Å indicates that CS planes have been formed, which terminate at the surface. From the LEED and STM data alone it is not possible to determine if the CS planes propagate through the entire crystal or are only located in the near surface region. However, from the line of intersection of CS plane and the surface it is possible to reconstruct the simplest CS plane that would give that termination. Analysis of a variety of STM images should be made as the symmetry of the crystal dictates that CS planes may form in four equivalent directions and as we discuss below not all directions are favorable for determining the CS plane present.

Taking the general form of CS planes to be composed $[hkl] = p[121] + q(011)$ (p and q are positive integers)[1] the line of intersection of the CS plane on the surface is given by $[hkl] \times [110]$. There are eight symmetrically equivalent planes in the $[hkl]$ family ($[hkl]$, $[\bar{h}kl]$, $[h\bar{k}l]$, $[\bar{h}\,\bar{k}l]$, $[khl]$, $[\bar{k}hl]$, $[k\bar{h}l]$, and $[\bar{k}\,\bar{h}l]$) giving rise to four lines of intersection from the cross product above, $\langle \bar{x}x\bar{x} \rangle$, $\langle \bar{x}x\bar{y} \rangle$, $\langle \bar{x}xy \rangle$, and $\langle \bar{x}xx \rangle$, where $x = p + q$ and $y = 3p + q$. From this we see that all values of p and q used to define a shear plane will give rise to lines of intersection on the surface in $\langle \bar{x}x\bar{x} \rangle$ and $\langle \bar{x}xx \rangle$ directions. Thus, the observation of lines in these directions does not allow the determination of the CS plane terminating from the bulk as any CS plane may be present. However, observation of lines of the form $\langle \bar{x}x\bar{y} \rangle$ or $\langle \bar{x}xy \rangle$ allows the simplest form of the CS plane to be deduced as we can solve for p and q.

The STM and LEED observations of CS plane steps along the $\langle 1\bar{1}2 \rangle$ and $\langle \bar{1}12 \rangle$ directions is consistent with formation of the {132} family of shear planes, which have been observed experimentally in TiO_2 using bulk structural techniques.[1] This is different to the {112} family of planes proposed by Nörenberg et al.[7,9] from their observation of $\langle \bar{1}10 \rangle$, $\langle \bar{1}1\bar{1} \rangle$, and $\langle \bar{1}11 \rangle$ directed half height steps. The {112} family cannot be composed from combinations of p and q to form CS planes as described above, as the authors point out, and so we are unsure as to their relation to our paper.

As mentioned above the separation of the CS planes is a measure of the local stoichiometry. We observed considerable variation in the CS plane spacing (20–80 Å) indicating that the local surface stoichiometry was inhomogeneous. Aono and Hasiguti[18] found that more than 1000 h of heating to 1273–1673 K were required in order to obtain an homogeneous single-crystal specimen of TiO_{2-x}, although in this case they obtained CS planes from the {121} family.

Our LEED data is also consistent with the STM images. The direction of the streaks observed in the LEED patterns are in agreement with the CS step directions observed by STM. The variation in CS plane step density across the surface would cause the streakiness while some of the larger and better ordered regions [Fig. 4(a) for example] would produce some of the spots on the streaks. The LEED patterns shown are to our knowledge the first reported for a surface containing CS planes. Rohrer, Henrich, and Bonnell only observed a (1×1) LEED pattern for their surface even though STM revealed the presence of CS planes. This was attributed to the CS plane density being extremely inhomo-
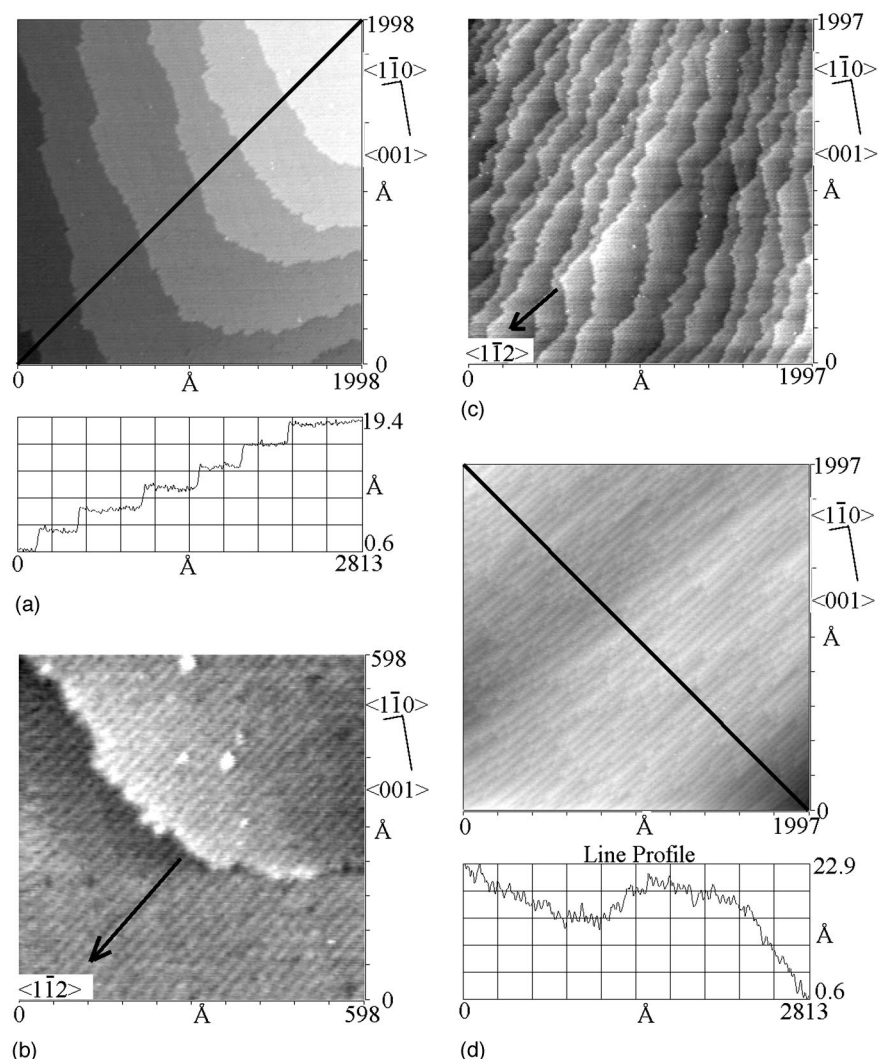
FIG. 4. STM images of the $TiO_2(110)$ sample vacuum annealed to 1223 K for 6 h showing variations in mesoscopic morphology over the surface. (a) (1 nA, 1 V) Large terraces containing CS planes, which are shown in more detail in (b). The line profile in (a) clearly shows 3.2 Å step heights associated with the bulk $TiO_2(110)$ interlayer spacing. (c) shows an area of the crystal several thousand angstroms to the left of (a), (b) exhibiting higher step density with some steps aligning with the CS plane direction. (d) Several thousand angstroms further left again showing a large area of crystal, which is facetted with step edges principally aligned with the shear planes. The line profile across the STM image in (d) indicates the extent of the facetting.

geneous and/or too low in concentration to be apparent in LEED.

There is, however, one minor discrepancy between the LEED and STM results, namely the observation of $\langle 1\bar{1}1 \rangle$ directed steps in LEED but not in STM. This may be due to the CS planes bunching within the crystal[1] producing localized areas of each CS plane. As we can only scan a small region at the center of the crystal by STM we may miss some orientations formed in the edge regions, which are, however, probed in LEED. It is also possible that reliable imaging is easier to achieve on $\langle 1\bar{1}2 \rangle$ directed regions and so we inadvertently preferentially select images from those regions.

Nörenberg *et al.* link CS plane formation with the segregation of Ca to the surface.[7] Others have also shown that Ca segregation to the surface can be significant in TiO_2.[8,19] Our results show that although CS plane formation was accom-

panied by Ca segregation we cannot conclude that Ca causes CS plane formation. It is important to note however that in our case the CS planes were still observed when the Ca was almost entirely eliminated from the surface region. Though this does not show whether Ca segregation is a cause or merely a consequence of CS plane formation it does demonstrate clearly that the surface structures observed both by LEED and STM were not maintained because of the presence of Ca at the surface.

V. CONCLUSIONS

We have demonstrated conclusively that CS shear planes produced by extensive vacuum annealing of $TiO_2(110)$ terminate at the surface and can be imaged by STM. The CS planes produce well-ordered linear structures on the surface

aligned in specific crystallographic directions and as such dominate the LEED pattern as stripes in the $\langle 1\bar{1}2 \rangle$ direction (and symmetric equivalents). These LEED patterns are the first reported for a $TiO_2(110)$ single crystal reduced to the extent that CS planes are formed. The surface was observed to roughen on both macroscopic (rippled surface observed by eye) and nanoscopic length scales which suggests CS planes induce facetting of the crystal. Ca segregation was observed to accompany CS plane formation, however after re-

moval by sputtering and annealing CS planes remained terminating the surface.

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