Ordered Overlayers of Ca on TiO_2(110)-1×1

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Scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) have been used to examine the structure of ordered adlayers of Ca on TiO_2(110)-1×1 formed by metal vapor deposition. A comparison is made with structures formed by segregation of Ca from the bulk, with similar structures being found for the two preparation methods below a monolayer coverage. At low coverages, rows of width ~0.6–0.9 nm develop in the [1$\bar{1}$0] and [001] azimuths. At coverages equivalent to a single calcium layer, a c(6×2) overlayer is formed. At coverages above a single layer, a disordered structure develops and a LEED pattern with $\begin{pmatrix} 2 & 0 \\ -0.1 & 1 \end{pmatrix}$ symmetry is observed.

1. Introduction

Alkali and alkaline earth metals are known to behave as reaction modifiers on a variety of substrates, including metal oxides.[1–8] Understanding their role in terms of structure, both physical and electronic, is a key challenge, with practical applications in areas such as gas sensors and microelectronics.[9] The deposition and segregation of metals on titanium dioxide has been a particular focus of attention (for a review, see ref 10).

Calcium is a common impurity of commercial titanium dioxide single crystals. The segregation of Ca impurities from the bulk to the surface of rutile TiO_2(110) has been previously studied by Zhang et al.[4] and Nörenberg and Harding.[5–7] These two groups reached different conclusions. A c(6×2) structure was proposed by Zhang et al.[4] based on their low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) results. The STM images exhibit rows along the [001] and [1$\bar{1}$0] directions of the TiO_2(110)-1×1 substrate, which were assigned to the formation of a $CaTiO_3$-like compound. In the more recent studies, Nörenberg and Harding[5–7] reported a highly ordered p(3×1) adlayer and explained the observed c(6×2) LEED pattern in terms of antiphase boundaries. This interpretation was supported by atomistic simulations.

Nörenberg and Harding also reported (7×2) and (1×4) reconstructions.[7] They found that the p(3×1) reconstruction can convert into a (1×4) reconstruction by annealing or by electron beam irradiation. The (1×4) structure forms trenches that run in the [001] direction. The 1×4 structure is disordered in the [001] direction and can coexist with the p(3×1) reconstruction on the same terrace.

Here we adopt a different approach, forming Ca overlayers by metal vapor deposition (MVD). This avoids any complications that may arise from population of the selvedge by Ca during the segregation process. We show that the ordered overlayers obtained by MVD have a genuine c(6×2) periodicity rather than a p(3×1) periodicity reported in refs 5–7. Evidence is presented of a new reconstruction, which is formed at high Ca coverages. We also compare the MVD results with those obtained by bulk segregation (BS), finding that they are equivalent in the low-coverage regime.

2. Experimental Section

The MVD experiments were performed with an Omicron GmbH UHV low-temperature STM operating at a base pressure of 1×10^{-11} mbar. The BS experiments employed an Omicron GmbH ultrahigh vacuum (UHV) room-temperature STM/atomic force microscope (AFM) operating at a base pressure of 1×10^{-10} mbar for the STM experiment. A UHV chamber described elsewhere[11] was used for the X-ray photoelectron diffraction (XPD) measurements. In this work, the base pressure was 2×10^{-10} mbar.

The rutile crystals (Pi-Kem) were slightly reduced and transparent blue. For the segregation experiments, sample preparation was carried out by Ar^+ ion bombardment (1 keV) and annealing to ~1100 K in a vacuum until the presence of Ca was detected by Auger electron spectroscopy (AES) and the corresponding c(6×2) LEED pattern was observed. No other contaminants were present in the Auger spectra. For the vapor deposition experiments, the sample was prepared by repeated cycles of Ar ion bombardment (1 keV) and annealing to ~1100 K. The cleanliness of the sample was checked with AES before Ca was deposited by using a well-degassed evaporator. The presence of Ca on the surface was checked with AES and the sample was subsequently annealed up to 1100 K to order the Ca at the surface. The ordering was monitored with LEED. All the measurements (MVD and BS) were carried out at room temperature.

All STM images were recorded in constant current mode with a tungsten tip held at ground potential with the sample biased positively (empty states regime) in the range 1.2 to 1.8 V, with

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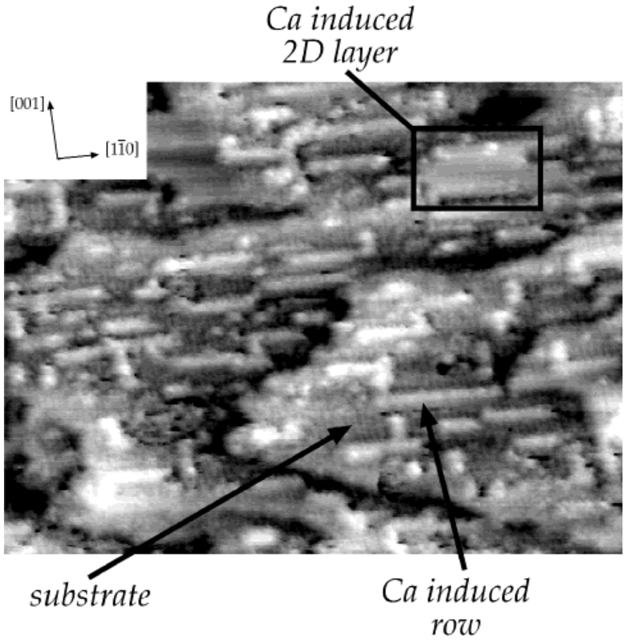

Figure 1. STM image (50 nm × 40 nm) of ~0.4 ML of Ca/TiO_2(110) prepared by Ca metal vapor deposition.

the tunneling current in the range 0.04 to 1.2 nA. Ti atoms are usually imaged as bright rows by STM under these conditions.[12] The room temperature microscope was calibrated with atomically resolved images of Si(111)-7×7 and the low-temperature microscope was calibrated with Cu(100)−(2×1)O. The Ca coverages are estimated on the basis that the c(6×2) overlayer defines 1 ML of Ca.

The XPD data were recorded on a VSW/Omicron EA125 analyzer with a five-channeltron detection system and unpolarized Mg Kα ($h\nu = 1253.6$ eV) radiation. An analyzer pass energy of 20 eV and analyzer lenses operating in low magnification mode were employed to record the data. These settings give an X-ray source-limited energy resolution $\Delta E = 0.7$ eV [full width at half-maximum (fwhm)] and an angular resolution $\Delta\theta = 2°$ (fwhm) for all the measurements.

3. Results

3.1. Low Coverage: Row Structure. Figure 1 shows a STM image of ~0.4 ML coverage of MVD Ca on the TiO_2(110) surface. The image shows the substrate 1×1 rows together with short added rows in the [001] and [1$\bar{1}$0] directions. The rows have a height of 0.21 ± 0.05 nm and a width of 1.1 ± 0.2 nm (fwhm), in very good agreement with the values reported by Zhang et al.[4] Their lengths in the [001] and the [1$\bar{1}$0] directions are up to ~5.0 nm and up to ~10 nm, respectively. At this coverage, a weak c(6×2) LEED pattern can be observed and Ca starts to form 2D layers (see Figure 1).

Consistent with earlier work,[4] similar structures are obtained by BS. At ~0.3 ML Ca coverage (Figure 2), rows extending up to ~6.5 nm in the [001] direction are formed, whereas the length of the rows in the [1$\bar{1}$0] direction remains at ~4.5 nm. In the image of Figure 2, oxygen vacancies/hydroxyl groups can be seen between the rows which can be used to identify the bright rows of the substrate as in-plane Ti atoms.[12] At higher calcium coverages obtained by MVD or BS, a denser arrangement of the Ca induced rows is formed. The rows cover most of the surface, with those in the [1$\bar{1}$0] direction extending across entire terraces.

3.2. Monolayer Coverage: c(6×2) Overlayer. When the coverage approaches saturation of the first layer, STM images

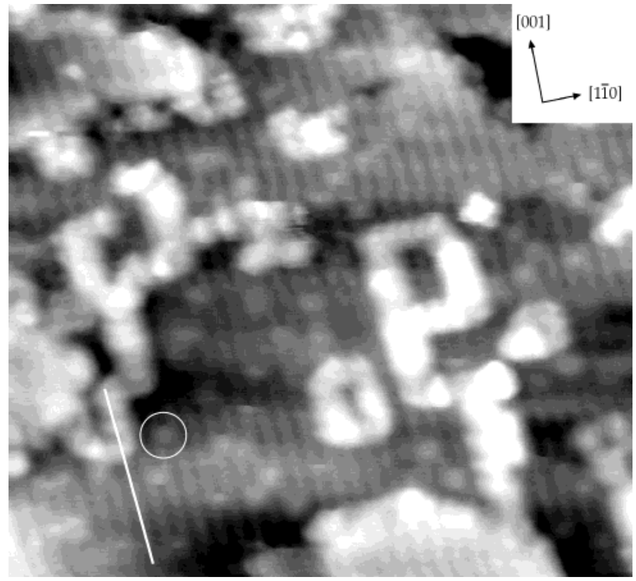

Figure 2. STM image (20 nm × 20 nm) of ~0.3 ML of Ca/TiO_2(110) prepared by segregation. The circle indicates the presence of an O-vacancy or a terminal hydroxyl group. The center of the overlayer Ca rows is on the bright lines of the substrate.

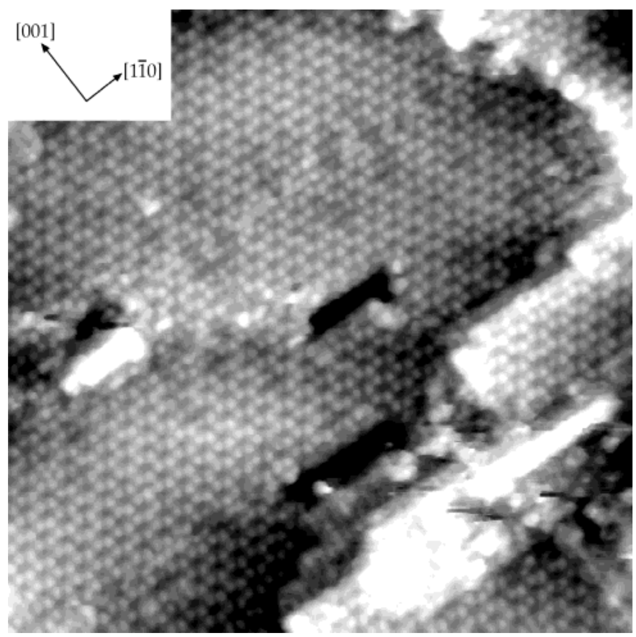

Figure 3. STM image (30 nm × 20 nm) of 1 ML of Ca/TiO_2(110) formed by Ca metal vapor deposition.

evidence an overlayer with a c(6×2) honeycomb structure [shown in Figures 3 and 4a], which completely covers the rutile substrate. The corresponding LEED pattern is sharp (see Figure 5). The honeycomb network is shown schematically in Figure 4b. In the [001] direction, the bright features are separated alternately by two substrate TiO_2(110) unit cells (2 × 0.296 nm) then four TiO_2(110) unit cells (see line profile in Figure 4c). The same configuration of bright features is seen in adjacent [001] direction rows but they are shifted three unit cells along the [001] direction with respect to each other. Equivalent [001] direction rows are separated by two TiO_2(110) unit cells (2 × 0.65 nm) in the [1$\bar{1}$0] direction.

Ordered overlayers can also be prepared by BS (see Figure 6) leading to the same c(6×2) honeycomb structure as the overlayer formed by calcium MVD. However, it is more difficult to control the coverage by BS than by MVD preparation.

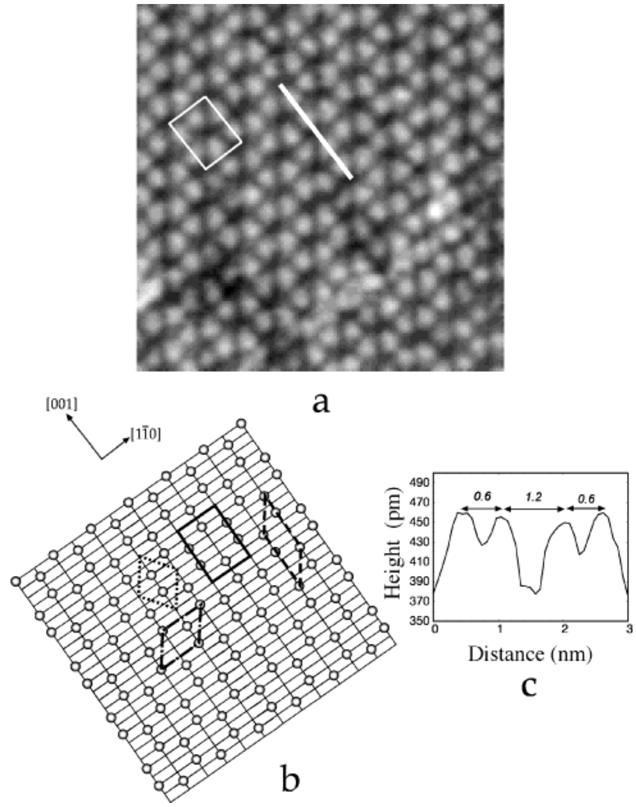

Figure 4. (a) STM image (9.4 nm × 9.4 nm) magnified from Figure 3. A c(6×2) unit cell is superimposed. (b) Schematic representation of the c(6×2) overlayer superimposed on a grid representing the TiO_2(110) unit cell. The $\begin{pmatrix} 6 & 0 \\ 0 & 2 \end{pmatrix}$ unit cell (full line) in the Park and Madden notation is indicated together with three other equivalent unit cells $\begin{pmatrix} 3 & 1 \\ 3 & -1 \end{pmatrix}$ (dotted), $\begin{pmatrix} 6 & 0 \\ 3 & 1 \end{pmatrix}$ (dashed), and $\begin{pmatrix} 3 & 1 \\ 0 & 2 \end{pmatrix}$ (dot dashed). (c) Line profile along the white line indicated in part a. The distance between peaks is indicated in nanometers.

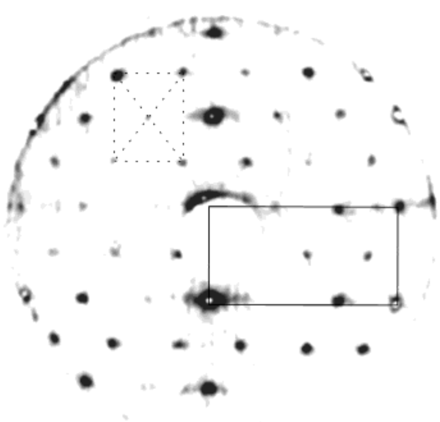

Figure 5. LEED pattern recorded from the Ca covered TiO_2(110) surface ($E = 60$ eV). The reciprocal unit cells of the TiO_2(110) substrate and of the Ca induced c(6×2) reconstruction are represented respectively by solid and dotted lines.

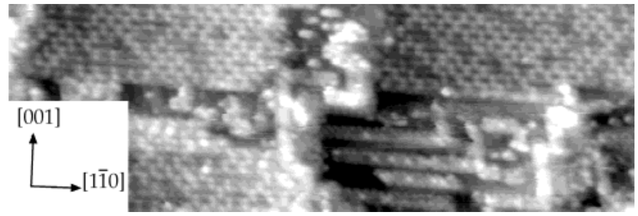

Figure 6. STM image (50 nm × 17 nm) of 0.7 ML of Ca/TiO_2(110) prepared by segregation of Ca.

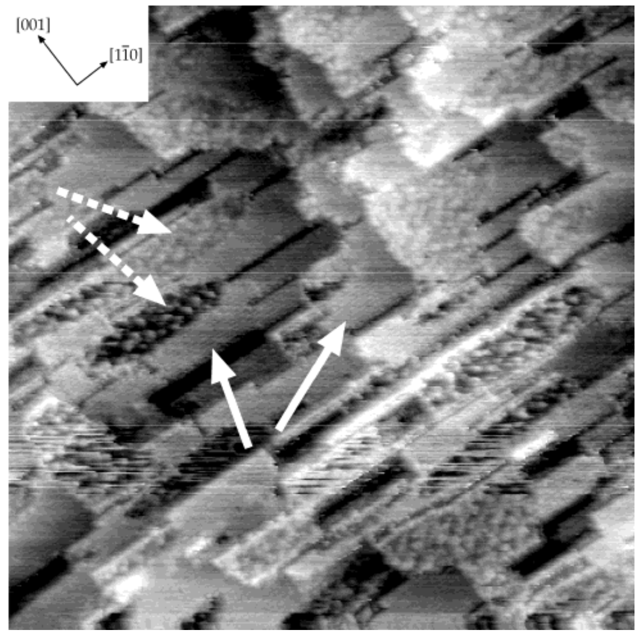

Figure 7. STM image (50 nm × 50 nm) of 1.2 ML of Ca/TiO_2(110) prepared by Ca metal vapor deposition. Two coexisting structures are observed: the ordered c(6×2) (indicated with solid arrows) and the "disordered " structure (dashed arrows).

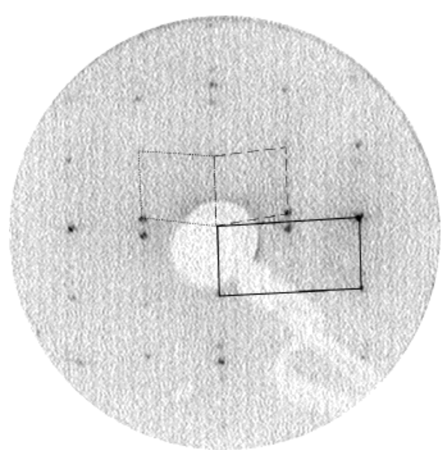

Figure 8. LEED pattern of the $\begin{pmatrix} 2 & 0 \\ -0.1 & 1 \end{pmatrix}$ overlayer on TiO_2(110) ($E =$ 110 eV). The TiO_2(110) reciprocal unit cell is indicated with full lines. The two domains of the reconstruction are indicated with dotted and dashed lines.

3.3. High Coverage: $\begin{pmatrix} 2 & 0 \\ -0.1 & 1 \end{pmatrix}$ Structure. All the coverages presented in this section have been prepared by MVD. At doses slightly above 1 ML, an additional structure is formed, which looks disordered and is difficult to image (see Figure 7).

At higher calcium coverages, only the "disordered" structure is found and it completely covers the rutile substrate. The LEED pattern of this structure has a high background and very weak spots (Figure 8). In this LEED pattern, the previous c(6×2) pattern can no longer be seen, although the 1×1 unit cell of the titania substrate is still visible. A new pattern with a parallelogram symmetry is superimposed. Due to the *p*2*mm* symmetry of the TiO_2(110) surface there are two symmetry equivalent domains. The new reconstruction layer and the TiO_2(110) surface are related by a $\begin{pmatrix} 2 & 0 \\ -0.1 & 1 \end{pmatrix}$ matrix in real space. The titania surface and the new reconstruction are commensurate in the [1$\bar{1}$0] direction.

4. Discussion

In the low-coverage regime, results from the BS experiment are essentially the same as those found for MVD. The results for Ca coverages up to ~1 ML indicate a 2D layer growth mode consistent with Ca/TiO_2 interfacial interaction being stronger than the Ca−Ca interaction. This is consistent with the predictions of Hu et al. based on thermodynamic criteria for the growth mode of different metals on $TiO_2(110)$.[13]

As for the ordered overlayer up to a monolayer coverage, our STM results show clearly that the well-ordered overlayers form a genuine c(6×2) overlayer (Figure 3). Hence, a previous explanation of the c(6×2) LEED pattern in terms of antiphase boundaries between different domains of a p(3×1) structure[5,6] does not seem to be appropriate. Moreover, our high-resolution STM images evidence an overlayer with very large domains. Due to the symmetry of the titania substrate only translational or mirrored domains of a p(3×1) structure could exist. Such p(3×1) domains, in the limit of very large domain approximation (see, for example, ref 14), would yield a p(3×1) LEED pattern and not c(6×2).

In attempting to construct models for the well-ordered layers from the STM and LEED data presented, it is clear that a definitive model is not possible with the data available to date. The c(6×2) overlayer is described by the basic symmetry model shown in Figure 4b. Zhang et al. have suggested a model where calcium atoms replace in-plane oxygen atoms to form a locally $CaTiO_3$-like structure with the bridging oxygen and the 6-fold coordinated Ti atoms.[4] In part this was based on their XPS-based observation that Ca^{2+} is present. However, our ancilliary Ca 2p X-ray photoelectron diffraction (XPD) results do not contain modulations, which rules out a model where calcium substitutes in-plane oxygen atoms. Nörenberg and Harding have suggested that Ca substitutes the 5-fold Ti atoms of the titania substrate,[5,6] although the calculations were based on a p(3×1) unit cell.

Other models cannot be discarded. Several experimental and theoretical studies of alkali metals on $TiO_2(110)$-1×1 point to a 3-fold hollow site (for a review, see ref 10). A similar site for Ca seems plausible. Models of such structures are presented in Figure 9. Combinations of techniques such as surface X-ray diffraction and further theoretical calculations are necessary to determine the exact structure of the c(6×2) reconstruction.

Finally, we discuss the $\begin{pmatrix}2 & 0\\ -0.1 & 1\end{pmatrix}$ structure. The weak spots in the LEED pattern (Figure 8) suggest that either the overlayer has some order or it modifies the titania substrate in an ordered fashion. The apparent complete lack of periodicity of the "disordered" structure in the STM images makes the second possibility more plausible. A disordered (1×4) structure, obtained by BS, was reported by Nörenberg and Harding.[7] In their STM images, the periodicity along the [1$\bar{1}$0] substrate direction was evidenced by the presence of trenches every four substrate unit cells. Since we did not see any trenches in our experiment, the structure we have observed is, most likely, not the same as the (1×4) reported in ref 7. Another possibility is that the trenches develop under particular conditions. The origin of the "disordered" structure is due, evidently, to the increased amount of Ca on the surface, although from our STM results it is not clear how the calcium excess affects and modifies the ordered c(6×2) overlayer and the substrate. Given the expected variation in charge transfer with coverage, it would be instructive

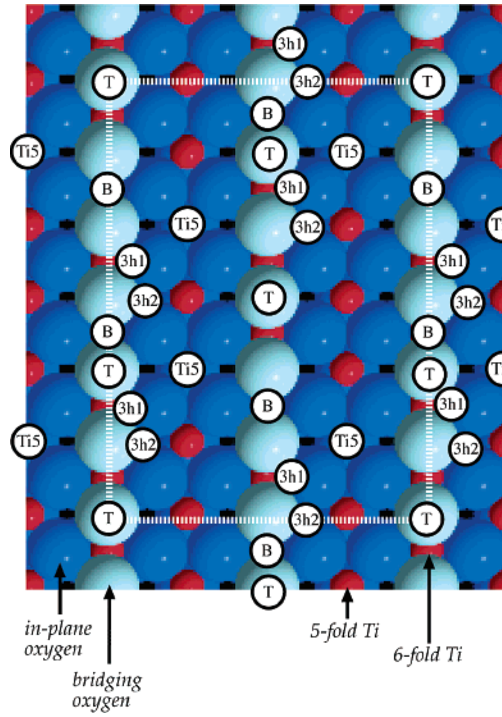

Figure 9. Ball model of possible high-symmetry adsorption sites of Ca in a c(6×2) overlayer on $TiO_2(110)$: T (top), B (bridge), Ti5 (substitution of in-plane Ti^{5+} ions), 3h1 (between two bridging oxygens and one in-plane oxygen atom), and 3h2 (between one bridging oxygen and two in-plane oxygen atoms).

in future work to investigate the oxidation state of Ca and the work function through the transition from the ordered to disordered phases.

5. Conclusions

The low-coverage Ca reconstructions obtained by vapor deposition or bulk segregation are similar, in particular a well-ordered c(6×2) overlayer is formed. With vapor deposition to coverages above a monolayer, the Ca excess gives rise to a highly disordered overlayer structure and is thought to induce a modification of the titania substrate.

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