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MIES and UPS(HeI) studies on reduced TiO₂(110)

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We have studied reduced TiO₂(110) surfaces by combining metastable impact electron spectroscopy (MIES) and UPS(HeI). The reduced Ti species were preparation-induced: their number density was modified either by adsorption of K atoms or by a combined annealing/oxygen exposure procedure. The emission from the bandgap state (binding energy 0.9 eV), caused by reduced Ti^{3+} 3d species, was monitored. Bandgap emission is seen clearly with UPS(HeI) and thus can be used to monitor the number density of the near-surface reduced species. A corresponding spectral structure cannot be seen with MIES. We propose that the excess charge density introduced either by preparation-induced oxygen vacancies or by K adsorption is delocalized over several surface and subsurface Ti sites; this, together with the partial shielding of the reduced Ti species, prevents detection of the reduced Ti species with MIES.

The re-oxidation and restructuring of the reduced TiO₂(110) surface, caused by simultaneous oxygen exposure and annealing, was studied at temperatures between 400 and 770 K, again by recording the Ti^{3+} 3d emission (0.9 eV bandgap state) with UPS(HeI). The surface can be completely re-oxidized by oxygen exposure at any selected annealing temperature in the range given above. Morphology changes, leading to a partially reduced surface, take place when the re-oxidized surface is further annealed at $T > 600$ K under reducing conditions. The results give support to the assumption that the re-oxidation is caused by the growth of additional titania whereby the Ti stems from the bulk and the oxygen originates from the gas. The restructuring of the re-oxidized surface upon annealing under reducing conditions appears to be due to diffusion of Ti interstitials to the surface. Copyright © 2004 John Wiley & Sons, Ltd.

INTRODUCTION

A better understanding of the functionality and improvement of the selectivity and efficiency of catalysts is one of the driving forces for surface investigations on titania.[1–3] Often, heterogeneous catalysts consist of small metal particles on oxide supports. Metal particles on oxide surfaces are relevant to crystal growth, catalysis, gas sensor operation, bonding in composites, etc. Moreover, when metal particles are deposited on reducible metal oxides, interesting surface chemistry can take place. Consequently, many growth studies of metals on titania were performed in the past.[1]

The discovery that finely dispersed Au particles supported on TiO₂ oxidize CO at low temperatures[4] has found considerable interest in the surface science community. So far, the underlying phenomena responsible for the oxidation process appear not to be well understood. The growth and properties of Au nanoparticles on TiO₂(110) depend on the surface restructuring, type and number density of defects at the surface produced during surface preparation prior to Au

deposition. Moreover, the Au–titania interaction itself is still subject to much speculation. For rutile (110) there is indication from scanning tunneling microscopy (STM) that the clusters nucleate at defect sites.[5] This could, on the one hand, bond the clusters firmly to the substrate, and, on the other hand, provide some excess charge leading to the production of anionic Au species.[6]

Normally, titania surface preparation is made by combining annealing, oxygen exposure and sputtering.[1] Titanium, as a reactive element, can be expected to react with O₂ provided that the surface is oxygen-deficient. Naively, one could anticipate that oxygen just fills the preparation-induced surface oxygen vacancies. However, there are numerous indications that the situation is more complicated. The bulk of non-stoichiometric TiO₂ contains, in addition to oxygen vacancies, Ti interstitials that possess a high diffusivity at elevated temperatures.[1] When these interstitials appear at the surface, they can react with gaseous oxygen. As a consequence, Ti–O complexes may be formed at the surface. Thus, reoxidation by filling the oxygen vacancies via the dissociation of gaseous oxygen may, at the same time, lead to oxygen-induced surface restructuring. As STM shows, the resulting surface morphologies will depend on sample temperature, anneal time, gas pressure, etc.[7] As a consequence,

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the catalytic activity of the surface may strongly depend on its history prior to deposition of the metal particles.

In the present work, the focus is on the MIES/UPS signals from preparation-induced reduced Ti species whose number was modified by either supplying extra charge to the system when adsorbing K atoms or by the re-oxidation of oxygen vacancies. The studies were made with the intention of obtaining information on the localization of the excess charge related to the presence of oxygen vacancies or supplied by metal adatoms.

EXPERIMENTAL

The experiments were carried out at the two cooperating laboratories in ultrahigh vacuum (UHV) systems (base pressure $<2 \times 10^{-10}$ Torr) equipped with X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS(HeI, II)), Auger electron spectroscopy (AES) and metastable impact electron spectroscopy (MIES), and are described in detail elsewhere.[8–10]

Briefly, in MIES, metastable helium atoms ($2^3S/2^1S$) are utilized to eject electrons from the substrate surface. Both MIES and UPS spectra are measured simultaneously using a cold-cathode discharge source that provides both ultraviolet photons (HeI) and metastable He($2^3S/2^1S$) atoms with thermal kinetic energy. Metastable and photon contributions within the beam were separated by means of a time-of-flight method using a mechanical chopper. This methodology yields MIES spectra free from UPS contributions; however, owing to the broad kinetic energy distribution of the metastable helium atoms, ~1.6% of the MIES intensity appears in the UPS spectra. In some of the measurements, particularly those concerned with the O_2–TiO_2 interaction, a pure HeI beam was obtained by removing the metastable component from the beam by (He*–He) small-angle scattering. Detailed introductions in MIES and its various applications in molecular and surface spectroscopy can be found in recent reviews.[11,12] The energy scales in the figures are adjusted in such a way that electrons emitted from the Fermi level (denoted by E_F, i.e. electrons with maximal kinetic energy) appear at the fixed energy $E_B = 0$ eV. In cases where the kinetic energy of the ejected electrons versus their intensity gives a direct image of the density of occupied states at the substrate surface, the energy distribution of the emitted electrons is presented as a function of their binding energy scale with respect to the Fermi energy, E_F, of the metallic Mo target-holder. For the chosen preparation conditions (see below) no charge-up occurs in MIES or in UPS. Consequently, the Fermi level of the Mo sample-holder can be used for calibration of the energy scale and E_F corresponds to the maximum kinetic energy at which electrons can be measured with MIES and UPS from a metallic substrate. Because substrate and analyzer are in electrical contact, the Fermi energy appears, irrespective of the substrate work function, at a constant position in the spectra. The energy scale of the UPS spectra was adjusted in the same way as described above for MIES. The work function of the surface is determined from the high-binding-energy cut-offs of the spectra; any variation reflects a corresponding change of the work function. As pointed out, the Fermi level appears at

a constant position in the spectra; any variation reflects a direct corresponding variation of the work function.

The K atoms were dosed by employing carefully outgassed commercial dispenser sources (SAES getters). The procedure to calibrate the K coverage is described elsewhere for Cs/TiO_2(110).[13] The sample can be cooled with liquid nitrogen and heated by electron bombardment. The temperature was measured with a thermocouple in direct contact with the front of the single crystal. A temperature range of 130–2000 K is accessible. The polished TiO_2(110) single crystals were introduced into the UHV chamber, Ar sputtered for ~30–45 min at 1 keV and annealed for 2, 2 and 0.5 min at 1065, 1105 and 1160 K, respectively.[14] The single crystal showed a (1×1) low-energy electron diffraction (LEED) pattern; a small amount of contamination by carbon was indicated by AES. After the series of experiments described in this paper, the color of the crystal turned deep blue and the crystal is of the type 'cube 1' shown in fig. 5 of Ref. 1.

RESULTS

The UPS results

The HeI results for the K-exposed TiO_2(110) surface are displayed in Fig. 1(a) in the submonolayer regime (the corresponding MIES results are presented in Fig. 1(b)); those for the O_2-exposed surface are shown in Figs 2 and 3. The shape of the O 2p valence band emission is slightly different in Fig. 1 compared with Figs 2 and 3 because the energy analysis is done with a hemispherical analyzer rather than a double-pass cylindrical mirror analyzer. In Fig. 1(a), exposure to K takes place at 130 K and the spectra are presented as a function of the K coverage starting from the bare surface. The small hump seen beyond E_F comes from contributions induced by HeII photons. The emission seen at binding energies larger than ~12 eV is affected by secondary electrons and will not be analyzed in the present work. In Figs 2 and 3 the crystal is held at 400 and 750 K, respectively, during oxygen exposure. Oxygen exposure is carried out in the following manner: in both cases oxygen exposure is increased stepwise until Ti(3d) (attributed to reduced Ti^{3+} 3d species; see below) has disappeared; the time between two consecutive spectra is ~2 min. Obviously, the required exposure depends strongly on the crystal temperature. Finally, the oxygen exposure is lowered slowly to zero over a period of 15 min. Corresponding data also were collected at 550, 600, 650, 700 and 800 K (not shown). At all studied temperatures Ti(3d) disappeared as a consequence of the chosen combined annealing/oxygen exposure procedure; this is not the case for $T > 850$ K. When the crystal temperature is chosen above 600 K, we find that Ti(3d) reappears during lowering of the exposure rate to zero; on the other hand, for crystal temperatures below 600 K the Ti(3d) structure does not reappear.

In general, the O 2p contribution to the UPS(HeI) spectra displays a double-peak structure. Emission peaked at around $E_B = 4$ eV can be attributed to the ionization of states in the upper part of the titania valence band, mainly representing the states located at the bridging oxygen, whereas emission peaked at around $E_B = 7$ eV is dominated by oxygen species
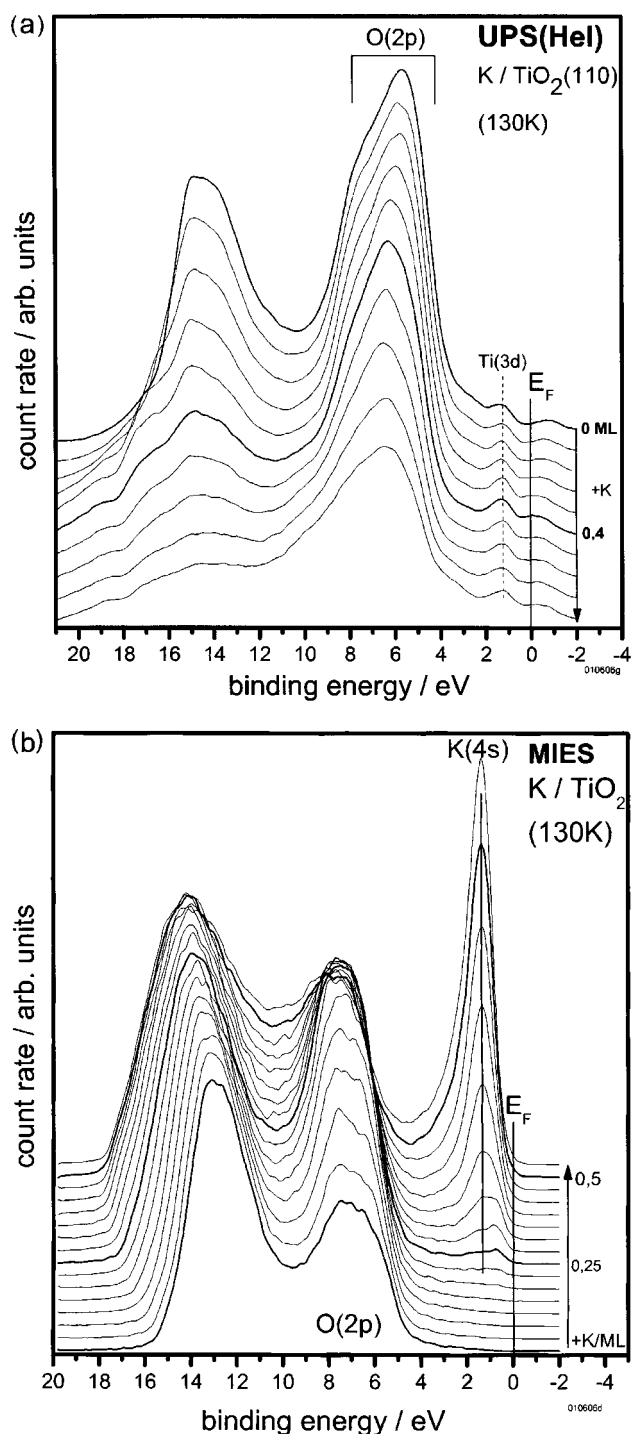
Figure 1. The UPS(HeI) (a) and MIES (b) spectra for K adsorption on TiO$_2$(110) at 130 K versus the K coverage.

from the oxygen planes.[15] Weak emission is seen around $E_B = 0.9$ eV; as in Refs 13 and 16–18, we attribute this feature, Ti 3d, to photoionization of preparation-induced reduced Ti^{3+} 3d cations (0.5% of a monolayer). As Fig. 1(a) shows, Ti 3d becomes more pronounced with K exposure, reaching its maximum at ~0.3 ML K coverage. No contribution from the K(4s) electron (analogous to K 4s in MIES; see Fig. 1(b)) appears in the UPS(HeI) spectra for coverages of >0.25 ML. This is due to the generally very low sensitivity of HeI for the detection of alkali valence electrons.[12]

Turning to the O$_2$/TiO$_2$(110) results, it can be seen from comparison of the top spectra at different substrate temperatures that the chosen method for substrate preparation leads to reproducible results. The preparation-induced intensity from reduced titania species Ti^{3+} 3d is ~0.5% of the area of the O 2p valence band emission structure. Assuming similar cross-sections for photoionization of O 2p and Ti 3d, we estimate that the number density of oxygen vacancies in the near-surface region is 0.5% of that of regular oxygen species.

At this point it is worth noting that in bulk Ti$_2$O$_3$ the 3d states located just below the Fermi level are also occupied; they are responsible for its semiconducting properties and UPS detects these 3d states. Their energetic position is almost indistinguishable from that of the 3d states populated during the creation of oxygen vacancies[2] and hence we need to consider the possibility that Ti 3d produced during the annealing procedure under simultaneaous oxygen exposure may be due to the presence of patches of substoichiometric titania.

The MIES results

Figure 1(b) shows MIES spectra for bare TiO$_2$(110) and those collected during K exposure at 130 K for coverages up to ~0.5 ML; results at larger K exposures will be presented elsewhere.[19] We do not discuss the emission at binding energies larger than ~13 eV because it is affected by secondary electrons. The surface was exposed to K atoms in order to enhance the detection sensitivity of MIES for the reduced Ti species. The presence of K atoms at the surface manifests itself in the following way. In the initial stage of K coverage (up to ~0.4 ML) the work function decreases by ~2 eV, starting with 4.4 eV for the bare titania substrate, as can be noticed from the corresponding variation of specal onset with coverage at large E_B values. Up to ~0.25 ML the presence of K species at the surface cannot be detected directly with MIES; the K atom is fully ionized and thus the K 4s electron is not available for interaction with He*. However, at ~0.25 ML K(4s) appears just below E_F. Up to 0.35 ML both Auger de-excitation of He* species and autodetachment of He^{-*}(1s 2s^2) negative ions (He^{-*}(1s 2s^2) $\rightarrow$ He(1s^2) + e(W_{kin})), formed by resonant transfer of the K(4s) electron to the He* probe atom, contribute to K(4s),[12,13] accounting for the two-peaked structure. At larger exposures, i.e. for smaller work functions, K(4s) is dominated by autodetachment. Our finding of only partial ionization of the surface-adsorbed K species above ~0.25 ML is at variance with the finding (based on EXAFS studies) that Na is nearly fully ionized at submonolayer coverages on TiO$_2$(110).[20]

As discussed in detail in Ref. 13, the emission from bare titania is due to the resonance ionization–Auger neutralization process sequence whereby the He* probe atom is first resonantly ionized; its re-neutralization involves two O 2p electrons, one of which is emitted.[11,12] Superimposed on the resulting structure (between 10 and 16 eV) is a contribution of secondary and scattered electrons. The structure between 5 and 9 eV also is attributed to processes involving O 2p electrons: the considerations made in Ref.
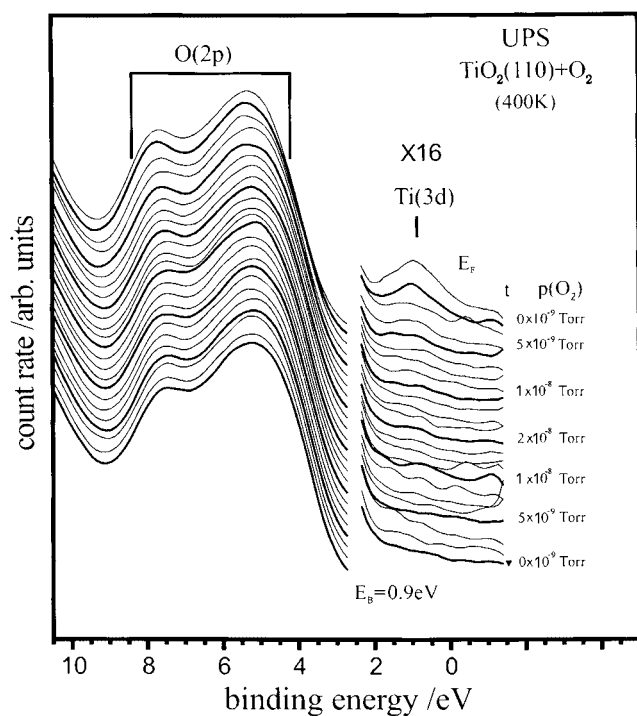
Figure 2. The UPS(HeI) spectra for $TiO_2(110)$ exposed to oxygen at 400 K. The time between two spectral scans is ~100 s. Pressure changes were made after fixed time intervals.
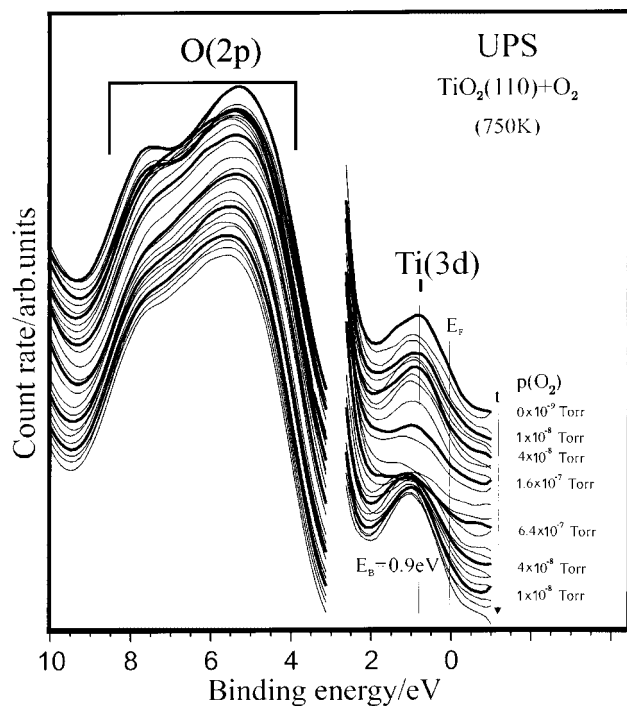

Figure 3. The UPS spectra for $TiO_2(110)$ exposed to oxygen at 750 K. The time between two spectral scans is ~100 s. Pressure changes were made after fixed time intervals.

21 suggest that for bare titania and coverages below 0.3 ML it is mostly due to Auger neutralization, involving both Ti 3d electrons from reduced cations (created by the transfer of the He 2s electron to the surface) and O 2p electrons. Auger neutralization involving only Ti species is not seen because

double occupation of Ti 3d would be prerequisite for this process; such species are not produced during preparation or during K adsorption. Thus a peak from the reduced Ti species is not expected from clean titania, and the MIES spectra from stoichiometric and defective clean $TiO_2(110)$ are like the bottom spectrum of Fig. 1(b).

Below a work function of 3.5 eV, i.e. for coverages beyond ~0.15 ML, the mechanism responsible for O 2p is dominated by Auger de-excitation involving only one O 2p electron. However, in contrast to UPS (Fig. 1(a)) there is still no indication of a contribution from the reduced Ti^{3+} 3d species, either from the preparation-induced species or from those due to K-induced reduction. Their contribution to the spectra would, as in UPS, be expected to produce a peak at $E_B = 0.9$ eV and an enhancement should be seen with increasing K exposure.

DISCUSSION AND INTERPRETATION

Delocalization of the excess charge introduced by oxygen vacancies or by K adsorption

We concentrate on the finding that there is no evidence in MIES for the presence of Ti^{3+} 3d species at the bare and K-covered surface whereas these species are clearly seen with UPS. In UPS(HeI) K adsorption enhances the Ti 3d signal already present after surface preparation. This enhancement is correlated with a decrease of the surface work function. Consensus exists that alkali adsorption on titania leads to the transfer of the weakly bound s-electron to the surface; the excess charge becomes accommodated at surface and near-surface cations, thus enhancing the Ti 3d signal from reduced Ti species.[1,13,22–24] On bare titania the absence of Ti 3d in MIES is due to the fact that the reduced Ti species become involved in Auger neutralization processes.[13,21] However, as soon as the work function is lowered to 3.5 eV, reduced Ti species become detectable with high probability via Auger de-excitation. Indeed, reduced Ti^{3+} 3d species were seen with MIES from $TiO_2(110)$, heavily reconstructed under reducing conditions, i.e. produced by annealing in UHV to ~1150 K.[25] Moreover, a pronounced Ti^{3+} 3d signal was seen from a TiO_x ($x \sim 1$) film on MgO.[26]

A possible explanation for the absence of any Ti 3d signal in MIES may come from a recent theoretical analysis of the nature of the extra state created upon the introduction of additional charge to $TiO_2(110)$.[22] On the basis of first-principles density functional theory (DFT) calculations it was concluded that for Na adsorption the extra state is essentially localized on substrate Ti cations, with a dominant weight on those lying in the subsurface plane, just below the surface fivefold-coordinated Ti species. It was, in addition, demonstrated that localization of the excess charge is insensitive to the particular way in which the extra charge is introduced. We assume that the analysis of Ref. 22 can be applied to K as well, and propose that the excess charge delivered by the K atom is delocalized over several surface and sub-surface sites.[22] Thus, not being confined to particular surface cations, the excess charge cannot be accessed efficiently with MIES. In addition, reduced Ti species may be masked partly by the K adsorbates. For K-precovered $TiO_2(100)c(2 \times 2)$ this delocalization goes

apparently even further, and the reduced species cannot be seen even with UPS.[23] In contrast, the reduced Ti species detected in Refs 25 and 26 may be located at the very surface, and thus can be accessed efficiently by MIES.

We can extend our reasoning to the preparation-induced reduced Ti species, related to surface oxygen vacancies: after reducing the work function below 3.5 eV we would expect to see reduced Ti species. Because this is not the case, we conclude that they are also not predominantly located at the very surface, and for this reason are again not accessible with MIES.

Reoxidation and restructuring of slightly defective TiO$_2$

The UPS results collected during the chosen annealing/oxygenation procedure can be summarized as follows: as a consequence of the oxygen exposure at elevated temperature, the Ti^{3+} 3d peak disappears, indicating that the near-surface region is re-oxidized. Apparently, the preparation-induced Ti^{3+} 3d peak is indeed the consequence of oxygen vacancies. As long as the crystal temperature is kept below 600 K (see Fig. 3), the bandgap of titania remains empty when the oxygen partial pressure is reduced while keeping the temperature of the titania constant, i.e. when annealing under reducing conditions. On the other hand, annealing at $T > 600$ K under reducing conditions leads to the reappearance of Ti 3d, i.e. signals the presence of Ti^{3+} 3d species.

For a qualitative interpretation we recall that the bulk of unstoichiometric TiO$_2$ contains, in addition to oxygen vacancies, Ti interstitials that possess a high diffusivity at elevated temperatures.[1] When these interstitials appear at the surface, they can react with oxygen atoms from the vacancy-induced dissociation of gaseous oxygen. We adopt the following scheme developed from combined STM, low-energy ion scattering and SIMS results:[7,27] the surface reoxidation and restructuring can be regarded as the growth of additional TiO$_2$ phases whereby the Ti comes from the bulk and the oxygen from the gas phase. The following phases could be identified, namely: regions with TiO$_2$ stoichiometry (pseudo-hexagonal rosettes); regions with presumably Ti$_2$O$_3$ stoichiometry (added Ti$_2$O$_3$ rows); and (1 × 1) islands.[7,27]

We propose that step 1 of the chosen surface treatment (annealing at temperatures between 400 and 800 K under simultaneous oxygen exposure) removes the reduced Ti species completely; surface restructuring leads to TiO$_2$ stoichiometry.[7,27] Some oxygen atoms from the defect-induced dissociation process may be left chemisorbed to the surface.

Our results suggest that below 600 K Ti diffusion to the surface continues to be of importance during step 2 (slow decrease of the oxygen exposure rate at the chosen anneal temperature between 400 and 800 K), eventually accompanied by oxygen desorption. Thus, the reappearance of Ti 3d for $T > 600$ K suggests that step 2 leads to the formation of Ti-rich structures possessing occupied Ti 3d states; they manifest themselves by the bandgap state at 0.9 eV, as seen for bulk Ti$_2$O$_3$ (see above). Added Ti$_2$O$_3$ rows constitute a possible example for such structures, as suggested by recent STM results.[7,27] At $T < 600$ K restructuring with the formation of regions with Ti$_2$O$_3$

stoichiometry does not occur, as concluded from the absence of the Ti^{3+} 3d signal. However, we have to be aware that the absence of bandgap emission does not necessarily imply that no restructuring of the surface occurs at all under the chosen reducing conditions. It merely follows that no formation of regions with Ti$_2$O$_3$ stoichiometry, detectable with UPS, takes place. Restructuring of the surface when it merely leads to TiO$_2$ stoichiometry does not produce a bandgap state, and thus it remains undetected with UPS.

SUMMARY

We have studied slightly defective TiO$_2$(110) surfaces by combining MIES and UPS(HeI). The reduced Ti species were preparation-induced: their number density was modified either by adsorption of K atoms or by a combined annealing/oxygen exposure procedure. The emission from the bandgap state (binding energy 0.9 eV) attributed to Ti^{3+} 3d species was monitored. Emission from reduced Ti^{3+} 3d species, both preparation and K-induced, is clearly seen with UPS but not with MIES. We propose that the excess charge, introduced by either surface oxygen vacancies or by transfer of the K 4s electron to the surface, is delocalized over several surface and near-surface Ti sites. Thus, owing to the negligible charge concentration at particular surface cations, it is not observed with MIES.

The re-oxidation of slightly defective TiO$_2$(110) surfaces during simultaneous oxygen exposure and annealing was studied at temperatures between 400 and 770 K. Emission from the bandgap state (binding energy 0.9 eV), caused by reduced Ti^{3+} 3d species, was monitored by UPS(HeI). In the entire studied temperature range the surface can be re-oxidized completely by oxygen exposure at the selected temperature. This proves that the preparation-induced surface point defects are indeed oxygen vacancies. We show that morphology changes, leading to a partially reduced surface, take place when the re-oxidized surface is annealed further at $T > 600$ K under reducing conditions. On the other hand, no partial reduction is observed when annealing the re-oxidized surface at $T < 600$ K. Our findings are consistent with the assumption that the restructuring and re-oxidation are caused by the growth of additional titania during simultaneous annealing and oxygen exposure; we propose hereby that the Ti is supplied by the bulk whereas the oxygen originates from the gas.

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