

Lithium adsorption on TiO₂: studies with electron spectroscopies (MIES and UPS)

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The adsorption of lithium atoms on rutile TiO₂(110) single crystals was studied with metastable-induced electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS(HeI)) between 130 K and room temperature. Some auxiliary measurements on W(110) required for data interpretation are also reported. At 130 K ionic adsorption at titania prevails up to 0.3 monolayer equivalents (MLE) as judged from the weak Li(2s) emission in MIES for these exposures. The reduction of the Ti⁴⁺ cation is manifested by the growth of an occupied bandgap state in UPS: the alkali s-electron is transferred to a near-surface cation, thereby reducing it to Ti³⁺ 3d. The transfer of the s-electron is responsible for the observed work function decrease up to ~0.5 MLE coverage. From the analysis of the UPS Ti³⁺ 3d signal, as well as from the Li(2s) emission, it is concluded that the degree of ionicity of the adsorbed Li decreases from 100% at 0.3 MLE to 40% at 0.7 MLE. Above 0.5 MLE the MIES spectra are dominated by an Li(2s)-induced peak indicating the presence of Li with an at least partially filled 2s orbital. At temperatures above 160 K this peak is almost absent. Excluding Li desorption at these temperatures, we suggest that Li moves into or below the rutile TiO₂(110) surface above 160 K. Lithium insertion into the surface and intercalation are discussed. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: MIES; UPS; alkali atoms; lithium; TiO₂(110)

INTRODUCTION

Metal particles and films on oxide surfaces are relevant to crystal growth, catalysis, gas sensor operation, bonding in composites, etc.^{1,2} Moreover, when metal particles are deposited on reducible metal oxides, interesting surface chemistry can take place. Usually, the metal adsorbate atoms are different from the metal cations of the oxide. Thus, there is interest in the properties of isolated metal adsorbate atoms on oxides that represent the initial stage of interface formation.

Alkali and alkaline-earth metals are known to readily donate electrons to transition-metal oxide substrates upon adsorption. Thus, their bonding to the surface possesses a strong ionic component. However, the idea that metal atoms interact only by electron transfer with the surface is too simplistic in general. The adsorption of metals may even disrupt the surface structure of the oxide, whereby considerable oxygen rearrangement can take place.

For alkali adsorption on titania, broad consensus exists that at low alkali exposures a complete transfer of the valence electron to the substrate takes place. However, although of technological importance, studies of Li adsorption on titania are rare (a recent summary can be found elsewhere³). No

studies with photoelectron spectroscopy on the Li/titania system are known to the authors. Numerous photoemission studies with Na, K and Cs have shown that alkali metal adsorption induces a reduction of Ti⁴⁺ cations to Ti³⁺ 3d.^{4–9} For brevity we have mentioned only studies on TiO₂(110), although the same behaviour is found for adsorption on TiO₂(100) as well.¹⁰ This has been interpreted as a charge flow from the adsorbate to Ti cations mediated by surface oxygen. In the photoemission spectra, the occurrence of the charge transfer is manifested by the presence of an occupied gap state with Ti 3d character and a significant decrease of the surface work function similar to that observed for alkali adsorption on metals. Consequently, one aspect of this work is the study of the charge transfer as a function of Li exposure. The UPS(HeI) technique is insensitive to the amount of charge of 2s character remaining at the adsorbate. However, for Cs and K/TiO₂(110)^{11,12} metastable-induced electron spectroscopy (MIES) has been demonstrated to be well suited to study this topic. In particular, MIES is rather sensitive to the presence of s-electrons at the adsorbate core.

Some evidence exists that the titania surface reconstructs when it becomes covered with more than a monolayer of alkali atoms.¹⁰ Oxygen extraction from the substrate by the adsorbate atoms may take place, just as for the adsorption of V on titania¹³ and Ba on SrTiO₃.¹⁴ In this way a surface layer may form in which the adsorbate atoms are oxidized. The MIES technique has been demonstrated to be rather

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sensitive to the detection of small amounts of oxygen-containing molecules, in particular the chemisorption of CO₂ on alkaline-earth oxides.¹⁵

Furthermore, Li intercalation is extremely interesting. For the rutile TiO₂ surface, small diffusion coefficients were reported for Li¹⁶ and insertion into the surface was suggested,^{3,17,18} whereas intercalation into anatase is known to be easier.^{16,18,19} With our surface-sensitive techniques the disappearance of Li from the surface will be easy to monitor; measurements versus the substrate temperature give some insight into the temperature dependence of an eventual insertion or intercalation.

In the present study we report MIES and UPS spectra for TiO₂(110) as a function of Li coverage starting from the clean titania substrate at 300 and 130 K in order to obtain information concerning the above-mentioned issues. We compare our results with corresponding results for tungsten, which are presented in this paper.

EXPERIMENTAL

The experiments were carried out in an ultrahigh vacuum (UHV) system (base pressure $<3 \times 10^{-8}$ Pa) equipped with low-energy electron diffraction (LEED), x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS(HeI, II)), Auger electron spectroscopy (AES) and metastable-induced electron spectroscopy (MIES). The system is described in detail elsewhere.^{20–22}

A cold-cathode helium-gas discharge source serves both as the source for an intense metastable helium beam for MIES (He*2³S/2¹S) with 19.8/20.6 eV excitation energy and as an HeI photon source for UPS (HeI with 21.2 eV). The metastable atoms and HeI photons eject electrons from the substrate surface. The contributions to the electron spectra from metastables and photons within the beam are separated by means of a time-of-flight technique. The incidence angle of metastables and photons is 45° with respect to the surface; electrons emitted in the direction normal to the surface are analysed. In MIES, the emitted electrons can stem from various Auger processes: Auger neutralization, Auger de-excitation of He* and autodetachment of He*^{-*} (1s 2s²). Provided that the electrons are due to Auger de-excitation, the spectra can, as in photoelectron spectroscopy, be presented as a function of the binding energy E_B of the ejected electron with respect to the Fermi energy (labelled E_F). The maximum binding energy with respect to the vacuum level probed by the He* atom equals its excitation energy, which is 19.8 eV for He*(2³S). A more detailed introduction to MIES and its numerous applications in molecular and surface spectroscopy can be found in recent reviews.^{23,24}

The particular processes taking place on titania pre-covered by >0.5 ML of K and Cs have been identified previously.^{11,12} In that work it has been established that the He* interaction with the alkali adsorbates causes a pronounced structure due to auto detachment. 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 the maximum kinetic energy appear at $E_B = 0$ eV. The position of E_F is determined from UPS spectra of a tungsten surface.

The maximum binding energy with respect to E_F (probed by the He* atom) equals its excitation energy (19.8 eV for He*(2³S)) minus the work function. Thus, the low-kinetic-energy cut-off in the spectra gives the surface work function directly, irrespective of the actual interaction process that produces the electrons. Evaluation of the work function was done by a linear fit of the onset of the spectra on the left side. The UPS spectra presented in this work were collected with a separate UV source (HIS 13, Omicron). This source provides higher HeI intensities compared with our MIES/UPS source and allows the collection of UPS(HeII) spectra, which is not possible with the combined MIES/UPS source. The energy resolution for both UPS and MIES is ~0.3 eV. The energy scale of the UPS spectra was adjusted in the same way as described above.

Lithium atoms were dosed by employing carefully outgassed commercial dispenser sources (SAES getters). The following procedure was used for calibrating the Li exposure: a W(110) single crystal, held at room temperature, was exposed to Li using the outgassed Li dispenser and the work function was monitored. The coverage at which the work function minimum is observed is at 5×10^{15} Li atoms cm⁻².^{25,26} For all measurements the Li doser was operated under the same conditions, therefore all exposures can be given in monolayer equivalents (MLE) in all cases (0.5 MLE is defined as the exposure that leads to a coverage of 5×10^{15} atoms cm⁻² in the case of W(110)). We chose this calibration because the TiO₂(110) surface has 5×10^{15} fivefold-coordinated Ti atoms per cm² as well as 5×10^{15} bridging oxygen atoms per cm². The dispensers typically operate at a rate of 0.05 MLE min⁻¹. The sample can be cooled by liquid nitrogen to 130 K and heated by electron bombardment to 2000 K. The temperature was measured by a thermocouple in direct contact with the front of the single crystal.

Polished TiO₂(110) single crystals were annealed at ~800 K for several hours. This procedure was used previously²⁷ and produces a (1 × 1) LEED pattern; furthermore, a small amount of carbon contamination was indicated by AES. Remaining contaminations were removed by Ar sputtering under grazing incidence. However, the sputter time was minimized to avoid the introduction of defects as much as possible. Additionally, some experiments were carried out on samples without previous exposure to Ar⁺ ions.

RESULTS

In this section the MIES and UPS results for Li-exposed TiO₂ surfaces are presented and compared with those from the Li/W(110) system. Primarily, the spectra are recorded as a function of alkali exposure.

The UPS and MIES spectra for the clean and Li-exposed (at 130 K) TiO₂ surface are shown in Fig. 1. The UPS spectra for clean TiO₂(110) are compatible with earlier investigations^{4–9} (see introduction) and display emission mainly from ionization of valence band states (with O(2p) character mainly) between binding energies of 3.5 and ~9 eV. The peak at $E_B = 1$ eV is known to originate from reduced Ti³⁺ states, which can be produced by ion bombardment,

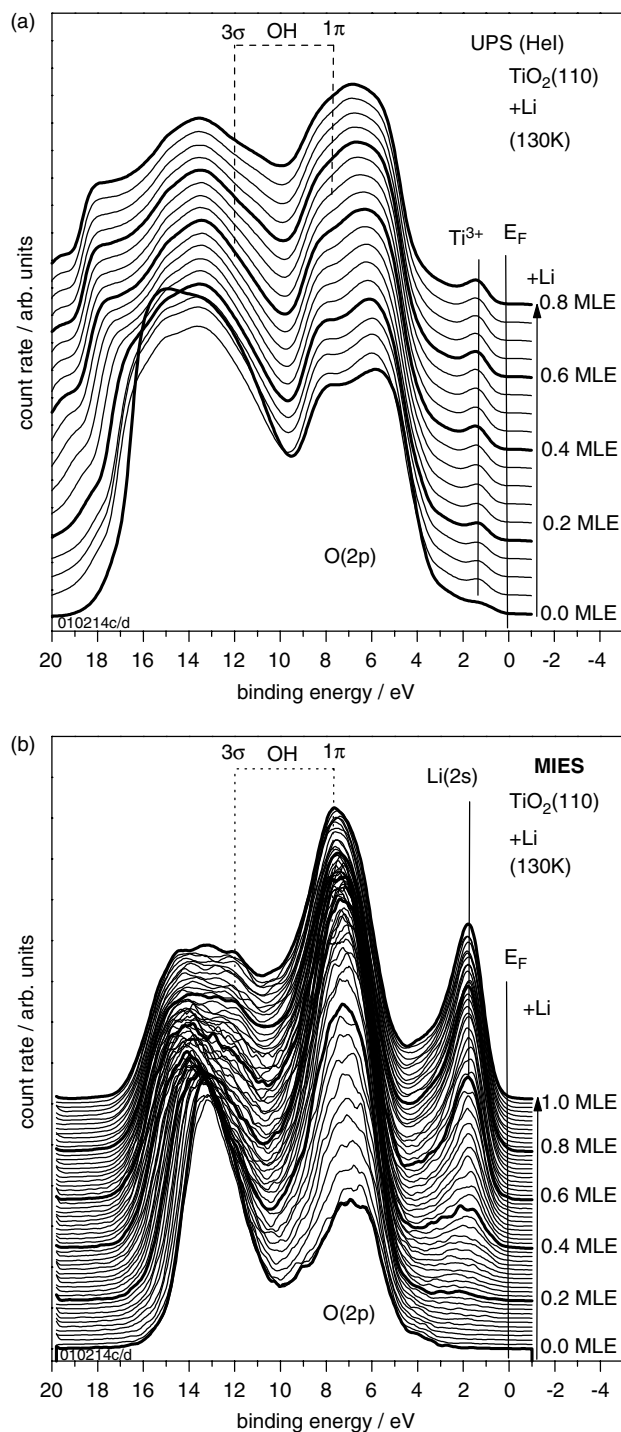


Figure 1. Lithium adsorption on TiO₂(110) at 130 K: (a) UPS(Hel) spectra; (b) MIES spectra.

heating and reducing adsorbates (see Introduction). For binding energies larger than ~ 12 eV (kinetic energies below ~ 6 eV) the UPS and MIES spectra are influenced to some extent by secondary and scattered electrons. The onset of the spectra on the left side (highest observed binding energy) in Fig. 1 is directly related to the surface work function (excitation energy minus work function), as already pointed out in the previous section.

The MIES results for the clean TiO₂ surface are in reasonable agreement with our previous results²² and those

obtained when a polycrystalline Ti surface is exposed to 110 L (Langmuir) of oxygen.²⁸ Briefly, the structures seen for binding energies between 4.3 and ~ 9 eV (O(2p)) are due to valence band emission in an Auger neutralization process that involves the He*-induced reduced Ti³⁺ 3d species. The resulting spectra are Auger de-excitation-like but are broadened and shifted by ~ 1 eV towards smaller kinetic energies than with a true Auger de-excitation process. At a work function of < 3.5 eV the Auger de-excitation process involving O(2p) states becomes dominating; this change in the interaction process is responsible, in particular, for the change in shape of the O(2p) peak with decreasing work function under Li exposure. The feature at low kinetic energies is also due to the ionization of valence band states, but in an Auger neutralization process involving two O 2p electrons from the surface.¹¹ A detailed discussion of the above-mentioned Auger processes was made for the interaction between He* and a strontium titanate surface, backed up by first-principles results with density functional theory (see Ref. 29). It is believed to be valid for titania surfaces as well.

For Li exposures up to ~ 0.5 MLE the onset on the left side of both the UPS and MIES spectra moves to higher binding (lower kinetic) energy due to a strong decrease of the work function. For exposures above 0.3 MLE a new peak close to E_F emerges in MIES. This peak, Li(2s), originates from interaction of the excited He atoms with the 2s electron of adsorbed Li atoms via Auger de-excitation.²¹ Contributions from the Auger autodetachment-process, efficient at work function < 2.5 eV, are small because the work function remains larger than 2.9 eV.

For larger exposures, some small contributions by peaks OH 3 σ and 1 π (at 7.5 and 11.7 eV, respectively) become visible in the MIES spectra. From earlier studies of the interaction of water with an alkali-precovered surface²² these contributions can be attributed to OH groups formed by the interaction of residual water molecules (coverage remains below ~ 0.1 ML coverage) with the Li-covered surface. In the UPS spectra the hydroxyl contamination is barely visible for all Li exposures due to the lower surface sensitivity of this technique.

The exposure dependence of Li(2s) in MIES and of Ti³⁺ observed in UPS is displayed in Fig. 2(a). The O 2p intensity observed by UPS (also shown in this figure) proves the stability of the UV-light intensity provided by the source. The observed change in work function under Li exposure is shown in Fig. 2(b). For the bare titania surface we observe a work function of 4.8 eV, in agreement with previous studies.^{11,22} The work function of the Li-covered titania surface is ~ 3.0 eV and is higher than the expected value for bulk Li (2.4 eV).³⁰ The exposure dependence of the Li(2s) and Ti³⁺ signals is rather different; although Ti³⁺ shows a maximum close to the minimum of the work function, Li 2s shows a strong rise in this region.

The interaction of Li with TiO₂(110) at room temperature was studied on samples prepared with and without Ar⁺ bombardment (in Fig. 3, MIES results for a sample prepared without Ar⁺ bombardment are shown). Both sets of spectra give the same results, which are different from those at 130 K (Fig. 1), especially at high exposures. As at 130 K, an initial

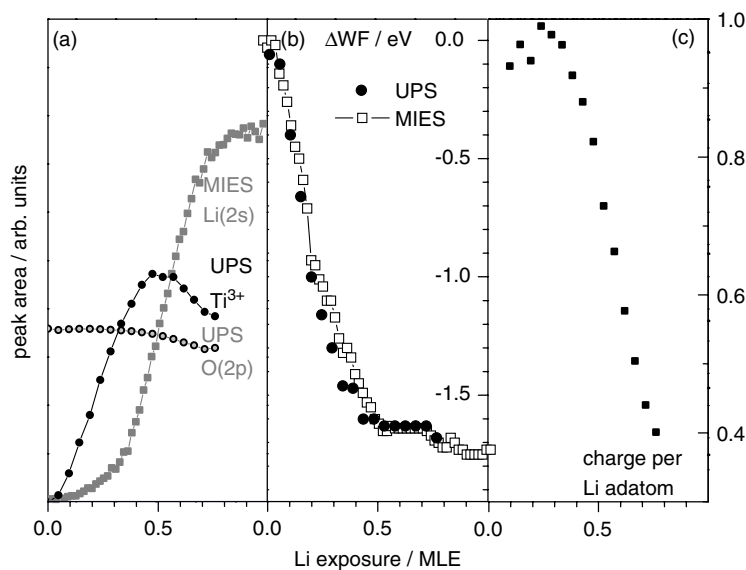


Figure 2. Exposure dependence of: (a) spectral features seen in Fig. 1; (b) the work function (WF); (c) the ionicity of the adsorbed Li.

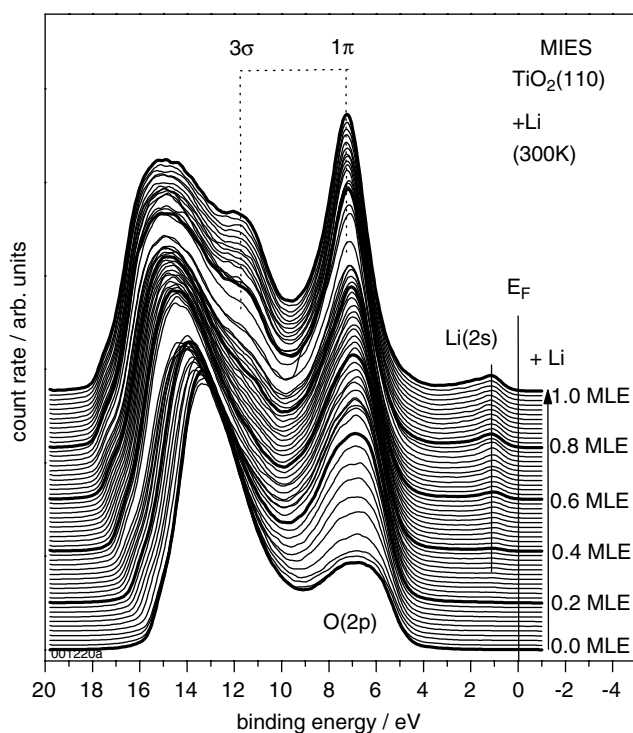


Figure 3. The MIES spectra for Li adsorption on TiO₂(110) at room temperature.

decrease of the work function and similar changes in O(2p) are observed. However, for exposures above 0.5 MLE the behaviour for 130 and 300 K differs significantly. The Li(2s) signal remains very weak under further Li exposure. The accumulation of hydroxyl species at the surface is stronger at 300 K but is still <0.1 ML; therefore it can be ruled out that the observed weak Li(2s) signal is due to the reaction of the supplied Li atoms with residual gas species (as f.i. water desorbing from the warm dispenser). However, it is important to note that the work function decreases further under Li exposure, reaching a value of ~1.9 eV at 0.8 MLE.

In Fig. 4(a) MIES spectra for W(110) exposed to Li at

room temperature are shown for comparison with those for TiO₂(110) (Fig. 4(b)). We will restrict ourselves on the discussion of the behaviour of the Li(2s) emission, whereby the 2s orbital is at least partially filled, as evidence for the presence of Li at the surface. For both Li adsorption on tungsten at 300 K and Li adsorption on titania at 130 K, the MIES spectra for high exposures are dominated by the Li(2s) signal, in contrast to the Li-exposed TiO₂(110) surface at 300 K where only a weak Li(2s) signal is observed. Figures 4(a) and 4(b) compare MIES spectra for the annealing of a tungsten surface precovered by 0.9 MLE Li (at 300 K) from 300 to 620 K (a) and a titania surface precovered by 1.4 MLE Li (at 130 K) from 130 to 290 K (b). For tungsten Li(2s) disappears between 400 and 500 K (Fig. 4(a)), whereas for Li-precovered titania Li(2s) starts to disappear at ~160 K. In parallel, the work function decreases to values of ~2.1 eV in this temperature range. As the work function behaviour and the comparison with tungsten show, this cannot be due to desorption into the vacuum. A weak signal at ~4.8 eV (O²⁻) is observed in the case of the tungsten surface; the identification of this spectral feature as O²⁻ follows from earlier studies investigating the interaction of Li with oxygen on W(110).^{31,32} Because no O²⁻ signal is observed for the titania surface, Li oxide formation involving oxygen from the TiO₂(110) surface is insignificant under the present conditions.

DISCUSSION

For the following discussion we assume a linear relation between exposure and the number of adsorbed alkali atoms for all cases (130 K and 300 K, as well as on W(110) and TiO₂(110)), which implies a constant sticking coefficient. Furthermore, we assume that the sticking coefficient is equal for both surfaces. These assumptions are supported by the similar behaviour of the work function with respect to the Li exposure and the fact that the multilayer desorption temperature of Li is well above room temperature.

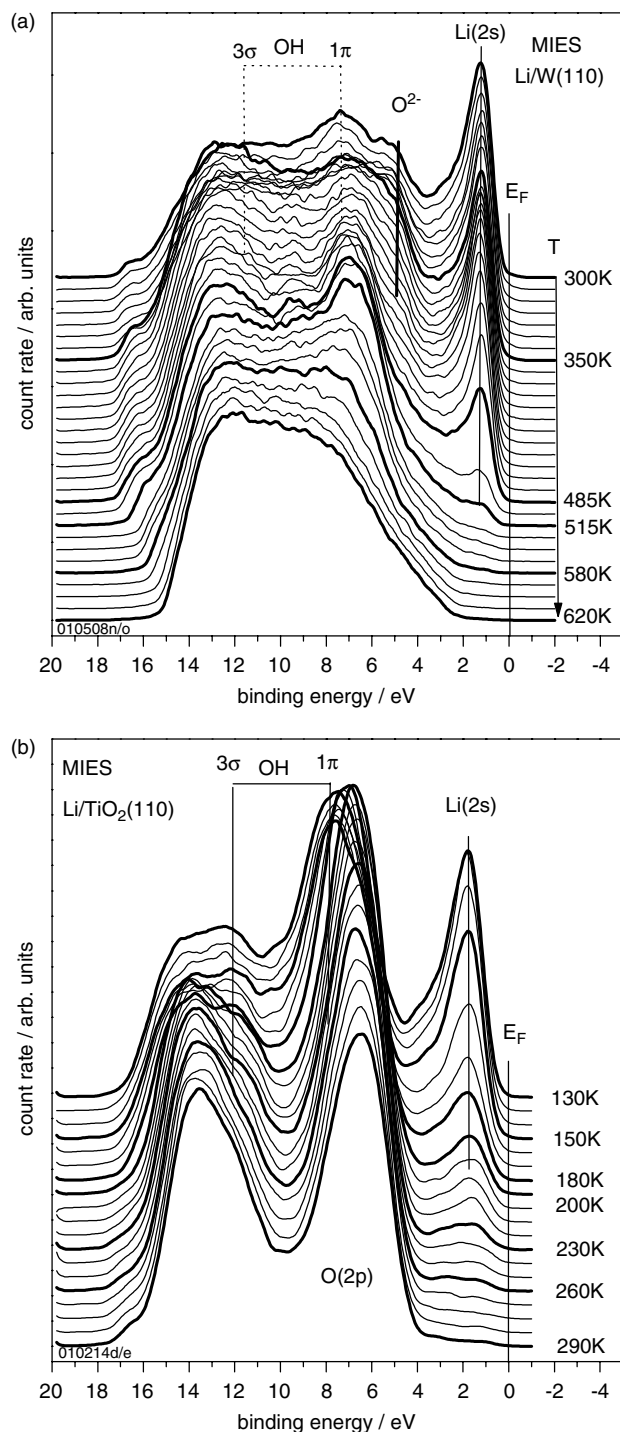


Figure 4. The MIES spectra recorded during the annealing of: (a) 0.9 MLE Li on W(110); (b) 1.4 MLE Li on TiO₂(110) as prepared in Fig. 1.

Lithium adsorption at 130 K

In UPS the feature Ti³⁺ close to E_F appears under exposure to Li, which is due to the reduction of Ti⁴⁺ to Ti³⁺. Obviously, the Ti³⁺ 3d signal is proportional to the number of adsorbates multiplied by the fraction of transferred charge to Ti per adatom (divided by the intensity loss due to the overlayer). As shown in Fig. 2, the Ti³⁺ 3d signal is proportional to the exposure for coverages Θ up to 0.3 MLE. For higher coverages the Ti³⁺ 3d signal deviates from a linear relationship with

respect to the exposure and saturates at ~ 0.5 MLE. Finally, the signal decreases towards higher coverages. This implies that for $\Theta > 0.3$ MLE the charge transfer to the substrate per adsorbate atom must deviate from its original value. The MIES spectra (Fig. 1(b)) suggest an initial adsorption of Li as Li⁺ (see discussion below) and this leads to the reduction of Ti cations. In this case a more quantitative analysis is possible and the degree of ionization of the adsorbates can be deduced from the Ti³⁺ 3d peak area at a given coverage. The expected area for a complete ionization of the outer shell (Li + Ti⁴⁺ \rightarrow Li⁺ + Ti³⁺) can be estimated by a linear fit of the Ti³⁺ 3d peak area for low exposures observed in UPS (see Fig. 2(a)). The stable intensity provided by the source is evident from the almost constant O(2p) intensity in the UPS spectra. The slight decrease of intensity seen in Fig. 2(a) can be explained by shielding of the underlying titania due to the adsorbed Li layer. However, this effect is rather small. Neglecting this effect, the observed Li-induced Ti³⁺ 3d peak area divided by the fitted peak area for complete ionization of the outer shell gives us the degree of ionization (Fig. 2(c)). We find that Li is adsorbed as Li ^{δ +} with δ equal to 1.0, 0.7 and 0.4 for $\Theta = 0.3, 0.5$ and 0.7 MLE, respectively.

The MIES results (Fig. 1(b)) support predominant ionic adsorption for $\Theta < 0.3$ MLE because the Li(2s) signal is small. Under the assumption that the Li(2s) signal is entirely due to Auger de-excitation, evaluation of the Li(2s) peak area (Fig. 2) leads to similar results. An ionic-to-neutral transition around $\Theta = 0.5$ ML was also postulated on the basis of ISS results for Cs-covered titania.⁹

Lithium adsorption at 300 K

The most striking differences from the 130 K results are the very weak Li(2s) signal for all coverages (indicating that no metallic Li overlayer is formed) and the low work function observed at higher exposures. We have already pointed out that an eventual accumulation of hydroxyl species at the surface (which is < 0.1 ML for all coverages) cannot be responsible for such behaviour.

Furthermore, as was discussed above, the weak Li(2s) signal in the case of titania is not due to reactions with surface oxygen leading to O²⁻ formation. Additional support that neither OH formation by interaction with the residual gas nor oxygen extraction from titania lattice occurs is provided by the results for K(Cs)/TiO₂(110).^{11,12} In these cases, the features K(4s) and Cs(6s) (corresponding to Li(2s)) persist up to saturation coverage at room temperature. This rules out consumption of the valence electrons 4s and 6s, respectively, by the formation of alkali–oxygen complexes, as well as by surface reactions with residual gas in these cases.

Lithium desorption into the vacuum at 160 K can be excluded in the case of the Li/titania system by comparison with the data for Li/W (see Fig. 4). Moreover, at > 160 K the onset of the spectra moves towards higher binding energies, indicating a work function decrease to ~ 2.1 eV, which is close to the observed value for titania exposed to Li at 300 K (see Fig. 3). Such values are not observed during the deposition at 130 K (Fig. 1(a)). Additional evidence against desorption comes from the fact that for heavier alkali atoms (K, Cs), where a lower desorption temperature is expected, the corresponding s-emission is observed in MIES at 300 K.

Because the absence of Li(2s) emission in MIES for temperatures of >160 K cannot be attributed to a chemical reaction at the surface or to Li desorption, we conclude that the Li is inserted into the surface or migrates into the bulk, lowering the surface work function. In the following we summarize some studies that provide a more detailed interpretation of the data presented here.

For the rutile surface very small diffusion coefficients have been observed experimentally,³³ as well as theoretically predicted.^{17,19} It has been shown that Li intercalation is favourable thermodynamically but that kinetic restrictions are important at room temperature.¹⁷ According to Stashans *et al.*¹⁹ the equilibrium position of the Li at room temperature is between two bridging oxygen atoms. The Li(2s) electron is transferred to the underlying Ti cation. An occupied bandgap state is produced, situated 0.7 eV above the valence band maximum and composed of the 3d and 4s Ti atomic orbitals. It was pointed out that, although Li bulk intercalation into anatase is easy, this is not the case for rutile. This was traced back to the much larger distortion of the lattice as a consequence of Li intercalation into rutile.

In the most recent theoretical work the diffusion of Li^+ ions into the rutile host lattice and the lattice's role as a kinematic constraint were discussed.¹⁷ In agreement with previous work,¹⁹ they report that intercalation into rutile at room temperature is not significant (the diffusion coefficients are of the order of 10^{-6} or 10^{-14} $\text{cm}^2 \text{s}^{-1}$, dependent on the direction). However, it is important to note that in our experimental study low Li fluxes are used and the overall exposure is very low. Therefore, even low diffusion coefficients of the order of 10^{-14} $\text{cm}^2 \text{s}^{-1}$ can be sufficient for considerable diffusion in our case. Moreover, electrochemical Li intercalation has been observed by EXAFS³⁴ and analysis of the results shows that a thin surface layer of the titania (a few nanometres in thickness) is changed by lithiation. At 120 °C Li intercalation is observed up to full loading. The intercalation influences the electronic structure of the rutile lattice, as demonstrated for $\text{Li}_{1/2}\text{TiO}_2$.¹⁷ Important consequences are: although the upper valence band of pure rutile consists of a two-peaked structure, a three-peaked structure is seen in the density of states of $\text{Li}_{1/2}\text{TiO}_2$; and a narrowing of the valence band occurs due to the Li-induced volume expansion, which causes a decrease of the valence band width by ~ 1 eV. An immediate consequence of this narrowing is a widening of the bandgap by ~ 0.6 eV.

Based on these results, we propose the following model for Li adsorption. At 130 K Li species adsorb above the rutile (110) surface, presumably on top or close to the oxygen bridges.^{35,36} Initially there is ionic adsorption whereas at larger exposures the adsorbed Li species are partially neutral in order to minimize their mutual repulsion. Above 160 K the Li species disappear from the surface. Excluding desorption into the vacuum, they most likely become, as proposed by Stashans *et al.*,¹⁹ inserted into the (110) surface between two bridging oxygen atoms. The model of Li insertion into the (110) surface is supported by two observations: the presence of a small Li(2s)-related peak in MIES above 160 K (Figs 3 and 4(b)) indicates the presence of a considerable amount of Li in the surface (note that the Li(2s) signal becomes visible in

the case of Li adsorption at 130 K for coverages of ~ 0.3 MLE); and the observed spectral features of the surface observed by MIES are in agreement with theoretical predictions. As a comparison of Fig. 1 and Fig. 3 shows, the Li insertion at room temperature leads to a valence band contraction of ~ 1 eV. This is consistent with the prediction that Li intercalation into rutile leads to valence band narrowing caused by the Li-induced volume expansion.

However, insertion into the surface alone cannot explain all of our experimental observations. By the proposed model only ~ 0.5 MLE Li can be inserted. However, in Fig. 4 we start from a nominal coverage of ~ 1.4 MLE. Consequently, insertion between the bridging oxygen is not the only active channel. This observation is strong evidence that part of the adsorbed Li atoms reach regions underneath the surface due to diffusion.

SUMMARY

Electron spectroscopy results for the interaction of Li with $\text{TiO}_2(110)$ are presented for the first time. Measurements were performed at 130 K and at 300 K and compared with those on tungsten. The present investigation is focused on two subjects: the change from ionic adsorption leading to a reduction of Ti^{4+} to neutral adsorption as a function of coverage; and the insertion and/or intercalation of Li at higher temperatures.

At 130 K Li is adsorbed ionically up to a coverage of 0.3 MLE onto the titania surface. Ionic adsorption leads to a reduction of Ti cations to Ti^{3+} , as manifested by the appearance of a bandgap state at $E_B = 1$ eV. For coverages above 0.3 MLE the transfer of the s-electron to the substrate is not complete anymore, and becomes increasingly less likely with increasing coverage. This leads to the following consequences: a strong signal occurs in the MIES spectra close to E_F due to Auger de-excitation involving the Li(2s) electron; and the surface dipole induced by the alkali adsorption becomes smaller as a consequence of the interaction between neighbouring surface dipoles, explaining the saturation of the work function. From analysis of the UPS Ti^{3+} 3d signal, as well as from the Li(2s) emission, we have concluded that the degree of ionicity of the adsorbed Li decreases from Li^+ at 0.3 MLE to $\text{Li}^{0.4+}$ at 0.7 MLE.

At 300 K, the initial (low coverage) adsorption state is similar to that at 130 K. However, for coverages above 0.5 MLE the adsorption differs significantly from that at 130 K. Upon annealing, the Li(2s) signal in MIES disappears at ~ 160 K for Li/ $\text{TiO}_2(110)$, whereas it persists up to 400 K on W(110). We conclude that above 160 K Li becomes inserted into the rutile (110) surface. Part of the Li most likely migrates underneath the rutile $\text{TiO}_2(110)$ surface.

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REFERENCES

1. Henrich VE, Cox PA. *The Surface Science of Metal Oxides*. Cambridge University Press: Cambridge, 1994.

2. Campbell CT. *Surf. Sci. Rep.* 1997; **27**: 1.
3. Diebold U. *Surf. Sci. Rep.* 2003; **48**: 53.
4. Onishi H, Aruga T, Egawa C, Iwasawa Y. *Surf. Sci.* 1988; **199**: 54.
5. Nerlov J, Christensen SV, Weichel S, Pedersen EH, Moller PJ. *Surf. Sci.* 1997; **371**: 321.
6. Heise R, Courths R. *Surf. Rev. Lett.* 1995; **2**: 147.
7. Heise R, Courths R. *Surf. Sci.* 1995; **331–333**: 1460.
8. Grant AW, Campbell CT. *Phys. Rev. B* 1997; **55**: 1844.
9. Souda R, Hayami W, Aizawa T, Ishizawa Y. *Surf. Sci.* 1993; **285**: 265.
10. Thomas AG, Hardman PJ, Muryn CA, Dharival HS, Prime AF, Thornton G, Roman E, de Segovia JL. *J. Chem. Soc. Faraday Trans.* 1995; **91**: 3569.
11. Brause M, Skordas S, Kempter V. *Surf. Sci.* 2000; **445**: 224.
12. Brause M, Kempter V. *Surf. Sci.* 2001; **476**: 78.
13. Zhang Z, Henrich VE. *Surf. Sci.* 1992; **277**: 263.
14. Andersen JET, Moller PJ. *Phys. Rev. B* 1991; **44**: 13 645.
15. Ochs D, Braun B, Maus-Friedrichs W, Kempter V. *Surf. Sci.* 1998; **417**: 390.
16. van de Krol R, Goossens A, Meulenkamp EA. *J. Electrochem. Soc.* 1999; **146**: 3150.
17. Koudriachova MV, Harrison NM, de Leeuw SW. *Phys. Rev. B* 2002; **65**: 235 423.
18. Koudriachova MV, Harrison NM, de Leeuw SW. *Phys. Rev. Lett.* 2001; **86**: 1275.
19. Stashans A, Lunell S, Berström R, Hagfeld A, Lindquist SE. *Phys. Rev. B* 1996; **53**: 159.
20. Stracke P, Krischok S, Kempter V. *Surf. Sci.* 2001; **473**: 86.
21. Krischok S. *Dissertation*, Clausthal University, Clausthal, Germany, 2001; Krischok S. Wechselwirkung zwischen TiO₂-Oberflächen und verschiedenen Adsorbatatomen und -molekülen (am Beispiel von Alkaliatomen, CO₂, H₂O, O₂ u.a. sowie anderen Kombination), dissertation.de - Verlag im Internet GmbH, Berlin, Germany, 2002.
22. Krischok S, Höfft O, Günster J, Stultz J, Goodman DW, Kempter V. *Surf. Sci.* 2001; **495**: 8.
23. Harada Y, Masuda S, Ozaki H. *Chem. Rev.* 1997; **97**: 1897.
24. Morgner H. *Adv. At. Mol. Opt. Phys.* 2000; **42**: 387.
25. Medvedev VK, Smereka TP. *Sov. Phys. Solid. State* 1974; **16**: 1046.
26. Loburets AT, Naumovets AG, Vedula YS. *Surf. Sci.* 1982; **120**: 347.
27. Guo Q, Oh WS, Goodman DW. *Surf. Sci.* 1999; **437**: 49.
28. Kurahashi M, Yamauchi Y. *Mater. Res. Soc. Symp. Proc.* 1998; **501**: 67.
29. Maus-Friedrichs W, Frerichs M, Gunhold A, Krischok S, Kempter V, Bihlmayer G. *Surf. Sci.* 2002; **515**: 499.
30. Ertl G, Küppers J. Low Energy Electrons and Surface Chemistry, in Ebel HF (ed.), *Monogr. Mod. in Chem.* Vol. 42nd edition, VCH, Weinheim, 1985.
31. Maus-Friedrichs W, Dieckhoff S, Wehrhahn M, Pülm S, Kempter V. *Surf. Sci.* 1992; **271**: 113.
32. Hermann K, Freihube K, Greber T, Böttcher A, Grobecker R, Fick D, Ertl G. *Surf. Sci.* 1994; **313**: L806.
33. Johnson OW. *Phys. Rev. A* 1964; **136**: 284.
34. Lützenkirchen-Hecht D, Wagemaker M, Keil P, van Well AA, Frahm R. *Surf. Sci.* 2003; **538**: 10.
35. Bredow T, Apra E, Catti M, Pacchioni G. *Surf. Sci.* 1998; **418**: 150.
36. San Miguel MA, Calzado CJ, Sanz JF. *J. Phys. Chem. B* 2001; **105**: 1794.