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Hydrogen adsorption on metal oxide surfaces: a reinvestigation using He-atom scattering

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Abstract

In this paper we will present recent results obtained for hydrogen adsorbed on metal oxide surfaces using helium-atom scattering (HAS). The hydrogen adlayers were prepared by exposing clean and well defined metal oxide surfaces to either molecular or atomic hydrogen. The HAS measurements were complemented by LEED and x-ray photoelectron spectroscopy. The results reveal the formation of ordered H(1×1) overlayers on rutile TiO₂(110), the polar Zn–ZnO surface and ZnO(10 $\bar{1}$ 0). On Al₂O₃(11 $\bar{2}$ 0) exposure to atomic hydrogen did not lead to the formation of an ordered hydrogen adlayer, whereas on the polar O–ZnO surface the hydrogen lifted the (1×3) reconstruction seen for the clean surface.

1. Introduction

When considering metal oxide surfaces one of the first questions to address is whether hydroxyl groups are present. Because of the strength of the OH bond even small amounts of water or hydrogen molecules can give rise to hydroxyl species and severely affect the chemical and physical properties of the metal oxide surface. In principle IR spectroscopy is the method of choice to detect such hydroxyl species and this technique has been successfully used for fairly comprehensive, detailed studies on the interaction of water and hydrogen with metal oxide powders such as ZnO, MgO and Al₂O₃ [1, 2]. Due to experimental problems, however, IR spectroscopy has not yet been used for systematic studies on hydrogen present on surfaces of single-crystalline metal oxide substrates. This is an unfortunate situation, since from related studies on metal surfaces (for a review see [3]) it is known that the adsorption of hydrogen can cause a variety of effects, ranging from the formation of a (1×1) adlayer on an otherwise unaffected substrate to a hydrogen-induced reconstruction of the metal substrate as in the case of Ni(110) [4, 5]. In addition, for a number of systems rather complicated overlayers are observed, which are interesting in themselves. The presence of hydrogen atoms can also have pronounced effects on the chemical activity of metal oxide surfaces and recently it has been proposed on theoretical grounds that e.g. the O-terminated Al₂O₃(111) surface is stable only

if the H atoms are present [6]. There are a number of chemical processes in heterogeneous catalysis where hydrogenation steps play a key role. An example is the synthesis of methanol from syngas (a mixture of CO, CO₂ and H₂), where the rate-limiting step is believed to be the addition of an H atom to a carboxylate species bound to a ZnO surface [7]. Also the growth of metals on metal oxide surfaces, a field of significant technological relevance, can be strongly affected by the presence of hydroxyl species (see e.g. [8]) since OH species will generally modify the wettability of the surface by the metal atom.

Scattering of thermal energy He atoms is particularly useful with regard to an investigation of hydrogen atoms adsorbed on a surface, since the cross-section of H atoms adsorbed on an otherwise perfect substrate is fairly large ($\sim 10 \text{ \AA}^2$, [9, 10]). In this context it should be noted that the standard method used for the determination of adlayer structures, low energy electron diffraction, or LEED, is not well suited to detect hydrogen overlayers on solid substrates due to the very small cross-section of hydrogen atoms for electrons.

The first demonstration of the strength of He-atom scattering with regard to an investigation of hydrogen layers adsorbed on solid substrates has been given by Rieder, who was able to detect several different ordered hydrogen adlayers on Ni(110) which in previous works using other techniques could not be seen [4]. In the past two decades He-atom scattering (HAS) has been applied to study hydrogen adlayers on a number of different metal surfaces (see e.g. [5, 11, 12]), semiconductors (Si(111) [13]) and insulators (diamond C(111) [12]). Applications to metal oxide surfaces have been rather scarce, although HAS has been used previously to investigate metal oxide surfaces; see [14–16] and [17] for studies on clean MgO, NiO and CoO. In the following we will present results obtained by He-atom scattering for hydrogen adsorbed on three different metal oxides, Al₂O₃, rutile TiO₂ and ZnO.

2. Experimental procedures

The measurements have been conducted using a molecular beam system described in detail elsewhere [18]. Briefly, a differentially pumped supersonic molecular beam source is attached to a scattering chamber and to a drift tube. At the end of the drift tube a magnetic mass spectrometer for the detection of the scattered He atoms is mounted. Whereas the total scattering angle (sum of incident and exit angles) is fixed, the angle of incidence, α_i , can be changed by rotating the sample around an axis normal to the scattering plane. The scattering chamber contains a second mass spectrometer LEED, and a differentially pumped sputter gun. The ZnO substrates used in this study (obtained from MaTeck crystals) have been cleaned by a procedure consisting of cycles of Ar⁺ sputtering (0.8 keV, $\sim 1 \mu\text{A}$, $T_s = 650 \text{ K}$) followed by annealing in oxygen ($1 \times 10^{-6} \text{ Torr}$, $T_s \sim 850 \text{ K}$, 2 min) and in UHV ($T_s = 850 \text{ K}$, 5 min), as described in previous publications (see [19]). After a few preparation cycles a pronounced LEED pattern and a distinct specular He peak revealed the presence of a structurally well defined surface. The aluminium oxide surfaces were prepared following the preparation procedures established in previous studies [20–22]. The samples were first cleaned by repeated cycles of Ar⁺ sputtering (1 keV) at elevated temperatures (800 K) followed by annealing to temperatures of 1150 K for 10 min. After this procedure highly ordered sapphire surfaces were obtained as evidenced by well defined (1×1) LEED and He-atom diffraction patterns. Investigations of this surface with XPS did not reveal the presence of any contamination above the XPS detection limit. For the TiO₂ surfaces a preparation procedure identical to that used for zinc oxide (see above) was employed. The gases used in this study are of research purity (99.9999% for He and 99.99% for CO from Messer Griesheim). Additionally, LN₂ traps are mounted in the hydrogen and He gas lines, respectively, in order to avoid a contamination of the

samples with H₂O. Exposure of the sample to atomic hydrogen was carried out by backfilling the scattering chamber (typically 1×10^{-6} mbar) through a leak valve and by dissociating H₂ on a hot tungsten filament which was placed in line-of-sight (distance 3 cm) from the substrate surface. The crystal could be cooled down to a substrate temperature, T_s , of approximately 50 K by means of liquid helium. The reading of the thermocouple, which was tightly clamped against the side of the substrate, has been calibrated by thermal desorption measurements (heating rate of 1 K s^{-1}) of n-butane multilayers (desorption temperature $T_D = 111 \text{ K}$) (see e.g. [23]).

3. Results

3.1. Aluminium oxide

Alumina, or sapphire (α -Al₂O₃), is used in a number of technical applications, in particular as substrate for heteroepitaxy and in heterogeneous catalysis, where alumina constitutes a widely used support for catalysts. Previous studies have shown that very smooth, atomically flat sapphire surfaces can be obtained by polishing and subsequent annealing in air at temperatures between 1000 and 1400 °C [20]. In several investigations a stable fourfold reconstruction along the [0001] direction was found [24, 25] after annealing the surface above 1400 °C, whereas sputtering and annealing to temperatures below 800 °C resulted in the formation of a (1×1) -structure [26]. The He-atom angular distributions reproduced in figure 1 essentially confirmed these previous findings and allowed us to propose a detailed model for the (12×4) reconstruction of this surface [27].

In order to investigate the reactivity of this surface to hydrogen the substrate was first exposed to molecular hydrogen. Helium-atom angular distributions recorded for the clean surface show a large number of diffraction peaks resulting from the rather large unit cell of the (12×4) reconstruction of this surface; see figure 1, top. The He-atom angular distribution recorded after exposing this surface to molecular hydrogen was virtually identical to that recorded for the clean surface. Since it is known from many other systems that the adsorption of hydrogen may be hampered by the fairly large energy required to dissociate the H₂ molecule, in a further set of experiments the surface was exposed to atomic hydrogen. The exposure to atomic hydrogen was carried out by placing a hot filament at a distance of about 5 cm from the sample after backfilling the UHV chamber with H₂ at a pressure of 1×10^{-6} mbar. For these experiments the sample was kept at room temperature. During exposure the intensity of the helium-atom specular peak was recorded; no variation for exposure times as large as 1000 s could be observed. Helium-atom angular distributions recorded after the exposure to atomic hydrogen (figure 1, bottom) were again indistinguishable from that recorded for the clean surface (figure 1, top). Both surfaces, the metastable low temperature (1×1) phase and the stable (12×4) phase obtained after annealing, yielded the same results. This is a surprising finding and, at first sight, appears to indicate that hydrogen atoms do not interact with the Al₂O₃ surface. This behaviour is in pronounced contrast to that seen for hydrogen atoms interacting with other semiconductor or insulator surfaces such as diamond C(111), the different types of ZnO surface (see discussion below) and Si(111). It is also known from infrared studies carried out for Al₂O₃ powders [2] and from theoretical calculations [6, 28] that OH species are also rather stable on the surface of Al₂O₃ particles.

We see two explanations to rationalize this unexpected absence of any structural changes on the alumina surface upon exposure to atomic hydrogen. The first would be that the surface is already terminated by hydrogen resulting from a high reactivity of the clean sapphire surface towards either molecular hydrogen or water, which are always present in the residual gas of

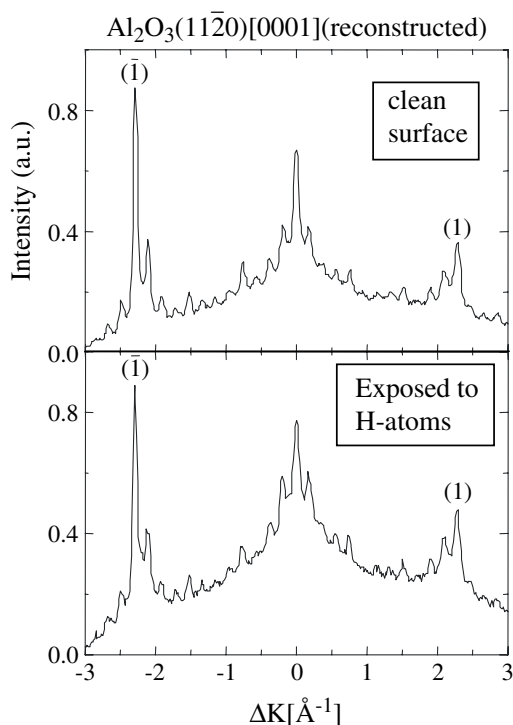


Figure 1. Top: He-atom angular distributions recorded along the [0001] azimuth of the reconstructed Al₂O₃(11 $\bar{2}$ 0) surface obtained after annealing to 1200 K. Bottom: the same surface exposed to atomic hydrogen. No significant changes are seen compared to the data for the clean substrate (top). The data are taken from [27].

the vacuum system. Note that a similar situation has recently been encountered for the (1×3) reconstructed oxygen-terminated polar surface of ZnO [29, 30]. In this case the reactivity of the O–ZnO surface towards molecular water was found [31] to be so large that it was very difficult to maintain a hydrogen free surface. We feel, however, that we can safely rule out this explanation for the Al₂O₃(11 $\bar{2}$ 0) surface since angular distributions recorded directly after annealing to 1200 K, a temperature for which previous work on the similar Al₂O₃ surface has revealed a substantial loss of hydrogen atoms [32], did not reveal significant differences.

The only possibility left open to explain the absence of surface structural changes when exposing the Al₂O₃(11 $\bar{2}$ 0) surface to atomic hydrogen is that hydrogen atoms adsorbed on the surface (most likely forming OH species) quickly react with subsequently impinging H atoms to form water molecules which then desorb from the surface. This situation would correspond to a hydrogen etching of the surface. Since this etching will preferentially occur at defect sites the change in reflectivity for the helium atoms will be small and also the helium-atom angular distribution will not be modified. A similar behaviour has been seen recently for a vanadium pentoxide (V₂O₅) surface exposed to atomic hydrogen. Also in this case no OH vibrations could be seen in EELS after exposing the surface to atomic hydrogen, indicating that under the experimental conditions OH species do not exist on the surface. Also in this case it has been proposed that continued exposure to hydrogen atoms leads to the formation of H₂O which desorbs from the surface [33].

In a future set of experiments we plan to expose the surface to hydrogen for even longer amounts of time. Since the hydrogen etching leads to a oxygen depletion of the surface, eventually the exposure to atomic hydrogen should result in structural changes of the surface. In a second set of experiments we plan to hydroxylate the surface using other, possibly *ex situ*, procedures. In the case of diamond surfaces it has been shown that well defined He-atom diffraction peaks could be observed for hydrogen-passivated diamond surfaces prepared *ex situ* by mechanically polishing with olive oil, which were only briefly annealed at 300 °C after transfer in the UHV system [12, 34]. The He-atom angular distributions recorded for the hydrogen-terminated diamond C(111) surface using this procedure was identical to those obtained for a hydrogen-terminated surface prepared by exposing the clean diamond surface to atomic hydrogen [12]. We expect that a similar procedure will also work in the case of sapphire.

3.2. TiO_2

Among all metal oxide surfaces, the rutile $TiO_2(110)$ surface is probably the one which has so far received the most attention. Basically all techniques available in surface science have been applied to this surface; a comprehensive review of the results is provided in the review article of Diebold [35]. The structure of the clean surface has been investigated in great detail and a general agreement has been achieved that different reconstructions exists on the surface. In addition to the different reconstructed surfaces a thermodynamically stable well defined (1×1) surface exists which can be prepared by appropriate annealing procedures. Although many studies have been reported on the structure and reactivity of titania surfaces, the question about the presence of hydrogen atoms on this titania surface has only rarely been addressed. Very recently, a few STM studies have appeared where protrusions seen in the STM micrographs were assigned to OH species. No lateral order for the adsorbed hydrogen atoms has been observed in the STM work [36]. Recent *ab initio* electronic structure calculations by Leconte *et al* have shown that OH species should be stable on the surface; on the basis of their results exposure to atomic hydrogen should also lead to the formation of TiH species [37]. It is a remarkable fact that it is unknown from an experimental point of view whether H atoms form an ordered overlayer on this prototype metal oxide surface.

In figure 2 we show a series of He-atom scattering angular distributions which were recorded along the [001] and $[1\bar{1}0]$ azimuthal directions of the rutile $TiO_2(110)$ surface. The angular distributions shown in the lower left and lower right have been recorded for the clean surface and reveal the presence of a high quality, clean rutile $TiO_2(110)$ surface; the HAS data are then fully consistent with previous results obtained by LEED and STM for this unreconstructed surface [35]. LEED data (not shown) recorded directly after the He-atom angular scans were indistinguishable from those reported in the literature [38]. Upon exposure to atomic hydrogen the relative intensities of the He-atom diffraction peaks strongly changed. This adsorption-induced change in the surface corrugation is most obvious along the [001] direction. For neither of the two azimuths are new diffraction peaks observed, revealing that the adsorption of hydrogen leads to the formation of a highly ordered hydrogen (1×1) overlayer. The widths of the diffraction peaks are essentially identical to those of the bare substrate, indicating that the average coherence length of the surface is not affected by the formation of the hydrogen adlayer. LEED patterns which were recorded simultaneously did not reveal any changes upon hydrogen adsorption. This observation demonstrates once more the very high sensitivity of helium atoms with regard to monitoring hydrogen adsorption on surfaces.

At present we are unable to answer the question of whether the unit cell of the (1×1) hydrogen adlayer contains one or two hydrogen atoms. One hydrogen atom would correspond

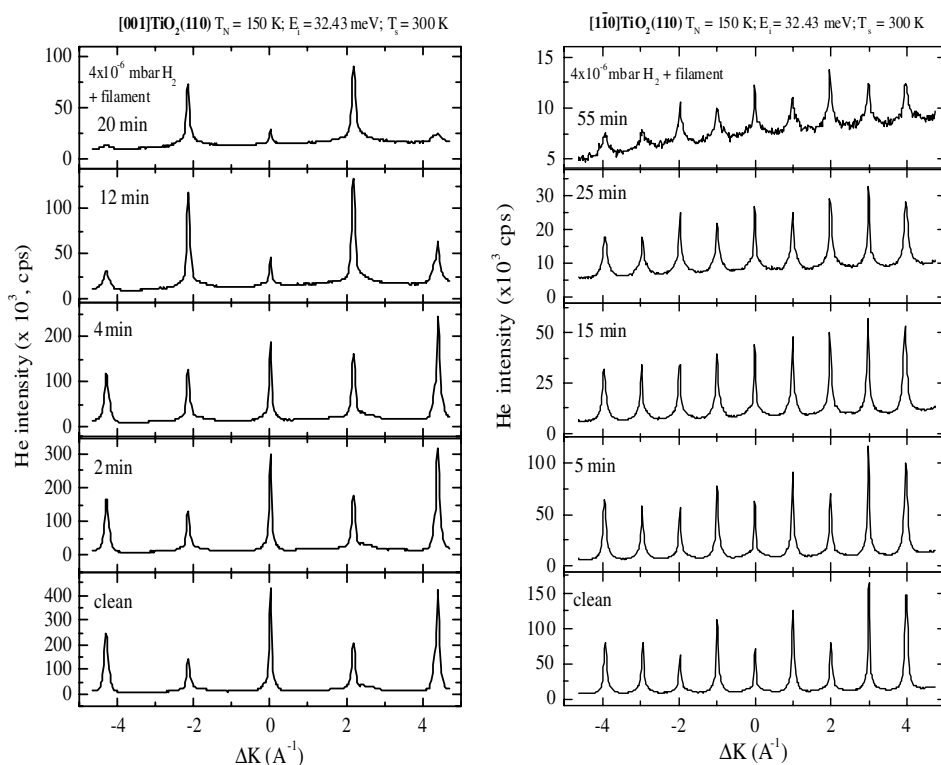


Figure 2. He-atom angular distributions recorded along the [001] (left) and the $[1\bar{1}0]$ (right) azimuth of the rutile $\text{TiO}_2(110)$ surface. The distributions shown at the bottom have been recorded for the clean surface. The angular distributions reproduced above were recorded for the surface exposed to increasing amounts of hydrogen atoms. Data are taken from [30].

to the presence of a hydroxyl species only whereas two hydrogen atoms would imply the existence of TiH species too, as suggested by recent theoretical calculations [37]. Preliminary results obtained from adsorption of carbon monoxide on the clean and hydroxylated surfaces were not consistent. At present we prefer a structural model where, at room temperature, the unit cell of the H-saturated $\text{TiO}_2(110)$ surface contains two hydrogen atoms as suggested in the previous theoretical calculations [37].

This present finding on the formation of an ordered (1×1) H-atom overlayer on the rutile $\text{TiO}_2(110)$ surface is, however, at variance with the results of recent STM work [36]. In the work by Suzuki *et al* the rutile $\text{Ti}(110)$ surface was also exposed to atomic hydrogen using basically the same experimental approach as that employed in this work, i.e. a hot filament placed in line-of-sight of the crystal surface. In the STM work it was reported that exposure to hydrogen leads to the formation of small, atom-sized protrusions on the surface with a maximum coverage corresponding to a quarter of a monolayer. An ordered $\text{H}(1 \times 1)$ structure corresponding to that seen in the helium atom diffraction could not be observed.

The only explanation we can currently offer for resolving this inconsistency is that the hydrogen atoms adsorbed on the surface are actually not seen in the STM micrographs, and that the small protrusions appearing in the STM work may correspond to surface defects generated by the impinging hydrogen atoms, e.g. by hydrogen etching. More experimental and theoretical work will be required to resolve this inconsistency.

3.3. ZnO

Also in the case of ZnO only a few studies on the interaction of hydrogen with single-crystal surfaces have been reported so far, namely on the non-polar ZnO(10 $\bar{1}$ 0) [39, 40] and polar ZnO [24, 40] surfaces. The interaction of hydrogen with ZnO powders, on the other hand, has been studied in considerably more detail [25, 41–44], and the experimental results obtained for ZnO surfaces have been reviewed by Campbell [45]. In previous work using LEED no changes in the structure of the clean surface were observed upon exposure to atomic hydrogen [40].

We will start the presentation of our new results by first focusing on the two polar surfaces of zinc oxide. When considering this particular type of ionic surface, one has to realize that on polar surfaces electrostatic interactions can cause surface instabilities and reconstructions. When the projection of the electric dipole moment of the (bulk) unit cell on the surface normal has a nonvanishing component, the corresponding surface can be shown to be unstable (i.e. the Madelung sum diverges). For most metal oxides this prediction (Tasker's rule) [46] is fulfilled and the clean surfaces exhibit strong reconstructions, but in the case of ZnO previous research has failed to clearly identify such instabilities for the two polar surfaces, ZnO(0001) and ZnO(000 $\bar{1}$). Instead, a general agreement has emerged in that the polar ZnO surfaces exhibit a (1 \times 1) unreconstructed top layer. The reason for this apparent violation of Tasker's rule is as yet not fully understood, but already in very early work it had been proposed [47] that the polar surfaces may be stabilized by a charge transfer from the O-terminated side to the Zn-terminated side. Theoretical studies employing density functional methods (DFT) support this hypothesis [48, 49] but more recent studies suggest that the models used in these previous calculations may have been too simplified [38, 50].

We will start the presentation of the He-atom scattering results by first considering ZnO(0001) (also denoted by Zn–ZnO). Although also this surface should not be stable according to Tasker's rule, generally (1 \times 1) diffraction patterns are observed in LEED. The stability of the clean Zn–ZnO surface has recently been explained by the formation of triangular-shaped terraces, where the step-edges are O terminated [38]. The helium-atom angular distributions shown in figure 3 reveal the presence of a well defined (1 \times 1) diffraction pattern and are fully consistent with this structural model. When exposing the Zn–ZnO surface to either molecular or atomic hydrogen, the angular distributions show characteristic changes as shown in figure 3. Here the angular distribution displayed at the top corresponds to the clean surface whereas those shown below have been recorded for increasing exposure times to molecular hydrogen. As in the case of TiO₂ only the relative intensities of the diffraction peaks are modified, and no new diffraction peaks are observed. The data shown in figure 3 have been recorded along the [100] direction. The data recorded along the [120] direction (not shown) are fully consistent with these results; also along this other high symmetry direction no new diffraction peaks are observed. As for the [100] direction, only the relative intensities of first and higher order (1 \times 1) diffraction peaks change upon exposure to hydrogen.

These observations clearly demonstrate that exposure to atomic or molecular hydrogen leads to the formation of a well ordered H-(1 \times 1) overlayer on the Zn–ZnO polar surface. LEED data recorded simultaneously showed no change between the clean and the hydrogen-exposed surface, again highlighting the low sensitivity of low energy electron diffraction towards hydrogen atoms adsorbed on the surface. Interestingly, these results also reveal that prolonged exposure to hydrogen (on the order of 10⁻⁴ L of molecular hydrogen at room temperature) leads to a strong disorder in the surface plane as can be seen in the angular distributions shown in figure 4.

Even when for the hydrogen-covered Zn–ZnO surface no diffraction peaks could be seen any longer (lowest figure in figure 4) we were still able to record fairly well defined LEED

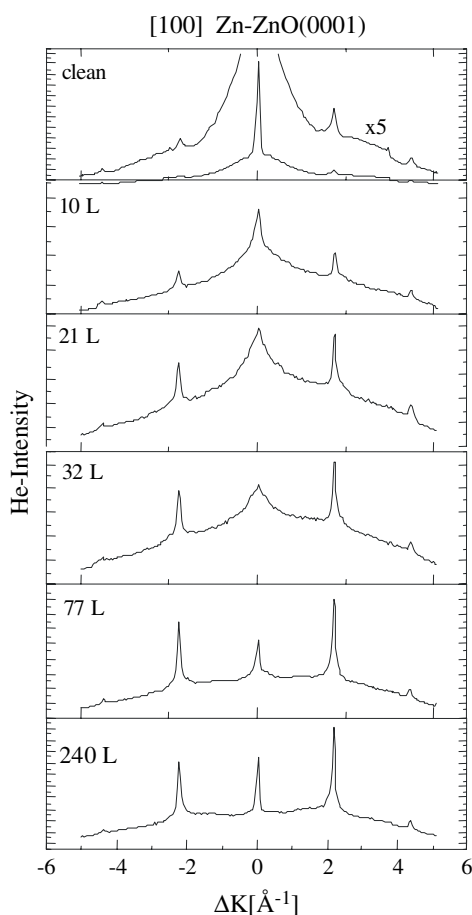


Figure 3. He-atom angular distributions recorded along the [100] azimuth of the polar Zn-ZnO surface. The data shown at the top were recorded for the clean surface. The data shown at the bottom were measured after increasing exposures to H atoms.

patterns from the surface, only the background was found to be slightly increased. This observation is related to the fact that the helium atoms are strictly surface sensitive whereas the low energy electrons used in LEED penetrate the first few layers. This consideration shows that in the case of a disordered, defective overlayer on top of essentially undistorted deeper layers it is still possible to observe a LEED pattern but no HAS diffraction pattern. In the present case the LEED and HAS data together reveal that the hydrogen-induced restructuring of the surface must be limited to the very top layer.

We have also employed the rather large cross-section of adsorbed H atoms in HAS (about 10 \AA^2) to determine the sticking coefficient governing the adsorption of hydrogen on the Zn-ZnO surface [51, 52]. For molecular hydrogen, the sticking coefficient is found to be on the order of 1×10^{-7} for Zn-ZnO surfaces for very low defect concentrations [51]. When on such a surface atomic hydrogen is adsorbed and subsequently desorbed by heating above the desorption temperature the sticking coefficient of molecular hydrogen is found to be significantly increased to about 1×10^{-3} . This unexpected increase of the sticking coefficient of H_2 to a fairly large value, which is actually comparable to

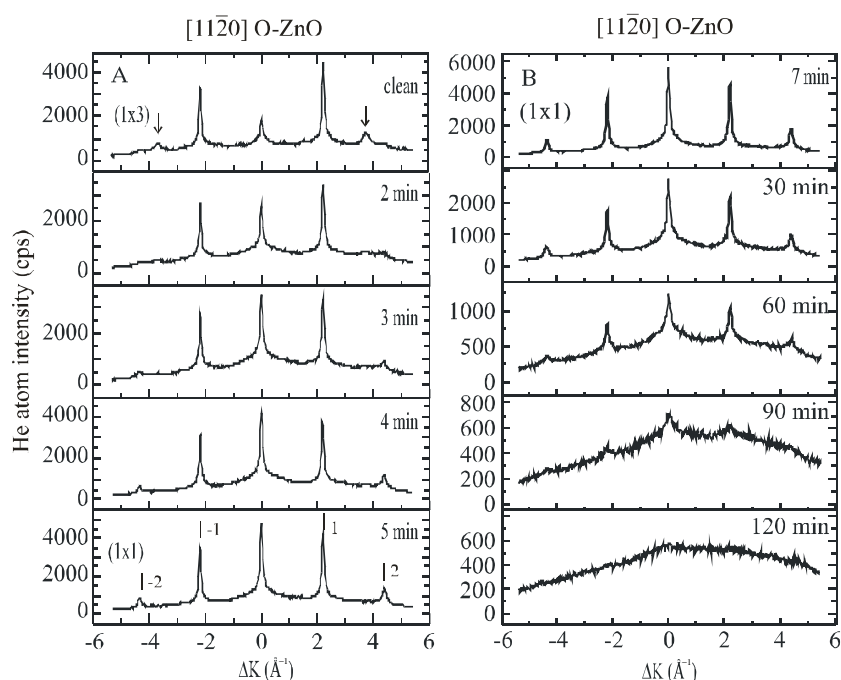


Figure 4. Set of He-atom angular distributions recorded along the $[11\bar{2}0]$ azimuth of O-ZnO for different exposures of atomic hydrogen. The data shown at the top were recorded for the clean surface. The angular distributions shown below have been recorded for increasing amounts of exposure to hydrogen atoms. Short vertical lines denote the positions of integral order diffraction peaks. The extra diffraction spots seen for the (1×3) reconstructed surface are marked by an arrow (top left). Data are taken from [29].

that seen for molecular hydrogen on Cu, is related to a hydrogen-induced restructuring of the surface, i.e. the generation of surface defects by hydrogen etching (see discussion above).

The binding energy of CO on the Zn-ZnO surface was determined by monitoring the reflectivity of the ZnO surface for He atoms as a function of temperature. Excellent agreement was found between the experimental binding energies and the results of precise, *ab initio* electronic structure calculations [50]. Briefly, it is noted that CO weakly chemisorbs on the Zn-ZnO surface, but only physisorbs on the $H(1 \times 1)$ Zn-ZnO substrate [50, 53].

A rather different picture on the interaction with hydrogen emerges from the HAS data recorded for the oxygen-terminated polar surface of zinc oxide, $ZnO(000\bar{1})$, also referred to as O-ZnO. In a first set of experiments the O-ZnO surfaces were prepared using the conventional procedure which consists of sputtering and annealing cycles followed by a slow cooling down to room temperature. About 30 min after the last annealing of the sample (the base pressure in our UHV chamber amounts to about 1×10^{-10} mbar) a well defined (1×1) diffraction pattern was observed, in full agreement with previous structural studies reported for this surface. Unexpectedly, the diffraction pattern did not show any changes when this surface was exposed to atomic or molecular hydrogen. At first sight this situation is similar to the one observed for the $Al_2O_3(11\bar{2}0)$ surface discussed above, where it was concluded that exposure to hydrogen does lead to an H-induced etching of the surface with no or only a small number of OH species present on the surface.

More detailed investigations, however, revealed that if the O–ZnO surface is cooled down very quickly after the last annealing process while maintaining a very low pressure in the UHV chamber ($<2 \times 10^{-10}$ mbar) a rather different HAS diffraction pattern is observed which is reproduced in figure 4. This diffraction pattern exhibits strongly different relative intensities of the diffraction peaks at the first order positions and, most notably, the presence of $1/3$ order diffraction peaks, indicating the presence of a (1×3) reconstruction. LEED investigations carried out for the same surface also show this (1×3) reconstruction which has not been reported before for this O–ZnO surface. When exposing the reconstructed (1×3) O–ZnO surface to atomic hydrogen or molecular water the HAS diffraction pattern is observed to quickly change to that observed for surfaces which were allowed to cool down slowly. XPS data which have also been recorded for the ZnO surface *in situ* (i.e. directly before and after the HAS distributions were recorded) reveal that for the clean (1×3) reconstructed surface a fairly symmetric XPS O 1s line can be observed. After exposure to hydrogen or to water a significant shoulder is detected at the high energy side of the O 1s line which can be unambiguously assigned to OH species formed on the O–ZnO surface.

Combining the experimental information gained from these experiments the following picture on the interaction of hydrogen with this particular metal oxide surfaces emerges. The clean O–ZnO surface is—as predicted by Tasker's rule—instable; the restructuring leads to a (1×3) reconstruction. When this surface is exposed to either atomic hydrogen or to water, the surface is stabilized by hydroxylation and the reconstruction is lifted, leading to a well defined, stable and rather inert (with regard to reaction with gas phase species) $H(1 \times 1)$ O–ZnO surface. From symmetry considerations all surface O atoms must be hydroxylated. This hydrogen (1×1) overlayer exhibits a characteristic HAS diffraction pattern which is shown in figure 4, bottom.

We explain the fact that the reconstruction of the O–ZnO surface has not been observed in previous LEED work by the very large reactivity of this surface towards molecular water. In a separate set of experiments [30] the interaction of water with a clean (1×3) O–ZnO surface has been studied. By using a molecular beam consisting of H_2 seeded in helium the sticking coefficient of water on the surface could be determined using the King and Wells methods. Surprisingly, even at surface temperatures as low as 200 K, the sticking coefficient amounts to 0.8 [31].

This is a very large sticking coefficient considering that we are dealing with dissociative adsorption for temperatures as low as 200 K, and the most likely explanation for this observation is that the (1×3) reconstruction actually consists of an ordered array of O vacancies, with one O atom missing in the (1×3) unit cell [29]. Such O vacancies are known to be very reactive and could well explain the pronounced reactivity of the surface.

Water molecules will interact fairly strongly with the oxygen vacancies forming the (1×3) surface and we expect the activation barrier for dissociation to be relatively low. Such a dissociation event will lead to an OH species filling the vacancy and supply on additional hydrogen atom which is adsorbed on a neighbouring oxygen atom, eventually leading to the formation of a $H(1 \times 1)$ phase.

Also in this case we have used the adsorption of a probe molecule, CO, to corroborate the experimental findings of clean and hydrogen-terminated O–ZnO surfaces. In a recent study a variety of different theoretical methods have been used to determine the binding energy of CO adsorbed on a hypothetical, ideally terminated (1×1) O–ZnO substrate [50, 53, 54]. In all cases the CO was found to only very weakly physisorb, in contrast to the experimental finding reported in the past by other groups in that CO chemisorbs on the O–ZnO surface. The weak binding of CO on a ideally terminated (1×1) O–ZnO surface can be rationalized by considering that the O^{2-} ion basically is unable to form any kind of chemical bond to CO [54].

When in the theoretical calculations the CO was allowed to interact with the $H(1 \times 1)$ O–ZnO surface it was found that the small dipole of the O–H bond is sufficiently strong to polarize the CO molecule, resulting in a weak binding to the surface. The corresponding theoretical binding energies are in excellent agreement with the experimental data [50, 53, 54].

We would like to remark, however, that the situation for the polar O–ZnO surface cannot yet be considered as fully resolved. The clean (1×3) reconstructed O–ZnO surface appears to be converted to the same structure after adsorption of both atomic hydrogen and molecular water. The clean (1×3) reconstructed surface most likely consists of an ordered array of oxygen vacancies [51]. It is evident that this oxygen deficit surface cannot be converted to an ideal (1×1) structure by adding one water molecule per (1×3) unit cell. The dissociation of one H_2O molecule per unit cell will provide only two H atoms per unit cell; one hydrogen atom is missing with regard to the formation of a perfect $H(1 \times 1)$ O–ZnO surface. Despite these considerations, the experimental HAS diffraction patterns measured after exposure to atomic hydrogen and molecular water are indistinguishable. We explain this apparent inconsistency by a low activation barrier for hydrogen atom diffusion along this surface which has also been found for other metal oxides. We propose that after formation of the hydroxyl species the hydrogen atoms are sufficiently mobile to form large (1×1) islands on the surface which may still contain a significant number of defects.

Another disturbing point is that the most recent theoretical calculations are still unable to explain the experimentally observed (1×1) O–ZnO surface. Even when the thermodynamic equilibrium with oxygen and hydrogen is considered [55] large electrostatic instabilities are found to be present. Further experimental as well as theoretical studies will be needed to fully clarify the situation for the polar ZnO surface.

In order to obtain another reference system concerning the interaction of hydrogen with ZnO surfaces we have also investigated the interaction of hydrogen with the mixed terminated non-polar ZnO($10\bar{1}0$) surface. In contrast to the two polar surfaces (see the discussion of Tasker's rule above) this surface is electrostatically stable [56].

In agreement with previous studies the helium-atom diffraction scans reproduced in figure 5 demonstrate that the conventional preparation scheme yields a well defined (1×1) surface. XP spectra recorded for the clean ZnO($10\bar{1}0$) surface reveal a rather symmetric O 1s line similar to that measured for the clean (1×3) O–ZnO surface, indicating the presence of a clean, hydroxyl-free ZnO surface. As in the case of TiO_2 and Zn–ZnO exposure to hydrogen atoms leads to a characteristic change in the relative intensity of the diffraction peaks, but no new diffraction peaks are observed. As for the TiO_2 and the zinc-terminated oxide surface this observation clearly indicates the formation of a highly ordered hydrogen (1×1) overlayer on the surface. XP spectra recorded after H-atom adsorption again reveal a high energy shoulder of the O 1s line characteristic for the presence of hydroxyl species on the surface.

We are currently unable to answer the question of whether the exposure to atomic hydrogen leads to the formation of OH species only (one H atom per surface unit cell) or whether Zn–H species (two H atoms per surface unit cell) are also formed. Theoretical calculations are currently being carried out which will help to answer this open question.

4. Summary

The results reported here obtained by He-atom scattering applied to metal oxide surfaces demonstrate that HAS is well suited to monitor the adsorption of hydrogen on these surfaces and to characterize the structure of the hydroxylated surfaces. Because of the fairly large cross-section of hydrogen atoms in He-atom scattering, the adsorption and subsequent formation of

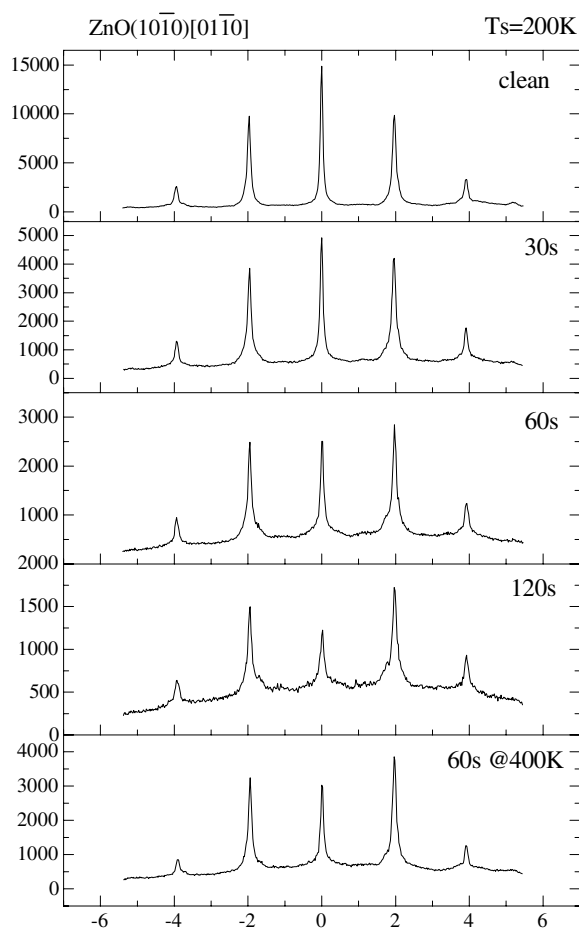


Figure 5. He-atom angular distributions recorded for the mixed-terminated ZnO($10\bar{1}0$) surface along the $[10\bar{1}0]$ azimuth for a surface temperature of 200 K. The data shown at the top were recorded for the clean surface, whereas the data shown in the lower part were measured after exposure to increasing amounts of hydrogen atoms. Prior to recording the angular distribution shown at the bottom the sample was annealed at 400 K for 60 s.

ordered hydrogen overlayers on these surfaces can be studied in a straightforward fashion. With other standard techniques for surface structure investigations such as LEED, the investigation of hydrogen overlayers on metal oxide surfaces has not yet been reported.

The results obtained for aluminium oxide, titania and zinc oxide demonstrate that the adsorption of hydrogen can lead to rather different structural changes of the metal oxide surfaces. Whereas on the Zn-terminated polar surface of zinc oxide and the mixed terminated ZnO surface and on rutile $\text{TiO}_2(110)$ the formation of an ordered (1×1) overlayer is observed, on aluminium oxide the formation of an ordered hydrogen overlayer could not be seen. Apparently, the sapphire surface is unstable with regard to hydrogen atoms and exposure to H atoms leads to etching of the surface. For the oxygen-terminated polar O-ZnO surface yet another scenario is observed: Here, the clean surface shows a (1×3) reconstruction which is removed when the surface is exposed to either water or hydrogen atoms. In both cases a hydrogen-terminated (1×1) surface is obtained.

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References

- [1] Griffin G L and Yates J T 1982 *J. Chem. Phys.* **77** 3744
- [2] Boehm H-P and Knoezinger H 1983 Nature and estimation of functional groups on solid surfaces *Catalysis. Science and Technology* ed J R Anderson and M Boudart (Berlin: Springer) p 39
- [3] Christmann K 1988 *Surf. Sci. Rep.* **9** 1
- [4] Rieder K H 1983 *Phys. Rev. B* **27** 7799
- [5] Rieder K H and Engel T 1979 *Phys. Rev. Lett.* **43** 373
- [6] Wang X G, Chaka A and Scheffler M 2000 *Phys. Rev. Lett.* **84** 3650
- [7] Askgaard T S, Norskov J K, Ovesen C V and Stoltze P 1995 *J. Catal.* **156** 229
- [8] Dulub O, Boatner L A and Diebold U 2002 *Surf. Sci.* **504** 271
- [9] Poelsema B, Ienz K, Bernasek S I, Verheij I K and Comsa G 1987 *Surf. Sci.* **189/190** 431
- [10] Poelsema B and Comsa G 1989 *Scattering of Thermal Energy Atoms from Disordered Surfaces (Springer Tracts in Modern Physics vol 115)* (Berlin: Springer)
- [11] Goerge J, Zeppenfeld P, David R, Büchel M and Comsa G 1993 *Surf. Sci.* **289** 201
- [12] Schaich T, Braun J, Toennies J P, Buck M and Wöll C 1997 *Surf. Sci.* **385** L958
- [13] Harten U, Toennies J P, Wöll C, Miglio L, Ruggerone P, Colombo L and Benedek G 1988 *Phys. Rev. B* **38** 3305
- [14] Brusdeylins G, Doak R B, Skofronick J G and Toennies J P 1983 *Surf. Sci.* **128** 191
- [15] Cantini P, Tatarek R and Felcher G P 1979 *Phys. Rev. B* **19** 1161
- [16] Rieder K H 1982 *Surf. Sci.* **118** 57
- [17] Witte G, Senet P and Toennies J P 1998 *Phys. Rev. B* **58** 13264
- [18] Hinch B J, Lock A, Madden H H, Toennies J P and Witte G 1990 *Phys. Rev. B* **42** 1547
- [19] Becker T, Kunat M, Boas C, Burghaus U and Wöll C 2000 *J. Chem. Phys.* **113** 6334
- [20] Yoshimoto M, Maeda T, Ohnishi T, Koinuma H, Ishiyama O, Sinohara M, Kubo M, Miura R and Miyamoto A 1995 *Appl. Phys. Lett.* **67** 2615
- [21] Beitel G, Markert K, Wiechers J, Hrbek J and Behm R J 1993 *Adsorption on Ordered Surfaces of Ionic Solids and Thin Films* vol 33, ed E Umbach and H-J Freund (Berlin: Springer)
- [22] Wölfling B, Theis-Bröhl K, Sutter C and Zabel H 1999 *J. Phys.: Condens. Matter* **11** 2669
- [23] Xu C, Koel B E and Paffett M T 1994 *Langmuir* **10** 166
- [24] Heiland G and Kunstmann P 1969 *Surf. Sci.* **13** 72
- [25] Watanabe M and Ito T 1980 *Japan. J. Appl. Phys.* **19** 1863
- [26] Chang C C 1971 *J. Vac. Sci. Technol.* **8** 500
- [27] Becker T, Birkner A, Witte G and Wöll C 2002 *Phys. Rev. B* **65** 115401
- [28] Tepesch P D and Quong A A 2000 *Phys. Status Solidi b* **217** 377
- [29] Kunat M, Gil-Girol S, Becker T, Burghaus U and Wöll C 2002 *Phys. Rev. B* **66** 081402(R)
- [30] Kunat M, Burghaus U and Wöll C 2003 *Phys. Chem. Chem. Phys.* **5** 4962-7
- [31] Kunat M, Girol S G, Burghaus U and Wöll C 2003 *J. Phys. Chem. B* **107** 14350
- [32] Ahn J and Rabalais J W 1997 *Surf. Sci.* **388** 121
- [33] Pepper B, Richter B, Dupois A, Kühlenbeck H, Huchou C, Schilbe B, Binyamo M and Freund H-J 2002 *Surf. Sci.* **64** 496
- [34] Braun J, Toennies J P and Wöll C 1999 *Phys. Rev. B* **60** 11707
- [35] Diebold U 2003 *Surf. Sci. Rep.* **48** 53
- [36] Suzuki S, Fukui K-I, Onishi H and Iwasawa Y 1999 *Phys. Rev. Lett.* **84**
- [37] Leconte J, Markovits A, Skalli M, Minot C and Belmajdoub A 2002 *Surf. Sci.* **497** 194-204
- [38] Dulub O, Diebold U and Kresse G 2003 *Phys. Rev. Lett.* **90** 016102
- [39] Göpel W 1978 *J. Vac. Sci. Technol.* **15** 1298
- [40] Moormann H, Kohl D and Heiland G 1980 *Surf. Sci.* **100** 302
- [41] Watanabe M 1980 *Japan. J. Appl. Phys.* **19** 1853
- [42] Idriss H and Barteau M A 1992 *J. Phys. Chem.* **96** 3382
- [43] Eischens R P, Pliskin W A and Low M J D 1962 *J. Catal.* **1** 180

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- [44] Ghiotti G, Chiorino A and Bocuzzi F 1993 *Surf. Sci.* **287/288** 228
- [45] Campbell C T 1997 *Surf. Sci. Rep.* **27** 1
- [46] Tasker P W 1979 *J. Phys. C: Solid State Phys.* **12** 4977
- [47] Nosker R W, Mark P and Levine J D 1970 *Surf. Sci.* **19** 291
- [48] Noguera C 1996 *Physics and Chemistry at Oxide Surfaces* (Cambridge: Cambridge University Press)
- [49] Wander A, Schedin F, Steadmann P, Norris A, McGrath R, Turner T S, Thornton G and Harrison N M 2001 *Phys. Rev. Lett.* **86** 3811
- [50] Staemmler V, Fink K, Meyer B, Marx D, Kunat M, Girol S G, Burghaus U and Wöll C 2003 *Phys. Rev. Lett.* **90** 106102
- [51] Becker T, Hövel S, Boas C, Kunat M, Burghaus U and Wöll C 2001 *Surf. Sci.* **486** L502
- [52] Becker T, Hövel S, Kunat M, Boas C, Burghaus U and Wöll C 2002 *Surf. Sci.* **511** 463 (erratum)
- [53] Meyer B and Marx D 2003 *J. Phys.: Condens. Matter* **15** L89–94
- [54] Shi S, Shi C, Fink K and Staemmler V 2003 *Chem. Phys.* **287** 183–95
- [55] Meyer B 2004 *Phys. Rev. B* **69** 045416
- [56] Meyer B and Marx D 2003 *Phys. Rev. B* 035403