The adsorption of hydrogen on the rutile TiO$_2$(110) surface

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The adsorption of hydrogen on a well defined single crystal rutile TiO$_2$(110) surface has been investigated using helium atom scattering (HAS). Whereas the adsorption probability of molecular hydrogen was below the detection limit ($S < 2 \times 10^{-7}$), the hydrogen adlayers were prepared by exposing the clean surface to atomic hydrogen. The results reveal the formation of a H(1 × 1) TiO$_2$(110) surface. In addition, the adsorption and desorption kinetics were studied by monitoring the reflectivity of the surface for helium atoms. The analysis of the data yielded two desorption maxima with activation energies for desorption of 99 kJ mol$^{-1}$ and 162 kJ mol$^{-1}$.

1. Introduction

Although rutile TiO$_2$(110) is probably the metal oxide surface which has been studied in most detail$^1$ precise information on the interaction of this substrate with hydrogen and the presence of hydroxyl species on this surface is very scarce. This is an unfortunate situation, since from related studies on metal surfaces (for a review see Christmann$^2$) 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).$^{3,4}$

In addition, for metal oxide surfaces the presence of hydrogen is expected to have significant influence on the chemical activity of the surface, which is frequently used as a support in heterogeneous catalysis. The most recent experimental information available on hydrogen atoms adsorbed on single crystal TiO$_2$ surfaces stems from scanning tunneling microscopy, or STM. In two studies small protrusions on the surface have been assigned to adsorbed hydrogen atoms$^{5,6}$ which, surprisingly, do not form an ordered overlayer. In previous work the influence of defects on the interaction with molecular hydrogen$^7$ and 50 eV hydrogen ions$^8$ has been characterized. Others studied the effect of vacuum-annealing on the formation of surface hydroxyls.$^9$

The 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 (ca. 10 A$^2$.$^{10,11}$). The potential of He-atom scattering with regard to a characterization of hydrogen atom overlayers on metal oxide and insulator surfaces has in the past years been demonstrated for a number of systems: Al$_2$O$_3$, ZnO$^{12,13,14}$ and diamond.$^{15}$ 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 well suited to detect hydrogen overlayers on solid substrates due to the very small cross-section of hydrogen atoms for electron scattering.

2. Experimental procedures

The measurements reported here have been conducted using a molecular beam system described in detail elsewhere.$^{16}$ 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, $\alpha$, can be changed by rotating the sample around an axis normal to the scattering plane. The scattering chamber contains a second quadrupole mass spectrometer, LEED, XPS, and a differentially pumped sputter gun. The TiO$_2$ substrates used in this study (obtained from MaTeck crystals) have been cleaned by a procedure consisting of cycles of Ar$^+$ sputtering (600 V, 1 $\mu$A, $T_s = 300$ K, 60 min) followed by annealing in oxygen ($1 \times 10^{-8}$ mbar, $T_s \sim 600$ K, 10 min) and in UHV ($T_s = 750$ K, 5 min), as described in previous publications (see ref. 17). The crystal was never heated above 850 K in order to avoid an excessive loss of oxygen. The crystal exhibited a light blue color, revealing the presence of a small amount of oxygen vacancies in the bulk. After a few preparation cycles a sharp LEED pattern and a distinct He-atom specular peak revealed the presence of a structurally well-defined surface. XPS showed no carbon containing species (contamination level <0.05 ML) and symmetric Ti 2p peaks that are characteristic for a stoichiometric crystal.$^{7,17}$ The gases used in this study are of research purity (99.9999% for He and for H$_2$ from Messer Griesheim). Additionally, LN$_2$ traps are mounted in the hydrogen and He gas lines, respectively, to avoid H$_2$O contamination of the sample. Exposure of the sample to atomic hydrogen was carried out by backfilling the scattering chamber (typically at 1–4 × 10$^{-6}$ mbar) through a leak valve and by dissociating H$_2$ on a hot tungsten filament which was placed in line-of-sight (distance 4 cm) from the substrate surface. The crystal could be cooled down to a surface temperature, $T_s$, of 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 $T_D = 111$ K) (see, e.g., ref. 18).

3. Presentation of the results

In Fig. 1 we present a schematic model of the TiO$_2$(110) surface. The two high symmetry azimuthal directions are denoted by [001] and [110], respectively. The surface consists of rows of bridging oxygen atoms along the [001] azimuth.