Water adsorption on the hydroxylated H-(1 × 1) O-ZnO(000-1) surface†

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Received 31st October 2005, Accepted 23rd December 2005
First published as an Advance Article on the web
DOI: 10.1039/b515418a

The adsorption of water multilayers on a well defined single crystal, hydroxyl-terminated ZnO-surface, H(1 × 1)-O-ZnO(000-1) surface has been investigated using infrared (IR) spectroscopy, helium atom scattering (HAS) and X-ray photoelectron spectroscopy (XPS). The results reveal the formation of well ordered mono-, bi- and multilayers of D₂O and H₂O on this substrate. On the bare hydroxyl-covered H(1 × 1) surface the OH-stretch vibration could be clearly identified in the IR-spectra. The water adsorption and desorption kinetics on this hydroxylated surface were studied by monitoring the reflectivity of the surface for helium atoms. The analysis of the data yielded activation energies for desorption of H₂O from the H(1 × 1) O-ZnO surface of 55.2 kJ mol⁻¹. The results reveal the formation of ordered mono- and bilayers. Further exposure to water at 113 K results in the formation of amorphous 3-D islands.

Introduction

Zinc oxide is a material of major industrial interest. Its semiconducting and optical properties make it a transparent conducting oxide ("TCO") suitable for front electrodes in thin film solar cells.2,12 ZnO is frequently used as gas sensor for hydrogen and carbon hydrides since the surface conductivity of the zinc oxide varies with gas pressure.3–5 Zinc oxide is used as a support in relevant technological processes involving heterogeneous catalysis. It acts, for example, as a support for copper nano particles for methanol synthesis from synthesis gas,6 for the water gas shift reaction7 and for steam reforming. The latter two reactions are important reactions in fuel cells. Though water is present in all major applications there is surprisingly little knowledge about the water-zinc oxide interaction. This is even more intriguing as wetting of metal nanoparticles in catalysis, for example, can be influenced substantially by the surface properties of the oxide.5 OH-anchor may also be relevant for anchoring dye molecules with carboxylic or phosphoric acid groups to nanostructured zinc oxide surfaces in new solar cells. The structure of the electrode ZnO surface via electrochemical deposition is influenced by the presence of the dye to be incorporated. Therefore OH-groups should have a direct impact onto the efficiency of the solar cell.9 ESR and conductivity measurements of Sengupta et al. indicated dissociative adsorption of water at powder ZnO samples.10 Very recent experiments on methanol synthesis using ZnO powders including kinetic measurements and characterisation of the probe revealed that polar surfaces are particularly efficient.11 Theoretical calculations showed that at pressures and temperatures typically employed in methanol synthesis the most stable structure was found to be a surface with a hydrogen-atom surface coverage of 50% where all surface electronic states are filled.12 OH groups are crucial for hydrogenation of the intermediate formyl species and H₂O is responsible for permanently providing active sites.

The issues mentioned above motivated a closer examination of the interaction of water with the polar ZnO(000-1) surface. For O-ZnO (short for ZnO(000-1)), like for other polar surfaces such as NiO(111)13,14 or CoO(111),15 hydroxylation of the surface occurs upon exposure to water.16 This is a major factor with regard to a stabilization of this polar surface which exhibits an inherent electrostatic instability.17 Upon heating the OH-groups desorb and the surface has to rearrange because of the reappearance of instability.13 This restructuring can either comprise a micro-faceting, which is an alternative way of stabilizing polar surfaces, or, as in the case of O-ZnO the formation of a (1 × 3)-reconstruction.17,18 Adsorption of water at a clean Fe₂O₃ (111) surface is more complex.19 The first third of a monolayer adsorbs dissociatively at Fe₂O₃ with OH being incorporated into the lattice and the remaining H-being highly mobile on the oxygen. However, the barrier for recombination is strongly influenced by the surface coverage. With increasing surface coverage features develop which are characteristic for hydrogen bonding of intact water molecules. The formation of dimers is concluded. OH groups have further been observed for Cr₂O₃(0001),14 MgO(100)20 and TiO₂21,22 where dissociative adsorption of water has been reported to occur mainly at defect sites.

Water adsorption on the mixed terminated ZnO(10-10) has very recently been studied by means of low-energy electron diffraction (LEED), He-scattering (HAS), scanning tunnelling microscopy (STM), He thermal desorption spectroscopy (H-TDS) and Car–Parinello ab initio simulations.23 Meyer et al. found a rather complex scenario, where every second molecule...