Structure of the Zn-terminated (001)-surface of hexagonal ZnO under ambient conditions with and without water from GIXRD experiments

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Introduction

The surface chemistry of oxide/liquid interfaces is a key issue in adhesion science and related areas such as corrosion science or electrocatalysis. ZnO is of particular interest in all these areas. The herein investigated single crystal ZnO(0001)-Zn surfaces have been extensively studied under UHV conditions within the last decades[1-3]. In contrast the literature on well-defined and crystalline ZnO(0001)-Zn surfaces under ambient conditions and in electrolyte solutions is not very comprehensive [4-7].

Experimental

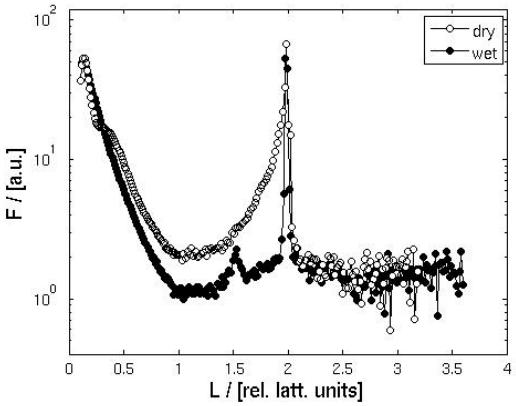
Polar ZnO(001)-Zn-terminated surfaces can be prepared as very well defined and single crystalline surfaces by hydroxide stabilization simply by introducing hydroxides via a wet chemical cleaning step. We present the first results of structure refinements of gracing incidence XRD experiments measuring crystal truncation rods of the ZnO(001)-Zn surface after hydroxide stabilization in both dry and humid atmosphere. The analysis shows that the surface is O-terminated and covered with a defect containing hydroxide/oxygen adlayer. The investigations also show that it is possible to obtain high quality single crystalline ZnO(0001)-O surfaces, which are stabilized by a disordered hydroxide/oxygen adlayer, in a simple way [8].

The experiment was performed at the surface diffraction beamline BM25B at the ESRF. For measurements with water film, a drop of water was introduced onto the crystal surface and maintained as a thin film covered with a Mylar foil to prevent evaporation. The intensity measurements on the ZnO(001)) surface was performed over a series of 8 symmetry

independent CTRs. The intensity profiles were corrected accordingly as described elsewhere[9].

Results and discussion

The refinement of the crystal truncation rod intensities measured in atmospheric conditions controlling relative humidity to 0 lead to a defect termination of the topmost O atoms with hydroxyl where 2/3 of the top sites were occupied (see Fig. 2, red spheres). No reconstruction and no significant deviation from the volume structure was observed. Adding water on top of the surface and protecting the water film from evaporation covering it with a mylar foil remarkably changed the intensity profile (see Fig. 1) indicating ordering of surface water molecules periodically on specific surface sites. The water molecule is located in the centre of the 6MR tunnel (see Fig. 2, white spheres), however with occupancy reduced to 1/3. This reduces steric hindrance of the surface terminating molecules and, at the same time, filling up all available space to completely cover the O-terminated surface.



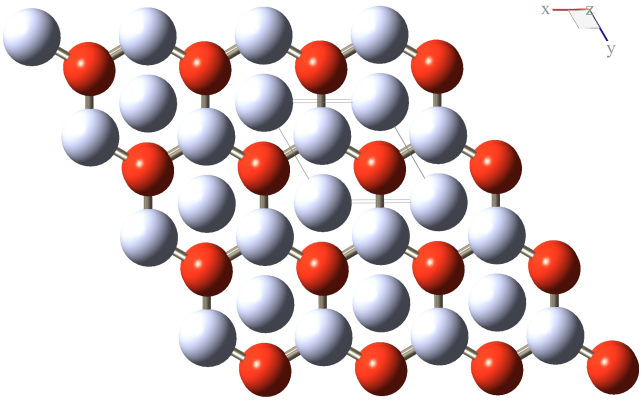


Fig.. 1: (0,0)-CTR of ZnO without and with ad-water. Fig. 2: Structure model of water on ZnO(001)-O

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