Preparation and calibration of ultrathin Zn layers on Pd(1 1 1)

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1. Introduction

The search for alternative sources of hydrogen as possible new energy carriers has become an important issue. A promising candidate is methanol which can be stored easily. The desired hydrogen is then gained by methanol steam reforming [1,2]. For processing the methanol effective catalysts are needed. Therefore the system Pd/ZnO has attracted increasing attention in the recent years due to its superior catalytic properties compared to the standard Cu and Cu/ZnO-based catalysts [3–6]. It could be shown that the reductive formation of a ZnPd alloy is mainly responsible for the good performance of Pd/ZnO catalysts [7–9]. The formation of ZnPd alloys on Pd single crystal surfaces was subject in a series of studies in the recent years [10–13]. However, the experimental work done on thin Zn layers on Pd(1 1 1) still shows some discrepancies. It is well known in the community that Zn evaporation is a delicate subject, but generally not discussed in the literature. A variety of methods was proposed to determine the Zn coverage like X-ray photoelectron spectroscopy (XPS) [12], CO titration experiments [12–14], standard quartz microbalance measurements [14] and comparison of thermal desorption spectra (TDS) of oxygen and Zn during decomposition of a fully oxidized ZnO layer [13]. The interpretation of the measured data is tightly linked to the correct quantification of the deposited Zn amount. Discrepancies between different works in the literature appear to be due to the different calibration methods used.

The success of spectroscopic methods like XPS or Auger electron spectroscopy (AES) for determining the coverage crucially depends on the film morphology. For CO titration the film morphology is also important but additionally one has to be sure that no configuration exists which allows binding of CO to already Zn covered surface areas, at least in a certain temperature range. Therefore deposition rates and consequently the coverage are usually controlled by a quartz microbalance. For a proper application of this method the sticking coefficient on the sample and on the microbalance has to be the same. In case of metal vapors which are deposited at not too high sample temperatures this condition is mostly fulfilled. It is generally assumed that metal vapors stick everywhere with a probability of unity. In this work we will show that this general statement does not hold for Zn which is vapor-deposited onto contaminated surfaces at room temperature and that consequently one has to be extremely careful by using a quartz microbalance for coverage calibration.

2. Experimental

The experiments were done in an ultra-high vacuum (UHV) chamber which provided a base pressure of $2 \times 10^{-10}$ mbar. The chamber was equipped with an Auger electron spectrometer (AES), a low energy electron diffraction (LEED) optics and an Ar−ion sputtering gun. In the main chamber a quadrupole mass spectrometer (QMS) was installed for residual gas analysis and monitoring of the preparation steps. A second quadrupole mass spectrometer was mounted in a line-of-sight (LOS) configuration in a differentially pumped detector chamber (base pressure $7 \times 10^{-11}$ mbar) for thermal desorption spectroscopy (TDS). Optionally the direct