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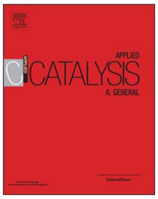

Feature Article

Ultrathin Zn and ZnO films on Cu(111) as model catalysts

Bo-Hong Liu, Irene M.N. Groot, Qiushi Pan, Shamil Shaikhutdinov*, Hans-Joachim Freund

Department of Chemical Physics, Fritz Haber Institute, Faradayweg 4-6, 14195, Berlin, Germany

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ABSTRACT

To prepare well-defined models of ZnO-based catalysts, in particular of Cu/ZnO used for methanol synthesis, we studied the structure of Zn and ZnO thin films grown on a Cu(111) single crystal surface using metal vapor deposition. Structural characterization was performed by scanning tunneling microscopy, Auger electron spectroscopy, and low-energy electron diffraction. In agreement with previous studies, Zn wets the Cu surface forming mixed surface layer depending on Zn coverage. Surface oxidation of the Zn film into ZnO, as monitored by STM, showed that the reaction starts at step edges and propagates inside the terrace at increasing temperature. However, the process is affected by Zn migration into the Cu bulk and hence the film formation critically depends on the heating rate. In another approach using Zn deposition in oxygen ambient and subsequent annealing in vacuum, the resulted films were well-ordered and showed a long-range coincidence structure, assigned to the formation of a single ZnO(0001) layer on top of Cu(111). Independent of preparations conditions, the ZnO overlayer did not cover the entire surface, leaving considerable areas exposing Cu(111) or Cu_2O/Cu(111) surface. Reactivity measurements for CO oxidation and reverse water gas shift reactions at nearly atmospheric pressures showed no promotional effects of the ZnO overlayer under conditions studied. Moreover, Zn irreversibly migrates into the Cu crystal bulk in an O_2 rich ambient, and the surface chemistry is governed, in essence, by a poorly defined Cu-oxide film. However, the ZnO/Cu model catalysts are fairly stable in a mixture of CO_2 and H_2.

1. Introduction

Zink oxide (ZnO) based catalysts show superior performance in methanol synthesis and water gas shift (WGS) reactions. Although Cu/ZnO/Al_2O_3 catalysts are commercially used in industry, the atomic structure of active sites in these catalysts remains debated in the literature. Among many proposed structures and reaction mechanisms, the crucial role of the ZnO/Cu interface has been highlighted (Refs. [1,2] and references therein). However, the metallic Zn-Cu sites were also considered as active [3–5]. In addition, several models invoke structures formed by Cu nanoparticles encapsulated by very thin ZnO overlayer [6–8]. This situation motivates research groups to perform studies on planar model systems such as metallic Cu nanoparticles and clusters deposited on ZnO single crystal surfaces [9–11]. Also the atomic structure and the formation of the Cu – Zn surface alloy received much attention. [12–14] In this respect, ZnO thin films supported on Cu can be considered as well-suited model systems for studying the reaction at the interface in order to rationalize the critical role of a ZnO phase in these catalysts. Moreover, ultrathin films supported on metals may show interesting catalytic properties in their own right [15–19].

Studies focusing on preparation of ZnO films on Cu singe crystals and foils were initiated more than twenty years ago using oxidation of metallic Zn overlayers [11,13,20–22]. Several attempts were made to fabricate thin ZnO films by oxidation of brass. [23] However, well-ordered ZnO films were not obtained in these studies. Preparation of crystalline ZnO films was first reported for a Ag(111) substrate employing pulsed laser deposition and vacuum annealing [24]. To date, crystalline ZnO films growing in the (0001) orientation have been prepared on Pd(111) [25], Pt(111) [26,27], and Au(111) [28]. On the basis of theoretical calculations, it is generally accepted that ZnO as an ultrathin film relaxes into a "depolarized" structure, in which Zn and O atoms are arranged in almost coplanar sheets as in the hexagonal boron-nitride structure.

In this work, we address the preparation of ZnO films on Cu(111) as a well-defined model system which could shed more light on chemistry of ZnO based catalysts. For this we use two different approaches frequently used in thin film growth. In the first one, Zn was vapor deposited onto clean Cu(111) and subsequently oxidized under UHV compatible pressure conditions. In the second approach, we employed Zn deposition in an oxygen ambient (so called "reactive" deposition) followed by annealing in vacuum. The structural characterization of the model catalysts was performed by scanning tunneling microscopy

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* Corresponding author.
E-mail address: shaikhutdinov@fhi-berlin.mpg.de (S. Shaikhutdinov).

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(STM), Auger electron spectroscopy (AES), and low energy electron diffraction (LEED). We also report results on the reactivity of this model system for CO oxidation and reverse (r-) WGS reactions at nearly atmospheric pressures and on structural and compositional changes induced by reaction ambient.

2. Experimental

The experiments were performed in an ultrahigh vacuum (UHV) chamber equipped with an STM (Omicron) and a four grid optics LEED apparatus used also for AES (from Specs). The Cu(111) crystal was clamped to an Omicron sample holder. The sample temperature was measured by a Type K thermocouple put into a small hole at the edge of the crystal. Clean surfaces were obtained by cycles of Ar^+-sputtering and annealing in UHV and 10^{-7} mbar O_2 to remove residual carbon. Zinc was deposited by heating a Zn rod (1 mm in diameter, 99.99%, Goodfellow) to 500 − 525 K by passing current through a thoriated tungsten wire wrapped around the rod. The deposition flux was controlled via the Zn rod temperature measured by a Type K thermocouple spot-welded to the edge of the rod. The Zn source is shielded by a metal cylinder having a small orifice (~ 5 mm in diameter) and placed about 2 cm away from a crystal.

STM images were obtained with commercial Pt-Ir tips (L.O.T.-Oriel) using tunneling parameters in the range of 1 − 2 V (bias) and 0.5–1 nA (current). The images were only subjected to plane corrections, if not specified.

3. Results and discussion

In the first approach, we employed Zn physical vapor deposition in UHV at room temperature and subsequent oxidation in 10^{-6} mbar pressure range at elevated temperatures. The amount of Zn deposited onto the clean Cu(111) was monitored by AES using the ratio of Zn (at 994 eV) and Cu (at 776 eV) peaks. Albeit the latter signal is significantly lower in intensity as compared to the principal Auger signal for Cu at 920 eV, it is the only one that does not overlap with the Auger transitions of Zn. Henceforth, this Auger ratio was used as a measure of the Zn coverage. Large-scale STM images (Fig. 1) of Zn/Cu(111) films at various amounts of deposited Zn showed no three-dimensional particles and aggregates, but flat terraces and ad-islands. This suggests that metallic Zn grows on Cu(111) in a layer-by-layer mode, as previously proposed on the basis of TPD and XPS results [14]. For the formation of a fully covered Zn monolayer, an estimate based on AES analysis [29] results in the above-mentioned Auger ratio value of ~ 1 (using a Zn layer thickness = 2 Å, and the mean free path of electrons = 10 Å). The STM images at such ratios (Fig. 1a) revealed wide terraces and irregularly shaped patches with a broad size distribution, probably due to a coalescence of smaller islands. When these islands merge with the step edges they do not exhibit any boundary with respect to a high-lying terrace, indicating that they share the same surface structure. Indeed, the monoatomic steps on Cu(111) (= 2.08 Å) and Zn(0001) (= 2.47 Å) differs substantially and hence must be readily detectable by STM. A peninsular-like morphology of the step edges clearly differs from that observed on the clean Cu(111) surface (inset in Fig. 1b). Such morphology can be rationalized in terms of Zn-Cu surface alloying, albeit the latter is thought to occur at higher temperatures [12,14]. Although the basal Zn(0001) surface has a much lower surface energy as compared to Cu(111) (i.e., 0.99 and 1.95 J/m^2, calculated [30]), previous STM studies [12] of the initial stages of Zn deposition on Cu(111) provided solid evidence that Zn ad-atoms substitute Cu in the surface layer at 300 K, in agreement with DFT calculations [31].

It has previously been proposed that Zn atoms adsorb at step edges and then migrate inside the upper terrace layer until a homogeneous distribution in the surface layer is reached. This scenario was inspected by theoretical calculations using Monte-Carlo simulations [32]. The results suggested that, at low coverage (0.25 ML), Zn ad-atoms coalesce forming compact islands with edges along the close-packed direction. At and above room temperature, the place exchange between the Zn ad-atoms and Cu atoms in upper terrace sets in, which is accompanied by the formation of Zn-decorated Cu islands. As the Zn coverage increases, an intermixing is less pronounced, favoring the formation of larger Zn islands within the adlayer, stable at higher temperatures. For 0.9 and 1.5 ML Zn, similar features are observed by simulations, i.e. the formation of a mixed, largely disordered Cu–Zn upper layer. Since the proposed Zn-Cu surface alloying mechanism involves surface diffusion, the resulted surfaces in our films may additionally be affected by the deposition flux.

Although it is difficult to discriminate pure Cu(111) and mixed Zn-Cu(111) surfaces in the presented STM images lacking atomic resolution, their close inspection showed that the step heights between the adjacent terraces (or patches) are often not identical. For example, the height difference between the areas labelled A and B in Fig. 2 is about 0.2 Å higher than between C and B. (The absolute step heights measured by STM (all in 2–2.5 Å range) may deviate depending on the tip and tunneling conditions). In addition, the areas B and C (but not A) show a long range modulation seen in STM as an irregular network of depressed lines (inset in Fig. 2b). In principle, this finding may be explained by Zn-Cu surface alloying, taking into account the difference in density of atoms in a mixed Zn-Cu layer (depending on Zn/Cu ratio) and the Cu(111) surface underneath, which may result in structure to some extent similar to the well-known "herring bone" reconstruction on the Au(111) surface. Another possible explanation would have to take

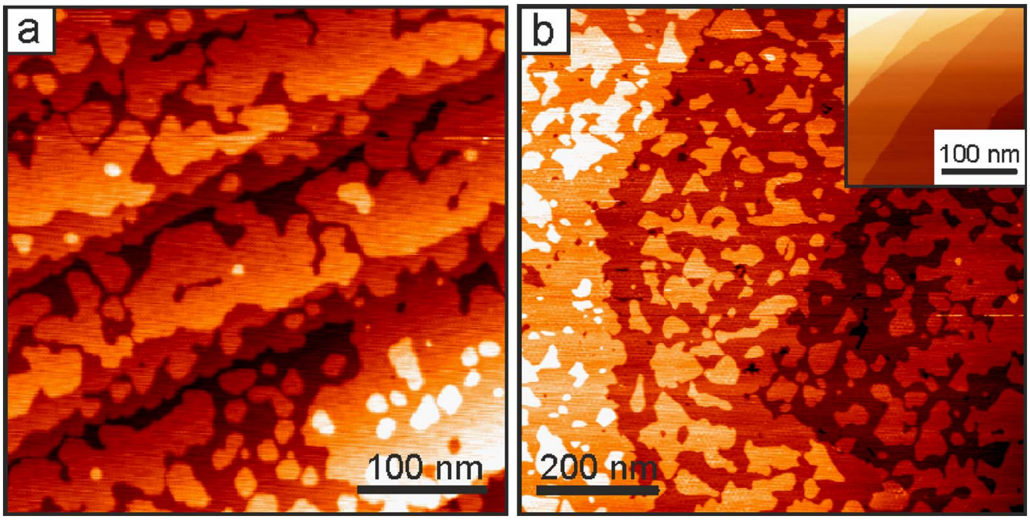

Fig. 1. STM images of Zn films on Cu(111) at 1.2 (a) and 2.5 ML (b) coverages determined by AES. Inset displays the STM image of the clean Cu(111) surface for comparison.