Thermal behavior of MOCVD-grown Cu-clusters on ZnO(10\(\bar{1}\)0)

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Scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS, AES) were used to study MOCVD of Cu-clusters on the mixed terminated ZnO(10\(\bar{1}\)0) surface in comparison to MBE Cu-deposition. Both deposition methods result in the same Cu cluster morphology. After annealing to 670 K the amount of Cu visible above the oxide surface is found to decrease substantially, indicating a substantial diffusion of Cu atoms inside the ZnO-bulk. The spectroscopic data do not show any evidence for changes in the Cu oxidation state during thermal treatment up to 770 K.

1. Introduction

Small, nm-scaled metal deposits on oxidic supports are important as active components in industrial catalysts, a prominent example are Cu-particles supported on ZnO used in the formation of methanol from syngas.\(^1,2\) Despite many years of intensive research the interaction of both components forming a complex interface is still not well understood.

As a first step to better understand the complex metal–substrate interactions in the case of the Cu/ZnO system, low-indexed surfaces of ZnO single crystals are investigated under UHV conditions with a broad spectrum of surface science tools as well defined model systems. One powerful tool to analyze the local geometric and electronic structure is scanning tunneling microscopy.\(^3\) STM investigations of different clean ZnO surfaces\(^4,5\) as well as Cu thin films deposited on the polar ZnO(0001)–Zn\(^6,7\) and on the mixed terminated ZnO(10\(\bar{1}\)0) surface\(^8\) have already been reported. On the ZnO(10\(\bar{1}\)0) surface Dulub et al.\(^8\) found Cu-cluster nucleation to occur preferentially at step edges orientated perpendicular to the [1\(\bar{2}\)10] atomic row direction.

In all STM-studies published up to now, Cu deposition on the ZnO substrate was accomplished by molecular beam epitaxy (MBE). In this article we present results for Cu particles obtained from metal–organic chemical vapor deposition (MOCVD) on the ZnO(10\(\bar{1}\)0) surface and discuss the annealing behavior of these Cu-clusters. In comparison to physical deposition techniques MOCVD allows higher deposition rates on substrates of random shape. In addition, in the present study some experiments have also been carried out for Cu deposited by MBE onto ZnO(10\(\bar{1}\)0) in order to clarify the question whether MBE deposited Cu-clusters exhibit the same morphology as the clusters deposited by MOCVD.

Experiments with MBE copper deposition on the Zn-terminated ZnO(0001) surface revealed a strong decrease of the Cu visible above the ZnO substrate level at elevated temperatures and gave a first hint to a substantial amount of Cu atoms diffusing inside the ZnO substrate.\(^7\) Thermally induced diffusion of Cu atoms into the ZnO substrate was also found recently in a combined HREELS and DFT-study on the polar O-terminated ZnO(10\(\bar{1}\)0) surface for temperatures above 800 K.\(^9\)

Jedrecy et al.\(^10\) concluded that during the early stages of Cu deposition on the same polar ZnO surface the O–Cu interaction is only weak. Already at room temperature a small decrease in the Cu2p binding energy was found in XPS-studies by Campbell et al.\(^11\) Therefore in this work the formation of Cu oxide could not be ruled out. Angle resolved photoemission studies\(^12\) on the valence electronic structure of Cu/ZnO(10\(\bar{1}\)0) during annealing point to the onset of oxidation of the Cu-clusters between 700 K and 800 K. Above 800 K the Cu deposits are found to be completely oxidized. In the present publication we mainly concentrate on the catalytically relevant temperature range below 700 K.

2. Experimental

The STM experiments were performed in two different ultrahigh vacuum systems with a base pressure of \(5 \times 10^{-9}\) Pa equipped with variable temperature scanning tunneling microscopes enabling in situ studies of growth and adsorption processes for sample temperatures up to 1000 K. The systems are equipped with ion guns for Ar\(^+\) bombardment, LEED optics and quadrupole mass spectrometers (QMA). ZnO(10\(\bar{1}\)0) substrates (MaTeck) were obtained in cut/polished form and fixed to a Ta-plate. Prior to loading into the UHV chamber the samples were cleaned in an ultrasonic bath in acetone and ethanol successively. The ZnO-samples were cleaned in a vacuum by cycles of Ar\(^+\) sputtering (\(\sim 0.9\) keV, 20 min, \(4 \mu\)A) and...