Surface Science 671 (2018) 1–5

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

On the growth mechanisms of polar (100) surfaces of ceria on copper (100)

Johanna Hackl[a], Tomáš Duchoň[a,b], Daniel M. Gottlob[a], Stefan Cramm[a], Kateřina Veltruská[b], Vladimír Matolín[b], Slavomír Nemšák[a,c,*], Claus M. Schneider[a]

[a] Peter-Grünberg-Institut 6, Forschungszentrum Jülich, 52425 Jülich, Germany
[b] Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University, 18000 Prague, Czech Republic
[c] Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA 94720, USA

ARTICLE INFO

Keywords:
Cerium oxide
X-ray photoelectron microscopy
Low energy electron microscopy
Epitaxy

ABSTRACT

We present a study of temperature dependent growth of nano-sized ceria islands on a Cu (100) substrate. Low-energy electron microscopy, micro-electron diffraction, X-ray absorption spectroscopy, and photoemission electron microscopy are used to determine the morphology, shape, chemical state, and crystal structure of the grown islands. Utilizing real-time observation capabilities, we reveal a three-way interaction between the ceria, substrate, and local oxygen chemical potential. The interaction manifests in the reorientation of terrace boundaries on the Cu (100) substrate, characteristic of the transition between oxidized and metallic surface. The reorientation is initiated at nucleation sites of ceria islands, whose growth direction is influenced by the proximity of the terrace boundaries. The grown ceria islands were identified as fully stoichiometric CeO_2 (100) surfaces with a (2 × 2) reconstruction.

1. Introduction

Model ultra-thin oxide catalysts grown on metallic supports have been a longstanding source of inspiration for the development of real-life catalysts [1]. Metal-supported ceria films are a prime example of a model heterogeneous catalyst related to industrial-scale chemical conversion, previously studied by numerous groups using a plethora of experimental and theoretical techniques [2–4]. The bulk of those studies were performed on substrates with three- or six-fold symmetries, which predominantly stabilize the (111) terminated cubic ceria phase [5–8]. Recently, several studies demonstrated the growth of (100) terminated ceria nanostructures on the three- or six-fold symmetric substrates [9–12], but the complexity of the yet unresolved interface presents an obstacle for understanding fundamental mechanistic steps of chemical conversion on/over these systems and poses a major challenge in their theoretical modeling. On the other hand, using a metallic substrate with four-fold symmetry offers a possibility to stabilize the energetically unfavorable (100) surface of ceria through a much more straightforward metal–oxide interface. This simplification could enable future coupling to theory and bring answers to many open questions, especially since the (100) surface in nanostructured samples is known to be more catalytically active in several reactions.

The defining feature of the (100) surface of ceria is that all the possible bulk terminations, either on an oxygen or a cerium plane, are “type 3” polar surfaces according to Tasker’s classification [13] and the dipole moment at the surface gives rise to compensating reconstructions. In the case of a thin film the most straightforward reconstruction involves termination of both surfaces on oxygen planes that have 50% of oxygen vacancies [10]. This keeps both the symmetry and stoichiometry of the CeO_2 (100) film. However, several other reconstructions were reported in the literature, specifically c(2 × 2) and (2 × 2) [9–12]. The two reconstructions are present as a function of various variables: ambient conditions, film thicknesses and consequently, substrate-ceria interactions. The interpretation of these is still under contention, but most recent density functional theory calculations indicate a preference for substoichiometric models of the reconstructions [9].

Here, we focus on the growth of epitaxial ceria films on a Cu (100) substrate as a means to reduce the complexity of the ceria–metal interface. By varying the deposition conditions, we explore growth modes of (100) terminated ceria on Cu (100) and demonstrate the flexibility of the physical vapor deposition in inducing different properties in the grown structures. Utilizing *in-situ* observation capabilities of a photoemission electron microscope (PEEM), we reveal a close connection between the growth mechanism and oxygen spillover between the metal substrate and supported oxide. The connection is realized through the surface chemical potential of oxygen that determines the orientation of steps on the copper single crystal. The as-grown ceria (100) islands exhibit a (2 × 2) reconstruction, revealed by low energy electron diffraction (LEED) measurement, while keeping the stoichiometry of CeO_2,

---

[*] Corresponding author.
E-mail address: s.nemsak@fz-juelich.de (S. Nemšák).

https://doi.org/10.1016/j.susc.2018.01.008
Received 17 November 2017; Received in revised form 8 January 2018; Accepted 16 January 2018
0039-6028/

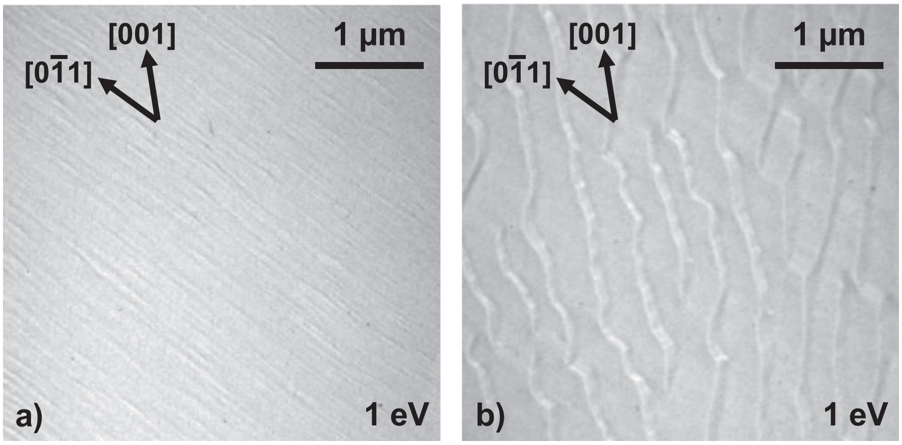

Fig. 1. LEEM images of Cu (100) substrate: a) 850 K in a vacuum, b) 850 K in 5×10^{-7} mbar O_2.

in contrast to previously proposed substoichiometric (2 × 2) terminations of the polar ceria (100) surface [9,4]. The relative simplicity of the ceria (100)/Cu (100) interface opens up a new explorable part of the structure–activity phase space of the cerium–oxygen–copper system, which can be utilized in bottom-up rational design of ceria-based heterogeneous catalysts.

2. Results and discussion

Cu (100) crystals were cleaned and conditioned by several cycles of Ar^+ sputtering and annealing in UHV and in oxygen, see the Methods section for details. As the last preparation step before the ceria growth, the clean Cu (100) crystals were annealed at 850 K and exposed to an oxygen ambiance of 5×10^{-7} mbar at the elevated temperature. The crystal step boundaries before and after oxygen exposure were imaged using low energy electron microscopy (LEEM), see Fig. 1a and 1b. The crystallographic orientations were determined using diffraction plane imaging, which provides equivalent information to the conventional LEED.

There is a stark difference in the shape and orientation of the step boundaries as the oxygen gets chemisorbed onto the Cu (100) surface. The clean Cu (100) surface exhibits step boundaries which are parallel to ⟨011⟩ crystallographic directions of the Cu crystal (Fig. 1a). The mean terrace size, in this case, was ~ 50 nm, without any other visible impurities or defects. On the other hand, the adsorbed oxygen causes a significant growth in terrace size and, more importantly, a change in the prevalent orientation of the step boundaries by 45°.

Similar effects were observed on various metallic crystals upon adsorption of different species [14], including the study of Mo (110) using low-energy electron microscopy [15]. The explanation of this phenomena lies in the preferred step boundary orientations of the metallic and the oxidized Cu (100) surface. For the metallic surface, the prevalent orientation of step boundaries is along the crystalline close-packed ⟨011⟩ direction [16]. However, the exposure of Cu (100) to oxygen at elevated temperatures leads to the formation of surface oxides [17] that prefer step boundaries oriented along the ⟨001⟩ direction (which is rotated by 45° with respect to the ⟨011⟩ direction) [18,19]. The reorientation of step boundaries is accompanied with a dramatic increase in the terrace size, from ~50 nm to ~500 nm, that can be interpreted in the light of recent observations of increased mobility of surface atoms of metal single-crystals in the presence of oxygen [11].

Interestingly, after removing the oxygen ambiance from the chamber and keeping the sample at an elevated temperature above 800 K, the step boundaries spontaneously reorient back to be parallel to ⟨011⟩ crystallographic direction. Studies examining the Cu (100) oxidation found that for temperatures in the range of 670 to 870 K, copper oxides become reduced in UHV [20,21]. Therefore, the repeatable step boundary reorientation by 45° is an indication of the oxidation and reduction of the Cu (100) surface.

The substrate temperature is one of the key growth parameters since it is directly connected to the mobility of the deposited material. Therefore, it is expected to have a dramatic impact on the ceria islands' growth mode. In our experiments, we used three substrate temperatures in the range between 720 and 850 K.

The growth at the lowest deposition temperature (720 K) did not lead to the formation of resolvable islands in the LEEM images, therefore they are not shown. The lateral resolution of images shown in Fig. 1a and 1b is around 10 nm. On top of that, electron diffraction did not reveal any new structural phase on the surface, excluding the possibility of a continuous epitaxial thin film of ceria. However, X-ray absorption spectroscopy (XAS) confirmed the presence of cerium atoms in 4 + state, which was deducted by the comparison with Ce^{3+} and Ce^{4+} reference spectra presented in the Fig. 2b having the well-known characteristic shapes for their respective states [26,27]. The XAS measurement also revealed that ceria was distributed uniformly on the sample within the achieved spatial resolution. Therefore, we conclude that the deposited film consists of a largely dispersed material with features too small to be resolved by our microscopic means and lacks the long-range ordering, otherwise detectable by LEED. This is well aligned with the low expected mobility of the deposited atoms and a pseudo-2D layer growth.

The results of the growth at the intermediate substrate temperature (800 K) are shown in the panels of Fig. 3. The Fig. 3a depicts the substrate surface right before the beginning of the deposition. Crystallographic directions of the substrate are again shown by two arrows in the top right corner and point out the preferential alignment of the terrace boundaries to be parallel to ⟨001⟩. As the growth progresses, the first changes in the step boundary preferential direction can be observed, although there is no clear direct observation of the deposited ceria islands (Fig. 3b). The growth was finished after 15 min of cerium deposition, which corresponds to 0.5 ML of the metal (Fig. 3c). In the course of cerium deposition, practically all of the step edges align with ⟨011⟩ directions. Even more interestingly, almost all of the ceria nanoislands (small dark objects in the microscopic image) reside in the corners of the terraces. The interpretation of the terrace step reorientation can be made in terms of the changed chemical environment, when the presence of cerium and sub-stoichiometric cerium oxide islands creates an oxygen-poor environment on the copper surface. One can assume that the nucleation of the cerium oxide islands happens at the terrace steps and, consequently, the boundary reorientation starts at these nucleation centers. As a result, the terrace step edges are pinned to the coalescing islands. XAS again confirmed the presence of the cerium oxide predominantly in its fully oxidized CeO_2 form (Fig. 2a). It is important to say that similar boundary reorientation was also observed upon the growth