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RHEED structural study of the novel tin-cerium oxide catalyst

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Abstract

We present our study of Sn interaction with CeO_2 (1 1 1) thin film supported by a Cu (1 1 1) single crystal. After deposition of metallic tin, tin-cerium mixed oxide is formed in the subsurface region by substitution of cerium atoms by tin in the cerium oxide crystal lattice. This process leads to transformation of the original fluorite structure of cerium dioxide to a simple cubic structure. The excessive metallic tin remaining on the surface forms three populations of small epitaxial clusters with tetragonal structure and the (0 1 0) crystallographic plane parallel to the surface. Two of these populations are favored over the third one, due to their better accommodation to the substrate lattice. After annealing the sample at 400 °C in oxygen atmosphere the metallic Sn clusters disappear and a very thin film of polycrystalline tin dioxide is formed.

Keywords: Tin; Cerium oxide; Mixed oxide; Electron diffraction; Photoelectron spectroscopy

1. Introduction

Cerium oxide, or ceria, is a material widely used in industry and catalysis. Catalytic systems consisting of active metals and cerium oxide are used for example in automotive industry for oxidation of CO and reduction of NO_x in waste gases or as a cathode material in the solid oxide fuel cells [1]. One of the most promising future applications of cerium oxide is its use as an electrode material in Proton Exchange Membrane Fuel Cells (PEMFC) [2,3].

The catalytic properties of cerium oxide originate from its easy transformation from CeO_2 to Ce_2O_3, which is accompanied by a release of oxygen (so called Oxygen Storage Capacity). During this process, the cerium atoms change their oxidation state from Ce^{4+} to Ce^{3+}. This transition has a relatively low activation energy, and can be reversed simply by annealing the catalyst in oxygen-rich atmosphere [4].

The desired catalytic properties of cerium oxide can be adjusted by suitable metal or oxide additives [5–8]. These additives may induce partial reduction of the cerium oxide either by creating oxygen vacancies at the surface or by redistribution of electrons between the cerium atoms and the additive. Tin, in particular, interacts very strongly with the cerium oxide. Previously, it was shown, that deposition of even a small amount of tin causes strong reduction of the cerium oxide and leads to formation of the Sn–Ce–O mixed oxide [9,10]. This mixed oxide exhibits greater catalytic activity than the individual tin and cerium oxides [11]. Similar behavior has also been observed for an inverse system, where metallic cerium was deposited onto a flat tin dioxide surface [12]. Formation of cerium-based mixed oxides was also reported for aluminum [13] and tungsten [14].

The fundamentals of the interaction of metallic dopants with the cerium oxide are still a subject of extensive research. Due to large complexity of conventional catalytic systems, these interactions are often studied on the so called "model systems," represented mainly by flat and atomically clean surfaces with deposited metal islands of defined structure and size. Although cerium oxide single crystals are available, they are not suitable for electron spectroscopic studies, since they suffer from charging effect due to low electrical conductivity. Another possibility is the preparation of thin and flat epitaxial cerium oxide film on a suitable metallic single crystal substrates. High quality cerium oxide thin film growth has been achieved on several metals like Pt [15], Ru [16] and Cu [17].

Photoelectron spectroscopy is a powerful tool for investigating the chemical state of cerium oxide, mainly the transition from Ce^{4+} to Ce^{3+} oxidation state is reflected by changes in

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the Ce 3d core level spectrum. The electronic structure of cerium oxide is characterized by empty 4f level for Ce^{4+} and $4f^1$ configuration for Ce^{3+} [18]. The resulting Ce 3d core level spectrum is composed of five spin-orbit split doublets. Three doublets belong to the Ce^{4+} state, while two others correspond to the Ce^{3+} state. A fitting procedure for deconvolution of Ce 3d spectra giving a very good reproducibility was proposed in [19]. Typically, the ratio of intensities belonging to Ce^{3+} and Ce^{4+} states is interpreted as a measure of the overall oxidation state of the sample. For homogenous samples, this ratio is in agreement with the Ce^{3+}/Ce^{4+} ratio calculated from Ce 4f core level resonant features measured with Resonant Photo-Electron Spectroscopy (RPES) [20].

Although the interaction of tin with cerium oxide and the creation of mixed oxide has already been described [9,10], the actual structure of the Sn–Ce–O mixed oxide is still a matter of discussion. In this work, we present our results of structural studies of the tin-ceria model system prepared by vacuum evaporation of metallic tin onto the epitaxial cerium oxide layer prepared on the (1 1 1) surface of copper single crystal. This system was investigated by Reflection High-Energy Electron Diffraction (RHEED) and X-ray Photoelectron Spectroscopy (XPS). Combination of these methods allowed us to describe the structural changes of the sample depending on its chemical composition and state.

2. Experimental

All experiments were performed in an UHV (Ultra High Vacuum) chamber with base pressure below 1×10^{-7} Pa. As a substrate we used a copper single crystal supplied by MaTecK (∅ 10 mm × 2 mm) with surface polished within 0.1° off the (1 1 1) crystallographic plane. The crystal was cleaned in situ by cycles of Ar^+ ion sputtering (1000 eV, 15 μA/cm^2) and annealing at 630 °C in vacuum, until no impurities were detectable by XPS and a sharp diffraction pattern was obtained by RHEED.

Cerium oxide epitaxial thin film with (1 1 1) surface orientation and thickness of approximately 1.6 nm (about 5 mono layers) was prepared by reactive evaporation of metallic cerium from molybdenum crucible heated by electron bombardment in the background pressure of 5×10^{-5} Pa of oxygen and at the substrate temperature of 250 °C. The cerium oxide thin film structure and its preparation are described in more detail in [21].

Tin was deposited in UHV by evaporation from sapphire crucible heated resistively by tungsten wire at the substrate temperature of 300 °C. The tin deposition rate was calculated from intensity decrease of the Cu 2p core level photoelectron spectrum. Assuming the mean free path of the Cu 2p photoelectrons in tin to be 1.5 nm, as calculated by the TPP2 formula [22], we estimated the value of 0.2 nm/min for the deposition rate of tin.

RHEED diffraction patterns were taken using a CCD camera acquisition system at primary electron beam energy of 25 keV. The sample lattice parameters were calculated from the distances of diffraction spots, which were determined by means of virtual camera and sub-pixel detection methods and fitted with analytical function to obtain precision better than 0.5% [23]. All XPS spectra were taken at $h\nu = 1486.6$ eV (Al K_α) and measured at normal emission angle by HA-100 electron analyzer supplied by VSW.

3. Results and discussion

The cerium oxide thin film was prepared by the previously described procedure and gave a sharp RHEED diffraction pattern which corresponded to the (1 1 1) surface plane of the fluorite crystal structure of cerium oxide [21]. The lattice parameter determined from the distance between diffraction lines in the direction parallel to the surface gave a value of 0.532 nm which is about 2% lower than the bulk value of 0.541 nm [24]. The XPS spectrum of the Ce 3d core level (Fig. 1a) was composed of three doublets, which correspond to different configurations of the Ce^{4+} photoemission final state. The O 1s core level spectrum (Fig. 2a) was composed of a single peak located at the binding energy of 529.6 eV, which originates from lattice oxygen atoms in cerium oxide. Both Ce 3d and O 1s spectra indicate a fully stoichiometric CeO_2.

In the next step of the experiment, approximately 1 nm of metallic tin was deposited onto the (1 1 1) cerium oxide surface at the temperature of 300 °C. The resulting Sn 3d core level spectrum (Fig. 3a) was composed of two distinct doublets. For simplicity in the following discussion we will be referring only to the Sn $3d_{5/2}$ peak. The peak located at the binding energy of 484.6 eV corresponds to metallic Sn, while the peak at 486.4 eV to an oxidized state of tin [25]. Resolving

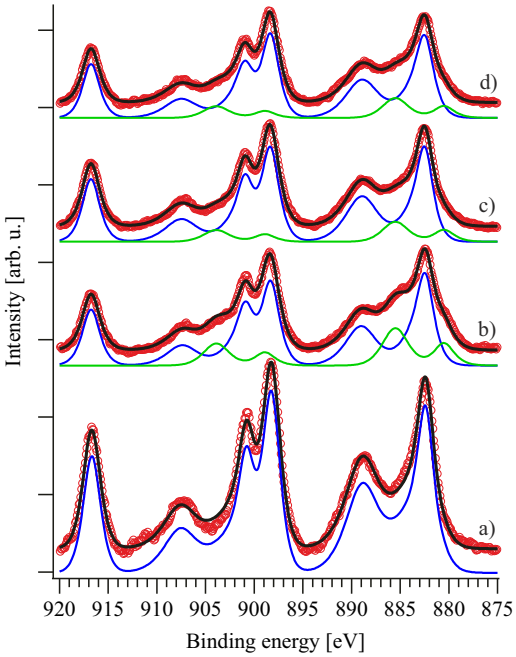

Fig. 1. The Ce 3d core level spectra taken at different stage of experiment: (a) cerium oxide substrate, (b) the first deposition of tin, (c) annealing in oxygen at 300 °C and (d) annealing in oxygen at 400 °C. Doublets corresponding to individual oxidation states were merged together – the blue line for Ce^{4+} state and the light green line for Ce^{3+} state.