RHEED and XPS Study of Tin Interaction with CeO_2 (111) Surface

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Abstract. In this study, we present our results of tin interaction with CeO_2 (111) surface supported by copper (111) single crystal. The system crystallography was characterized by RHEED (Reflection High-Energy Electron Diffraction), while the stoichiometry was investigated by XPS (X-ray Photoelectron Spectroscopy). The ceria thin film was prepared by reactive evaporation of metallic cerium in oxygen atmosphere.
Deposition of low amount of metallic tin onto the ceria substrate led to the formation of polycrystalline layer of tin oxide (SnO_x). The oxidation of tin is made possible by taking the oxygen from ceria surface, as indicated by evolution of peaks in XPS spectra belonging to Ce^{3+} state. Subsequent deposition of tin led to the coexistence of two phases on the surface—small epitaxial clusters of metallic tin with (010) crystallographic plane parallel to the surface and polycrystalline tin oxide. Annealing of the sample up to 250 °C in oxygen atmosphere resulted in the oxidation of metallic tin and disappearance of the epitaxial clusters.

Introduction

Cerium oxide, or ceria, is a widely used material in industry and catalysis. Catalytic systems featuring active metals and ceria 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 solid oxide fuel cells [1].

The catalytic properties of ceria originate from its easy stoichiometric transformation from CeO_2 to Ce_2O_3, which is accompanied by release of oxygen (so called oxygen storage capacity). During this process, the cerium atoms are transformed from Ce^{4+} state to Ce^{3+} one. This transition has relatively low activation energy, and can be reversed by a simple annealing in oxygen abundant atmosphere [2].

The desired catalytic properties of ceria can also be adjusted by suitable metal or metal-oxide additives [3–6]. It has been shown, that tin interacts very strongly with ceria in layers prepared by simultaneous sputtering of ceria and tin, leading to the formation of homogenous mixed Sn-Ce-O oxide, which is accompanied by strong ceria reduction [7]. Thus a large number of Ce^{3+} active sites are created on the surface. This mixed oxide shows greater catalytic activity than the individual pure oxides [8].

In this work, we present our results of study of tin-ceria model system, prepared by vacuum evaporation of metallic tin. This system was investigated by RHEED (Reflection High-Energy Electron Diffraction) and XPS (X-ray Photoelectron Spectroscopy). Combination of these methods allows us to describe the structural changes of the sample depending on its chemical composition and state.

Experimental

All experiments were done in an UHV (Ultra High Vacuum) chamber with a 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° of the (111) crystallographic plane. The crystal was cleaned *in situ* by cycles of Ar^+ ion sputtering (1000 eV, 15 $\mu A/cm^2$) and annealing at 630 °C in vacuum, until no impurities were detectable by XPS and a sharp diffraction pattern was obtained by RHEED.

Cerium was then evaporated from molybdenum crucible heated by electron bombardment in 5×10^{-5} Pa of oxygen. The preparation procedure of epitaxial cerium oxide layer is described in more detail in [9]. The ceria film thickness was estimated from relative decrease of Cu 2p photoelectron spectrum intensity. Tin was deposited in UHV by evaporation from sapphire crucible at the deposition rate of 0.2 ML (Mono Layers) per minute which was estimated from the evolution of intensity of the photoelectron spectra in a similar way to the ceria growth.

RHEED diffraction patterns were taken using a primary electron energy of 25 keV. All XPS spectra were taken at $h\nu = 1486.6$ eV (Al K_α) and measured by HA-100 electron analyser supplied by VSW.

Results and discussion

The epitaxial ceria thin film was prepared by evaporation at the substrate temperature of 250 °C. Its thickness was determined to be approximately 1.6 nm (which is equal to approximately 5 ML of ceria). Diffraction patterns of this surface taken in two main crystallographic directions are given in Figure 1a. Similar patterns repeated every 60° during the sample rotation along its surface normal. The patterns consist of sharp diffraction rods, which correspond to the (111) surface of fluorite crystal structure of ceria. Measurement of the diffraction rod distance gave the value of lattice parameter of ceria of 5.32 Å. This value is 2 % lower than the bulk value of 5.41 Å [10].

Figure 2a represents photoelectron spectrum of Ce 3d level taken from ceria thin film. Ceria electron structure is characterized by empty 4f level for Ce^{4+}, while the Ce^{3+} has $4f^1$ configuration [11]. During photoemission, this level can be filled with electrons from valence band, thus giving raise to different configurations in the photoemission final state. These configurations are seen as spin-orbit split doublets in the Ce 3d level spectra. Three doublets belong to the Ce^{4+} state, while two belong to the Ce^{3+} state. Deconvolution of these spectra, as seen in Figure 2a, is not straightforward, but it has been shown, that ratio of doublet intensities belonging to individual oxidation states is roughly equal to their true ratio in the sample [12]. The doublets belonging to Ce^{3+} are very small ($Ce^{3+}/Ce^{4+} = 0.02$). The small reduction of the oxide layer is probably caused by high-energy electron beam of the RHEED method, which was used to monitor the film growth.

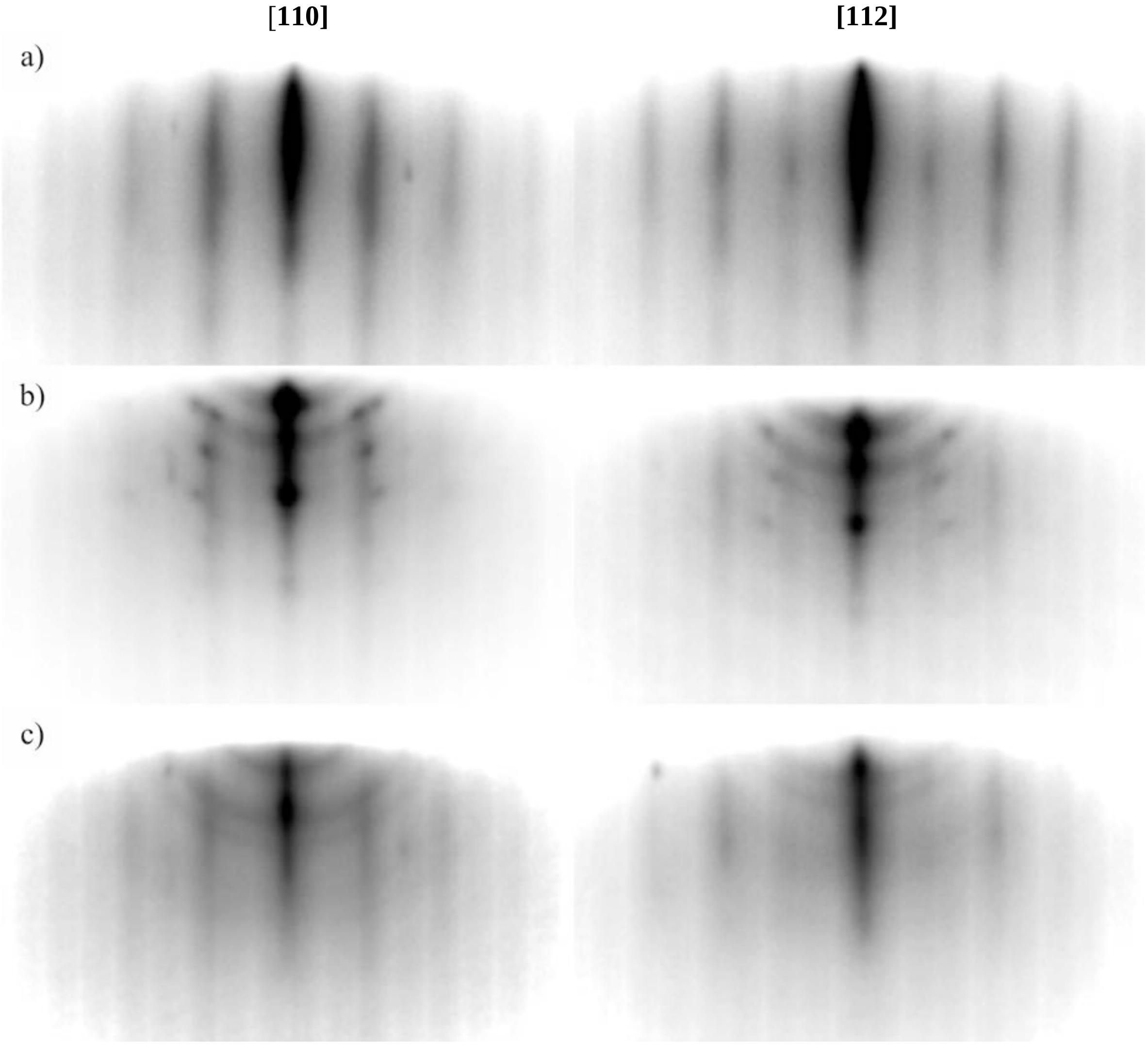

Figure 1. RHEED diffraction patterns taken during experiment at the [110] and [112] crystallographic directions of the substrate. (a) ceria layer, (b) epitaxial clusters of metallic tin, (c) after annealing in oxygen.

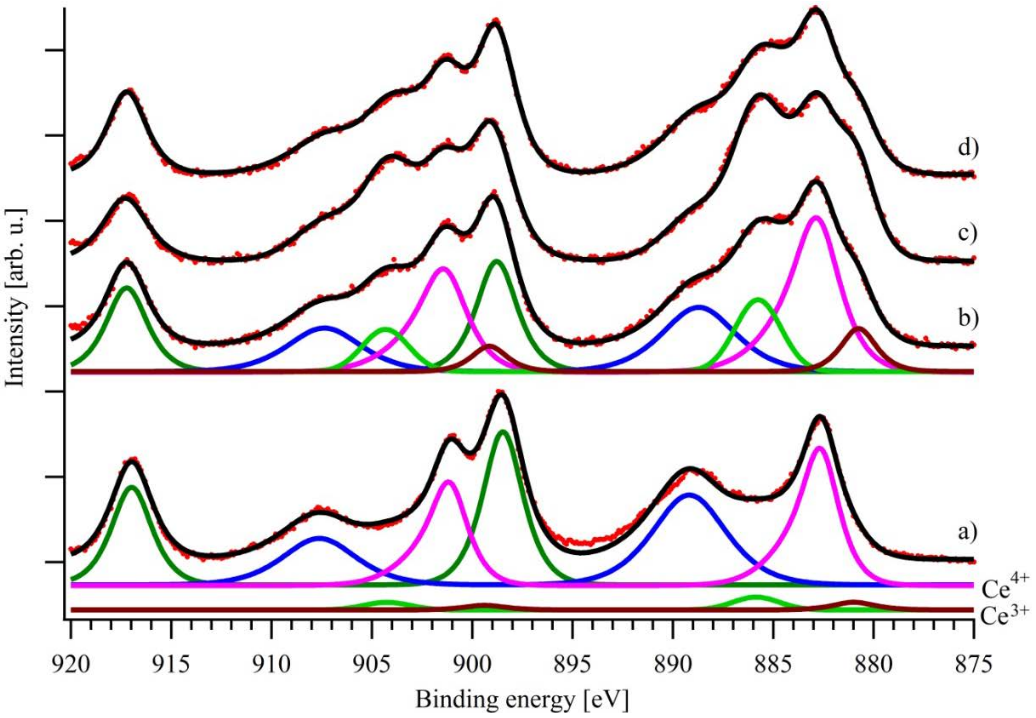

Figure 2. XPS spectra of the Ce 3d core level taken during experiment. Spectra are normalized to demonstrate the changes of the chemical composition of the sample. Spectrum: (a) of the ceria substrate, (b) after first deposition of tin, (c) after second deposition of tin, (d) after annealing in oxygen.

Approximately 2 ML of tin were deposited onto this substrate at room temperature. As expected, the deposition resulted in a strong ceria substrate reduction, which is evident from increasing intensity of peaks belonging to the Ce^{3+} state in the Ce 3d spectrum (Figure 2b). The Ce^{3+}/Ce^{4+} ratio was determined as 0.25. The Sn 3d spectrum (Figure 4a) is composed of two doublets with $3d_{5/2}$ peaks located at the binding energies of 484.6 eV and 486.4 eV, belonging to metallic tin and tin oxide (SnO_x) respectively [13]. The O 1s spectrum (Figure 3b) also exhibits two peaks: one belonging to ceria (529.4 eV) and the other to tin oxide (530.1 eV). Since oxygen peak intensity did not change significantly and signal belonging to Ce^{3+} state intensity increased, it is clear that tin was oxidized by taking the oxygen atoms from the substrate leading to the ceria reduction.

No diffraction features belonging to tin oxide were visible in the diffraction patterns. But the elevated intensity of diffuse background suggested, that the tin oxide has created a thin amorphous film or very small polycrystalline grains giving no diffraction.

At the next step of experiment, another 4 ML of metallic tin were deposited at the temperature of 250 °C. The deposition led to further reduction of ceria (Figure 2c, $Ce^{3+}/Ce^{4+} = 0.35$) and the Sn 3d spectrum has changed considerably (Figure 4b). The intensity of doublet belonging to metallic tin increased with respect to the oxide one. At the same time the oxide state component of Sn 3d spectrum increased almost twice in intensity as well as the tin oxide component in the O1s spectrum (Figure 3c).

Diffraction patterns taken after the second deposition of tin are shown in Figure 1b. Diffraction rods belonging to the epitaxial ceria are still visible. We can also see circles belonging probably to the polycrystalline phase of tin oxide. The main feature is the appearance of diffraction spots. They originate from transmission diffraction from small epitaxial islands and can be assigned to a metallic tin with tetragonal structure with lattice parameters a = 5.82 Å, c = 3.17 Å [10]. Since the surface (111) plane of ceria has six fold symmetry, the metallic tin grains are present in two orientations rotated by 90° in respect one to each other. Both orientations exhibit triple positioning and can be described with the following epitaxial relations:

$$\text{Sn}\ (010) \parallel \text{CeO}_2\ (111)$$
$$\text{Sn}\ [100] \parallel \text{CeO}_2\ [110]$$
$$\text{Sn}\ [100] \parallel \text{CeO}_2\ [112]$$

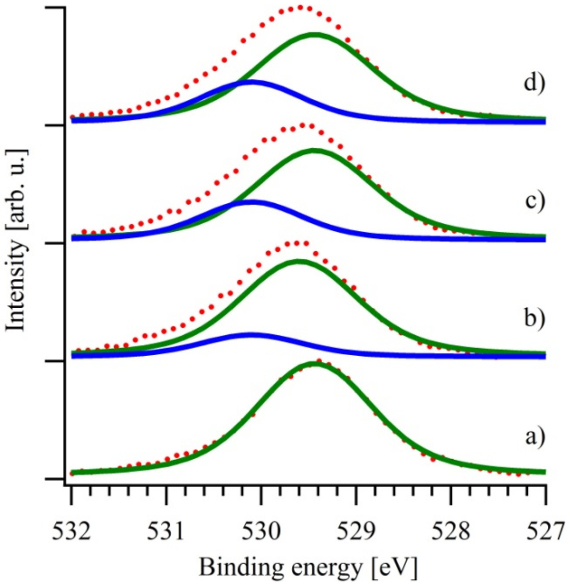

Figure 3. XPS spectra of the O 1s core level taken at different steps of the experiment. The peak at 529.4 eV corresponds to cerium oxide, while the peak at 530.1 eV belongs to tin oxide. (a) Spectrum of ceria substrate. (b) Spectrum after first deposition of tin. (c) Spectrum taken after the second deposition of tin. (d) Spectrum taken after annealing in oxygen

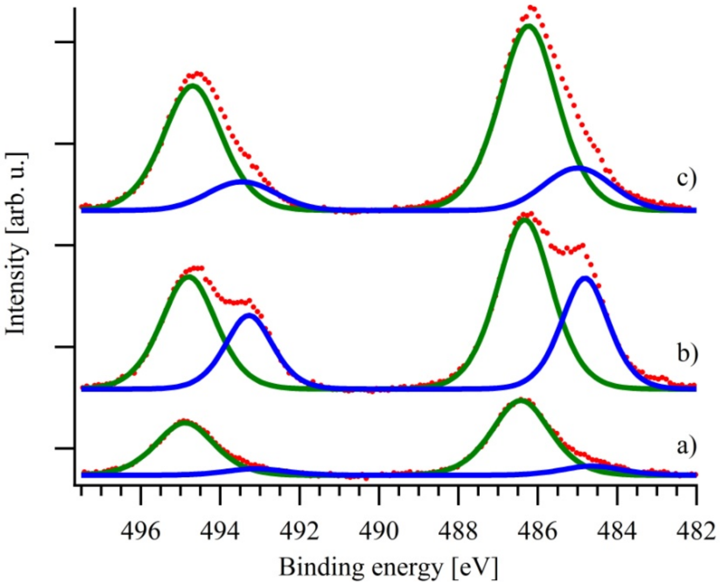

Figure 4. XPS spectra of the Sn 3d core level taken during experiment. The doublet with 3d5/2 peak at 484.6 eV belongs to metallic tin, while the one at 486.4 eV belongs to tin oxide. Spectrum: (a) after first deposition of tin, (b) after the second deposition of tin, (c) after annealing in oxygen.

From the presented results we deduce that the layer of tin oxide prevents the diffusion of oxygen atoms from the ceria substrate to the tin deposit, and in this way enables the growth of metallic tin clusters. Although this interface layer is not preferentially oriented, its low thickness enables the interaction of tin deposit and ceria substrate leading to the growth of epitaxial tin clusters.

The sample was then annealed at the temperature of 250 °C in 5×10^{-5} Pa of oxygen. In the diffraction patterns in Figure 1c, the diffraction spots corresponding to metallic tin clusters entirely disappeared, while the diffraction circles from tin oxide polycrystalline phase became sharper and the diffuse background more intense. The disappearance of metallic tin is also confirmed by XPS. The Sn 3d spectrum in Figure 4c shows increasing intensity of doublet at higher binding energy corresponding to the tin oxide at the expense of metallic doublet. The Ce 3d spectrum in Figure 2d indicates re-oxidation of ceria back to the state prior to the second deposition of tin ($Ce^{3+}/Ce^{4+} = 0.27$). This means, that the metallic clusters are rather unstable and oxidize to tin oxide when being exposed to oxygen.

Conclusion

We have shown that the deposition of small amount of metallic tin onto ceria surface resulted in the growth of polycrystalline layer of reduced cerium oxide, and amorphous layer of tin oxide. Further deposition of tin led to the growth of epitaxial metallic tin clusters. These clusters were oxidized after annealing in oxygen.

References

[1] W. Xiao, Q. Guo, G Wang, *Chem. Phys. Lett.* 368 (2003), 527.
[2] A. Siokou, R.M.Nix, *J. Phys. Chem. B 103* (1999), 6984.
[3] J. Guzman, S. Carrettin, A. Corma, *J. Am. Chem. Soc.* 127 (2005), 3286.
[4] D. Senanayake, J. Zhou, P. Baddorf, R. Mullins, *Sur. Sci.* 601 (2007), 3099.
[5] V. Nehasil, K. Ševčíková, T. Záhoranová, *Surf. Int. Anal.* 42 (2010), 931.
[6] V. Matolín, V Johánek, M. Škoda, N. Tsud, K. Prince, T. Skála, I. Matolínová, *Langmuir* 26 (2010), 12824.
[7] N. Tsud, T. Skála, K. Mašek, P. Hanyš, M. Takahashi, H. Suga, T. Mori, H. Yoshikawa, M. Yoshitake, K. Kobayashi, V. Matolín, *Thin Solid Films* 518 (2010), 2206.
[8] V. Matolín, M. Cabala, V. Cháb, I. Matolínová, K.C. Prince, M. Škoda, F. Šutara, T. Skála, K. Veltruská, *Surf. Int. Anal.* 40 (2008), 225.
[9] V. Matolín, J. Libra, I. Matolínová, V. Nehasil, L. Sedláček, F. Šutara, *App.Surf. Sci.* 254 (2007), 153.
[10] R. Wyckoff, Fluorite structure Crystal Structures 1, Interscience Publishers, New York (1963).
[11] S. Fabris, S. Gironcoli, S. Baroni, G. Vicario, G Balducci, *Phys. Rev. B* 71 (2005), 411.
[12] T. Skála, F. Šutara, M. Škoda, K. C. Prince, V. Matolín, *J. Phys.: Cond. Matt.* 21 (2009), 55.
[13] V. Jiménez, A. Fernández, J.P. Espinós, A.R. González-Elipe, *Surf. Sci.* 350 (1996), 123.