



	Experiment title: In-situ oxidation study of Pd nanoparticles	Experiment number: ME-867
Beamline: ID - 03	Date of experiment: from: 09.02.05 to: 17.02.05	Date of report: 24.02.05
Shifts: 18	Local contact(s): Ernesto PAISER	<i>Received at ESRF:</i>
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Report:

We have carried out an in-situ X-ray scattering study of the oxidation of Pd particles grown epitaxially on MgO (001) substrates. The experiment has been performed at a photon energy of 0.721 Å using the high-pressure Be – chamber, which allows at variation of the temperature of the sample as well as the partial pressure of the oxygen in a wide range.

The characterization of the particles size and shape has been done before starting oxidation. According to the literature [1], Pd particles grown at MgO (001) have a shape of the pyramids or octahedra restricted by the (111)_{fcc} planes [2] depending on the insize; the top and side corners are truncated by (100) planes (Fig. 1). The observed crystal truncation rods (CTR) coming from the particle facets (Fig. 2), indicate that the particles have a shape of pyramids or octahedral truncated on the top, as it is illustrated in Fig. 1. We have used in Figs. 2 the so-called “(100) surface” unit cell. The vectors of this unit cell are related to the vectors of

the *fcc* unit cell by the following equation:
$$\begin{pmatrix} \bar{a} \\ \bar{b} \\ \bar{c} \end{pmatrix}_s = \begin{pmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} \bar{a} \\ \bar{b} \\ \bar{c} \end{pmatrix}_{fcc}$$
 . It is easy to see, that the (111)_{fcc}

crystallographic planes correspond to the (101)_s planes in the used coordinate system. The measured widths of the Pd Bragg peaks for the studied sample correspond to the height of the particles $h \sim 2\pi/\Delta_{(001)} = 30$ Å and the lateral size $D \sim 2\pi/\Delta_{(100)} = 50$ Å. Here $\Delta_{(001)}$ and $\Delta_{(100)}$ are the FWHM of the Bragg peaks in the (001)_s and (100)_s directions of the reciprocal space, respectively.

The oxidation of the samples the temperatures in the range from 250 – 300 °C in an oxygen pressure range from $10^{-6} - 10^{-1}$ mbar leads to a strong decrease of the CTR intensity. It is known from the literature [3 - 5]

that the formation of so-called surface oxides set in during the oxidation of single crystalline surfaces at these conditions: $(\sqrt{5} \times \sqrt{5})R27^\circ$ structure has been found during the oxidation of Pd (001) [3, 4] and the $(\sqrt{6} \times \sqrt{6})$ 2D oxide lattice forms at the Pd (111) surface [5]. Our previous studies [6] have revealed also, that the size of the metallic Pd “core” of the nanoparticles gradually decreases at 350 °C if the pressure of oxygen increases from 10^{-6} up to to 10^{-1} mbar. We did not find any Bragg peaks

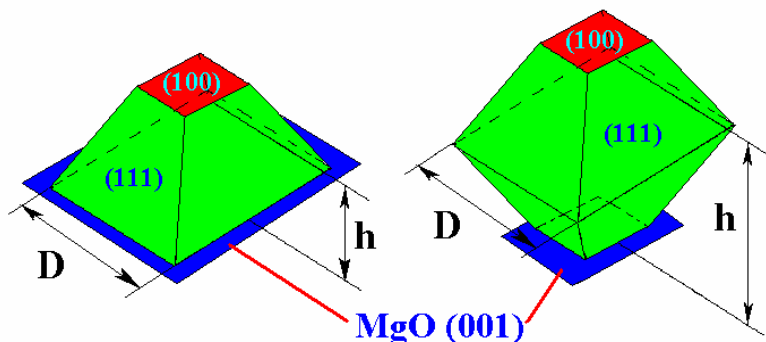


Fig. 1. Schematic representation of shape of Pd nanoparticles grown at MgO(001).

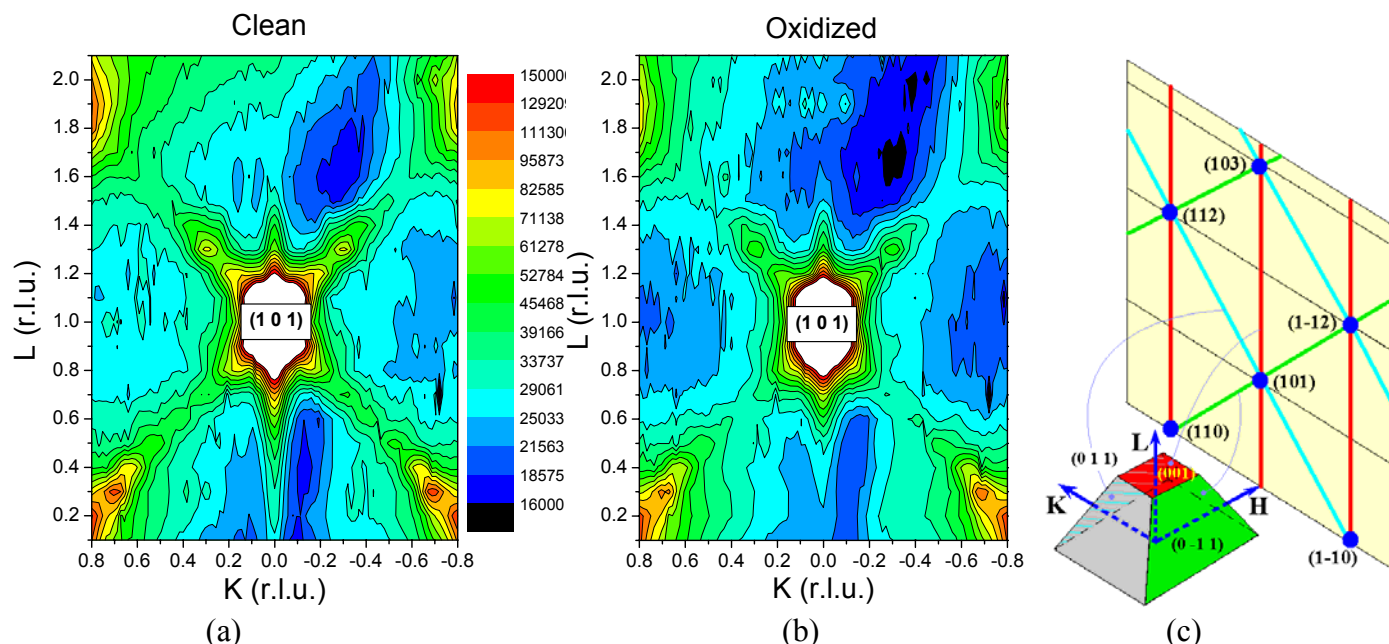


Fig. 2. The scattered intensity distribution in the (100) plane of the reciprocal space for the clean sample (a) and after the oxidation at $T=250\text{ }^{\circ}\text{C}$ and $p_{\text{O}_2}=5 \cdot 10^{-6}\text{ mbar}$ (b); (c) – an illustration of the mechanism of appearance of CTR.

corresponding to the surface oxides structures known for the single crystalline surfaces $(111)_{\text{fcc}}$ and $(100)_{\text{fcc}}$. The $(\sqrt{5} \times \sqrt{5})R27^{\circ}$ surface oxide at the Pd (100) hinders the further oxidation and growth of the 3D oxide at the temperatures below $370\text{ }^{\circ}\text{C}$ [3]. It was found in the present experiment, that the tetragonal bulk PdO [7] is growing during the oxidation of Pd nanoparticles even at the temperature as low as $T=300\text{ }^{\circ}\text{C}$, if the pressure increases above 10^{-1} mbar . In our opinion, these findings indicate formation of a 2D oxide layers or chemisorbed oxygen layer at the free surfaces of the nanoparticles. The decreasing CTR intensity indicates probably (i) that coordinatively unsaturated atoms at the edges of the particles get firstly oxidized, what leads to the “hogging” of the facets and (ii) the roughening of the facets. It can be suggested from these observations that the surface oxide at the free faces of nanoparticles does not have a pronounced crystalline structure.

The complete oxidation of the nanoparticles leads to the formation of the bulk PdO. Both the powder rings and the Bragg peaks from epitaxially grown PdO have been observed. Three different domains of the epitaxial PdO were found. They are presented schematically at the Fig. 3.

The reduction of the oxidized nanoparticles ($p < 10^{-9}\text{ mbar}$, $T \sim 670\text{ }^{\circ}\text{C}$) leads to formation of metallic Pd nanoparticles. The width of the Pd Bragg peaks and observed CTR indicate that the particles after reduction have the similar size as the particles before oxidation and show the same type of the facets, namely $(111)_{\text{fcc}}$ and $(100)_{\text{fcc}}$.

References

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- [2] Subscript *fcc* indicates, that the Miller indices are given in the frame of the face centered cubic unit cell.
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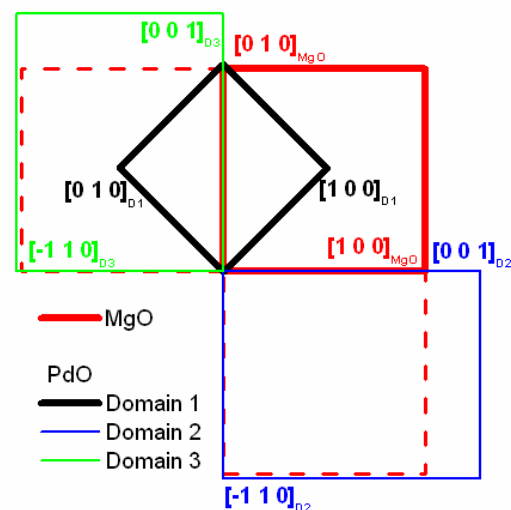


Fig. 3. Schematic presentation of the in-plane orientations of different domains of bulk PdO forming by the oxidation of Pd / MgO $(0\ 0\ 1)$. The plane of the figure is parallel to the substrate surface. Normal to the surface are $[001]$ direction for of the D1 and $[110]$ – for D2 and D3.