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RHEED investigation of lattice deformations of α-Al_2O_3 supported Pd particles

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Abstract. Pd particles were grown on (0001) and (2-1-10) surfaces of α-alumina single crystals by means of molecular beam epitaxy. Particles exhibited (111) epitaxy preferentially. The orientational relationship, as well as the precise values of lattice parameter, were determined from RHEED measurements. The Pd crystallographic lattice was found to be deformed via an important contraction of the lattice parameter in the direction perpendicular to the interface plane. This deformation was size-dependent, which made this study interesting from the point of view of size effect study in heterogeneous catalysis.

PACS. 61.14.Rq Other electron diffraction and scattering techniques for structure analysis – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 68.55.-a Thin film structure and morphology

1 Introduction

Investigation of metal–insulator interfaces as the first stage of thin metallic film growth is of great scientific interest. The interface formation determines the physical properties of the adlayer/insulator system-like adhesion and of the continuity and morphology of the deposited films, and plays an important role in numerous industrial applications.

In heterogeneous catalysis, the most frequently investigated model catalysts, single crystals, are very different from the real catalytic systems, and it is thus difficult to use them for investigation of the size effects. This has led to the utilization of more realistic model catalysts exhibiting metal particles deposited on a flat support. The insulator-supported epitaxial metallic particles can be used as well-defined model catalysts, permitting one to investigate mechanisms of catalytic reactions, including the effects connected with the catalyst particle size, morphology, interaction with support, and particle reconstruction.

The main aim in this work was to investigate the growth of small Pd particles on an α-Al_2O_3 (0001) and (11-20) substrate. As we have shown previously [1–3], the particles exhibited the (111) epitaxy, i.e., the (111) plane parallel to the substrate at different azimuthal orientation. We investigated the particle/substrate epitaxial parameters and the evolution of Pd lattice parameter during the growth by RHEED (reflection high-energy electron diffraction). The precise parameter measurement using the so-called subpixel detection method [4] showed the lattice deformation to be dependent on particle size.

2 Experiment

The deposits of palladium were prepared on Al_2O_3 substrates in ultrahigh vacuum conditions ($P < 1 \times 10^{-7}$ Pa). The special MEBES (micro electron beam evaporation source) evaporation cell allowed the preparation of very thin deposits at low evaporation rate. In this way, homogeneous populations of single-crystalline particles were prepared. The material to be evaporated, which was in the form of a tip on a high positive potential, was heated by impinging electrons emitted from a heated cathode.

The RHEED system consisted of a 40 kV electron gun, a CCD camera, and a computer system permitting the intensity measurements of diffracted electron beams and recording the real-time development of the diffraction pattern during sample treatment. This system has been described elsewhere.

Special software permitted us to obtain the position of diffraction spots with very high precision [4] and to evaluate the lattice parameters and deformations. A movable sample holder made it possible to change the angle of incidence as well as the azimuthal direction of the incident electron beam with respect to the sample surface. The chamber was also equipped with the fast entry air lock for rapid sample exchange. We prepared the (0001) and (11-20) Al_2O_3 mechanically and chemically polished substrates by heating them at 1470 K for four hours in air. Before the deposition, the substrates were heated at 820 K for half an hour in UHV conditions.

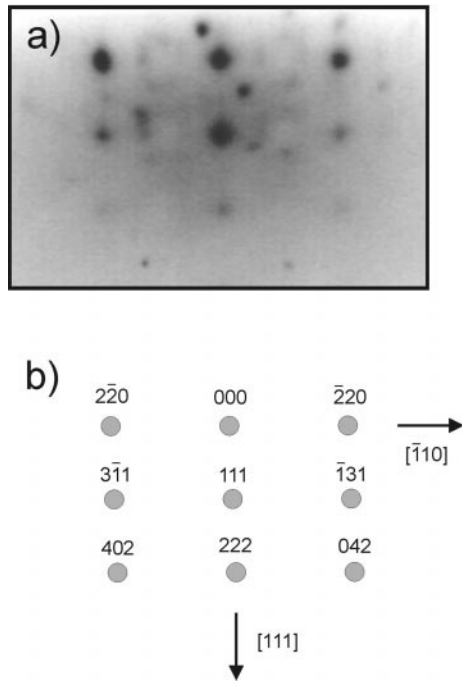

Fig. 1. The diffraction pattern of the Pd deposit on the (0001) Al_2O_3 substrate (a) and its interpretation (b). The primary electron beam is parallel to the [2-1-10] Al_2O_3 direction. The noninterpreted spots correspond to the diffraction from substrate surface and to double diffraction.

3 Results

3.1 The (0001)Al_2O_3 substrate

Pd was deposited at a constant deposit rate, and the RHEED diffraction pattern development was recorded in real time with a video recorder. It permitted us to treat the diffraction pattern later on in order to compare the particle lattice parameter values as a function of deposition time. After the whole deposition run, the particles' size and morphology were investigated by means of transmission electron microscopy (TEM) using the method of transfer carbon replica. The average particle diameter was found to be 6.2 nm, and the particle density $6.2 \times 10^{11}\,\mathrm{cm}^{-2}$; these values corresponded to the deposition flux of $7.3 \times 10^{12}\,\mathrm{atoms\,cm}^{-2}\,\mathrm{s}^{-1}$.

The final diffraction pattern is presented in Fig. 1a and the corresponding interpretation in Fig. 1b. The spot-like form of diffraction spots showed the three-dimensional growth of particles. It was confirmed by the TEM observations mentioned in the previous paragraph. The orientation relationship between substrate and deposit lattices were as follows:

$$(111)\mathrm{Pd}\ //\ (0001)\mathrm{Al_2O_3}\,,$$
$$[211]\mathrm{Pd}\ //\ [2\text{-}1\text{-}10]\mathrm{Al_2O_3}\ \text{(double positioning)}\,.$$

The precise measurement of distances between the diffraction spots permitted us to obtain the Pd lattice parameter value a in directions parallel and perpendicular to the substrate surface respectively. Both are plotted in Fig. 2. We can see that a_{parallel} kept the constant value slightly dilated with respect to the bulk value (0.389 nm), in contrast to the $a_{\mathrm{perpendicular}}$, which exhibited variable contraction, reaching a minimum at deposition time 150 s.

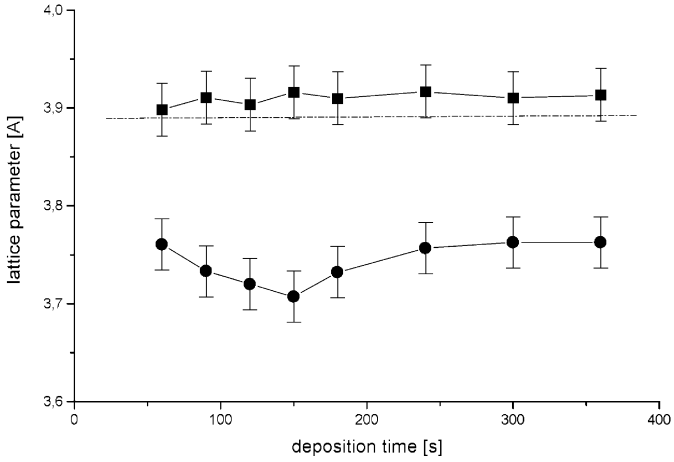

Fig. 2. The evolution of the lattice parameter value of Pd particles in directions parallel (■) and perpendicular (●) to the (0001) Al_2O_3 substrate surface during the growth.

The epitaxial relationships were calculated as a ratio of experimentally determined final distances between (0001)alumina oxygen atoms and (111)Pd atoms, $r = d_{\mathrm{O}}/d_{\mathrm{Pd}}$, in the [2-1-10] and [10-10] substrate directions:

$$r_{[2\text{-}1\text{-}10]} = 0.99\,,$$
$$r_{[10\text{-}10]} = 0.99\,.$$

These results show that Pd particles prefer to expand slightly even though the bulk (nonexpanded) close-packed (111)Pd surface matches the (0001) substrate perfectly. It seems reasonable to explain this slight expansion as a compromise between a dilatation tendency of palladium, observed, for example, in [5], and the effort to achieve matching along the most close-packed rows of these lattices. The appropriate hard ball model of one particle is presented in Fig. 3a. The important contraction along the [111] Pd direction confirms the previous observation using the same system [3], with little difference in the minimum form, and its time-location can be caused by deposition rate fluctuations.

3.2 The (2-1-10)Al_2O_3 substrate

The experiment was performed at the same evaporation rate as in the previous case. The RHEED diffraction pattern and its interpretation are shown in Fig. 4a and b, respectively. Two sets of diffraction spots indicated two particle populations. The more intense set of spots corresponds to the more extensive particle population of the orientation relationship

$$(111)\mathrm{Pd}\ //\ (2\text{-}1\text{-}10)\mathrm{Al_2O_3}\,,$$
$$[211]\mathrm{Pd}\ //\ [0001]\mathrm{Al_2O_3}\ \text{(double positioning)}\,.$$

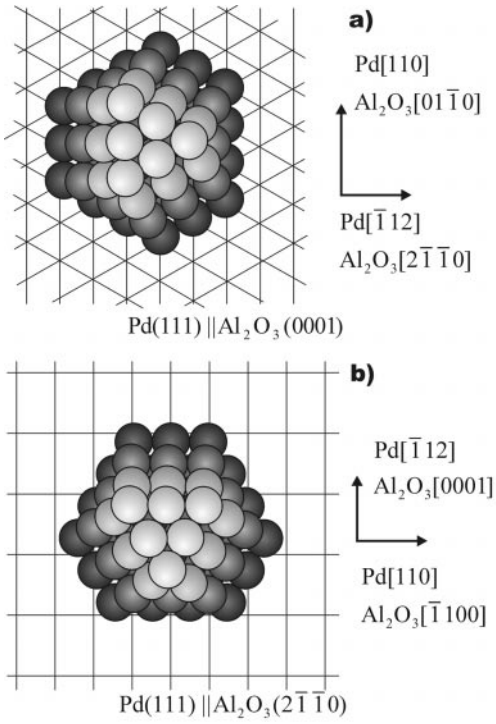

Fig. 3. Hard ball model of one Pd particle on (0001) (a) and (2-1-10) (b) α-Al_2O_3 substrates.

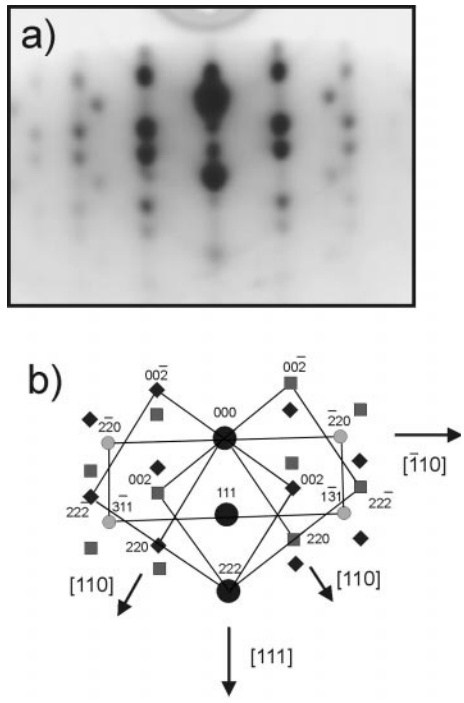

Fig. 4. The diffraction pattern of Pd deposit on (2-1-10) Al_2O_3 substrate (a) and its interpretation (b). The primary electron beam is parallel to the [-1100] Al_2O_3 direction. The noninterpreted spots correspond to the diffraction from substrate surface and to double diffraction.

that is depicted in Fig. 3b. The secondary population is rotated by 90° with respect to the first one ([211] Pd // [-1100] Al_2O_3 (double positioning)).

Lattice parameter variation versus deposition time is shown in Fig. 5. We can see that the a_{parallel} remained constant (slightly dilated with respect to the bulk value); this is similar to the case of (0001) alumina. The $a_{\text{perpendicular}}$ value exhibited decreasing contraction, reaching a maximum close to the bulk value at the deposition time of 600 s.

The epitaxial relationship r was calculated as a ratio of experimentally determined final distances between (2-1-10)alumina oxygen atoms and (111)Pd atoms along [0001] and [-1100] substrate directions:

$$r_{[0001]} = 0.91\,,$$
$$r_{[\text{-}1100]} = 1.00\,.$$

The small interfacial expansion of the Pd(111) surface led to the row matching along the [110]Pd and [-1100]Al_2O_3 direction. The important perpendicular contraction was size-dependent behavior, which was more pronounced in the case of smaller particles (average particle size should increase with the amount of deposited metal).

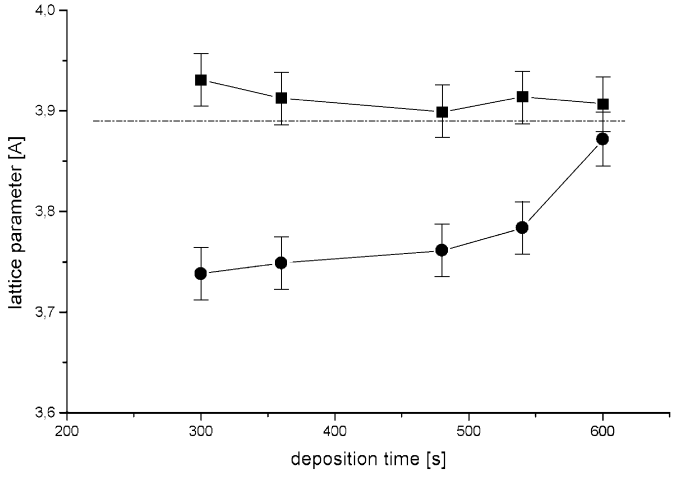

Fig. 5. The evolution of the lattice parameter value of Pd particles in directions parallel (■) and perpendicular (●) to the (2-1-10) Al_2O_3 substrate surface during the growth.

4 Conclusion

Palladium particles on (0001) and (2-1-10)α-Al_2O_3 surfaces grow preferentially with (111) epitaxial orientation. In both cases, the important lattice deformations are given by great perpendicular contraction and slight lateral expansion. One can assume that this deviation from the perfect cubic form of crystal lattices can bear on some catalytic size effects observed in the case of small supported particles.

Despite the very different substrate structures, the observed behavior of Pd lattice parameter is similar in the both cases. One can conclude that the perpendicular lat-

tice deformation is a property of (111) epitaxial Pd particles independent from the nature of the Pd/alumina interface. This idea is supported by the fact that the opposite behavior was observed in the case of (001)Pd particles deposited on NaCl. In that case, the lattice expanded in the direction perpendicular to the interface surface [3].

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