

STRUCTURAL CHARACTERIZATION OF Pd THIN FILM GROWTH ON Al₂O₃ USING PHOTOELECTRON AND ION SPECTROSCOPY

N.Tsud, D.Bača, K.Veltruská, V.Matolín

Department of Electronics and Vacuum Physics, Faculty of Mathematics and Physics,
Charles University, V Holešovičkách 2, 18000 Prague 8, Czech Republic

X-ray photoelectron spectroscopy (XPS) and low energy ion scattering spectroscopy (ISS) was used to investigate model catalyst thin film growth mode in the submonolayer region. Palladium was deposited step by step in-situ using an electron beam evaporator on different aluminum oxide substrates. The Pd growth process was monitored by means of the Pd3d_{5/2} binding energy, modified Auger parameter and full width at half maximum of the Pd3d_{5/2} peak. The deposited layer morphology was determined using the QUASES software based on analysis of the Pd peak shape and background. The relative coverage and the thickness of Pd films obtained on the different substrates are compared. The results showed that the oxide structure and the metal-substrate interaction (MSI) influenced the particle shape and growth.

Introduction

The interactions of small metal clusters with oxide substrates are presently a subject of great interest that is motivated primarily by the technological importance of metal clusters in heterogeneous catalysis. In the case of supported catalysts metal-substrate-interaction (MSI) could influence the adsorption and also morphological size dependent properties of particles. The smaller particles should exhibit the most important MSI.

Investigation of size effect upon CO adsorption on alumina supported particles showed a surprising effect – CO partially dissociated on small Pd clusters deposited on mica [1], γ -alumina [2] and thin aluminium oxide film [3]. It was found that smaller particles exhibited higher dissociative activity. On the other hand, CO adsorption was molecular on Pd clusters deposited on sapphire [4, 5] and Al₂O₃(111)/NiAl(110) [6]. However, the question of the mechanism of dissociation process enhanced by this unexpected behavior has not been explained yet. The possible origin of this phenomenon could be linked to the metal-substrate inter-

action (MSI), which may be influenced by the thickness, surface structure, and/or stoichiometry of the alumina support, that could be in relation with the MS charge transfer. This assumption was supported by a recent observation of Pd 3d_{5/2} initial state shift for Pd on γ -alumina prepared by thermal oxidation of aluminium that was associated to electron transfer in the direction substrate-deposit [7].

The MSI depends on two parameters: the electronegativity of the metal and the ionic-covalent character of the oxide surface [8, 9]. Moreover, stable oxide surfaces appear to be generally reconstructed or/and non-stoichiometric [10, 11]. It has been shown that the aluminum oxide surface can be identified by a characteristic electronic structure in the band gap [8] that is very sensitive to the surface ionicity. Then we can expect that growth mode would differ for different alumina modifications.

In this work, Pd/Al₂O₃ model systems are examined with X-ray photoelectron spectroscopy and low energy ion scattering spectroscopy. Especially, the aim is to characterize Pd thin film growth modes in the submonolayer region.

Experimental

In this study we present the results obtained for following substrates (10×10 mm in size): polycrystalline Al_2O_3 ($\gamma\text{-Al}_2\text{O}_3$) thin film on Al (G) exhibiting the cubic structure [12], and hexagonal $\alpha\text{-Al}_2\text{O}_3$ (0001) single-crystal (sapphire) (S), thin amorphous oxide Al_xO_y on Al (A). The $\gamma\text{-Al}_2\text{O}_3$ substrate was prepared by heating of chemically polished Al foil in air at 900 K for 24 h before inserting into vacuum. The $\alpha\text{-Al}_2\text{O}_3$ substrate was pre-treated by heating of mechanically polished sapphire crystal wafer in air at 1500 K for 2 h before inserting into vacuum. The (A) substrate was prepared by Ar^+ ion bombardment which removed partially the natural oxide layer on aluminum.

Experiments were performed in UHV chamber equipped with multichannel hemispherical analyzer OMICRON EA 125, dual Al/Mg X-ray source and differentially pumped ion gun OMICRON ISE 10. In this work the Mg $K\alpha$ line (1253.6 eV) was used for all XPS measurements. ISS was carried out using He ions at primary energy 2keV ($P_{\text{He}}=3 \times 10^{-5}$ Pa, current density of about $0.05 \mu\text{A}$).

The substrates were cleaned by Ar^+ ion bombardment (2.5×10^{-3} Pa, 500 eV, $1.5 \mu\text{Acm}^{-2}$) using the ion gun. The cleanliness of the surface as well as the possible effect of preferential sputtering of surface components, which may cause the changes in surface stoichiometry, was monitored during the cleaning by means of scattered ion analysis. Pd particles were deposited in-situ from the electron beam evaporation source permitting to control the evaporation rate by monitoring the Pd^+ ion current. The deposit layer morphology was investigated using QUASESTM software (the software package for quantitative XPS of surface nanostructures by analysis of the peak shape and background) made by Quases Tougaard ApS. The principles of the method are explained in Refs. [13,14]. The experimental set-up is described in details in [7].

Results and discussion

Ion scattering spectroscopy (ISS) is a surface analytical technique, that is sensitive to the very first atomic layer of the surface. The measured spectrum gives the intensity distribution of the scattered He ions versus their detected kinetic energy which is directly related to the mass of the target atoms. Fig. 1 shows the typical spectrum obtained from sputtered $\gamma\text{-Al}_2\text{O}_3$. Since the neutralization terms for Al and O in alumina are unknown, it is impossible to determine exactly stoichiometry for this layer. However, the ratio of Al to O intensity is directly proportional to the real surface stoichiometry. In tab. 1, the intensity ratio of Al and O is shown for all sputtered substrates. The value for $\gamma\text{-Al}_2\text{O}_3$ is closed to that for $\alpha\text{-Al}_2\text{O}_3$ while for thin oxide it is much higher.

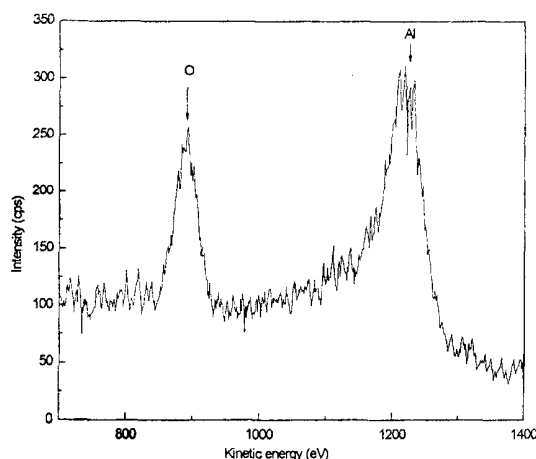


Fig. 1. ISS spectrum of sputtered $\gamma\text{-Al}_2\text{O}_3$

Table 1. The ISS intensity ratio of Al and O for all sputtered substrates.

Substrate	$I_{\text{ISS}}(\text{Al})/I_{\text{ISS}}(\text{O})$
$\alpha\text{-Al}_2\text{O}_3$	1.75 ± 0.01
$\gamma\text{-Al}_2\text{O}_3$	2.05 ± 0.01
amorphous Al_xO_y	5.68 ± 0.01

First we investigated the growth mode of Pd deposit on γ (G) and α (S) alumina. The evaporation cell was operated at constant evaporation flux for all deposits. In Fig. 1 we

plotted the Pd 3d_{5/2} peak intensity as a function of deposition time for both substrates. It can be seen that both curves have nearly identical shape showing the same growth mode (the identical deposit morphology for given deposited Pd amount should give an identical XPS signal). The final points corresponding to Pd3d_{5/2}/Al2p intensity ratio of 3.5 indicate that more than 1 monolayer of Pd was deposited. More detailed information about the layer parameters was obtained using the QUASES analysis. It was found that Pd formed the island (non-continuous) layer structure that explained the smooth (unbroken) form of the curves in Fig. 2.

In Fig. 3a we plotted the average island height *h* as a function of deposition time for the sample (G). The value of *h* rapidly reached the maximum at 1 nm and remained constant till the end of the deposition. In Fig. 3b we plotted the corresponding Pd/substrate relative coverage. Both curves clearly indicated that there were two time intervals of different growth modes. During the first deposition time interval from 0 to 9 minutes, labeled I, palladium formed three dimensional clusters. The second one, characterized by linear coverage increase (labeled II),

was the interval of the lateral growth mode giving formation of flat islands of constant height equivalent to 5 monolayers approximately. The sample A structure was not quantified by QUASES because it was designed for analysis of deposits on homogeneous substrates only.

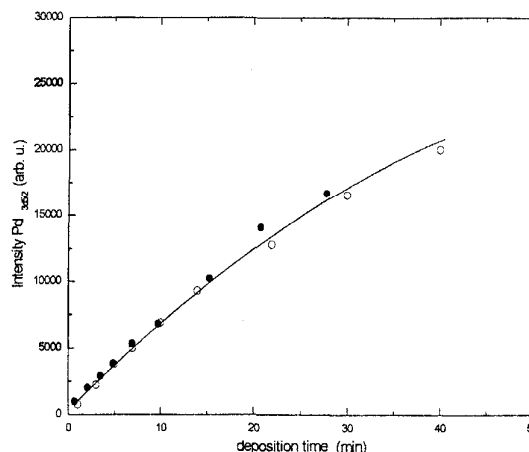


Fig. 2. The change of the Pd3d_{5/2} intensity as a function of the deposition time for substrate γ -Al₂O₃(O), α -Al₂O₃(•)

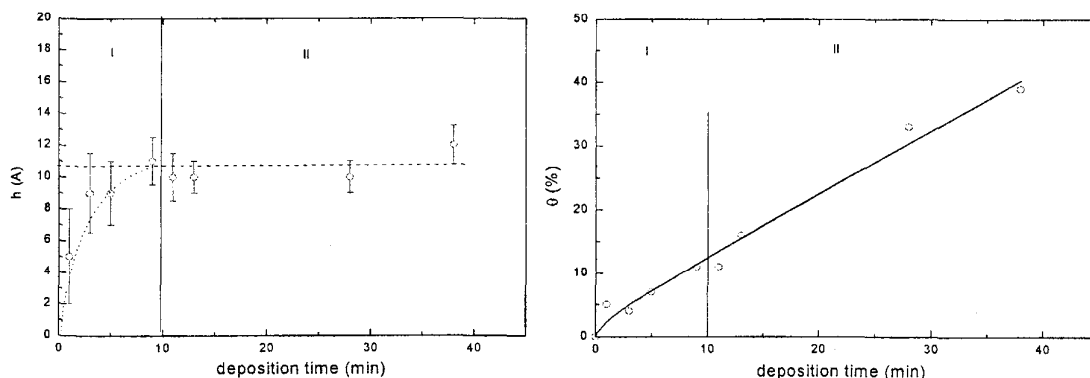


Fig. 3. Plots of the average island height *h* (a) and the Pd/substrate relative coverage (b) as a function of deposition time for γ -Al₂O₃ substrate.

The Pd core level binding energy shifts to higher values for smaller particles and full width at half maximum (FWHM) of peaks decreases during the growth. FWHM parameter variations are generally associated

with a mean coordination number of cluster atoms. We plotted FWHM of Pd 3d_{5/2} versus deposition time in Fig. 4. For samples G and S, it can be seen that FWHM decreases rapidly in the interval I whereas it remains con-

stant in the zone II. These results fit very well with the growth mechanism presented above. The average coordination number increases in I and remains constant in the “flat island” zone II, reaching the same value for both samples. On the other hand, for the sample A decrease of FWHM is much slighter and we can see that FWHM becomes constant after longer deposition time, i.e. at higher amount of Pd deposit. This behavior can be explained by difference in the initial phase of cluster growth. For the less reduced samples (G and S) the bonding of Pd atom to the substrate is weaker which results in higher surface mobility of the atom. The surface of the substrate A is, on the contrary aluminium rich. The excess of Al atoms on the surface may act as induced nucleation centers for the creation of new Pd islands, because metallic Pd-Al bonding is much stronger, forming a twofold covalent bond Pd-Al [9]. It means that the density of clusters should be higher and their size smaller, with lower average coordination number, for the sample A compared to the samples G and S.

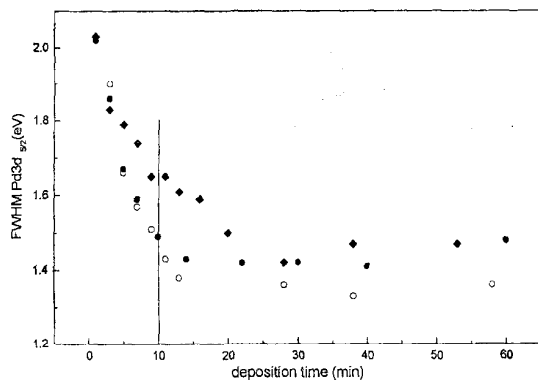


Fig. 4. FWHM of Pd3d_{5/2} peak variation versus deposition time for the substrates γ -Al₂O₃(O), α -Al₂O₃(●), amorphous Al_xO_y(◆)

Conclusions

In spite of that surface sensitive spectroscopy techniques permit to determine very precisely surface composition of heterogeneous catalyst, in-situ determination of ultra-thin layer morphology represents a key

problem limiting investigation of size effect in heterogeneous catalysis model studies. Since the use of scanning microscopy methods (STM, AFM) for this purpose is not sufficiently developed for the time, surface spectroscopies still remain a promising source of supported particle shape and size.

In this work we compared results of XPS and ISS studies of non-continuous Pd layer growth on different aluminium oxide substrates exhibiting different surface stoichiometry. Two different growth mode were determined. The formation of flat islands via lateral growth of several layer thick nucleus was characteristic for more stoichiometric substrate while on Al-rich surface Pd formed small clusters with higher density. The first growth mode was explained by higher Pd atom diffusion length on alumina surface, the second one was tentatively explained by more strong Pd-substrate interaction giving rather formation of high density nucleus and consequently smaller Pd clusters.

Acknowledgement

This work was supported by the Czech Grant Agency under the Grant No. 202/99/1714, and by the Czech Ministry of Education, Youth and Sports under the Project No. VS97116.

References

1. V. Matolin, E. Gillet, N. Krus, *Surf. Sci.* **186**, L541 (1987).
2. I. Stará, V. Matolín, *Surf. Sci.* **313**, 99 (1994).
3. D.R. Rainer, M.C. Wu, D.I. Mahon, D.W. Goodman, *J. Vac. Sci. Technol. A*, **14**, 1184 (1996).
4. I. Stará, V. Matolín, *Surf. Rev. Lett.* **4**, 1353 (1997).
5. H. Cordatos, T. Bunluesin, R.J. Gorte, *Surf. Sci.* **323**, 219 (1995).
6. M. Baumer, J. Libuda, A. Sandell, H.J. Freund, G. Graw, Th. Bertrams, H. Neddermeyer, *Ber. Bunsenges. Phys. Chem.* **99**, 1381 (1995).

7. N.Tsud, V.Johánek, I.Stará, K.Veltruská, V.Matolín, *Surf. Sci* (submitted 1999).
8. B.Ealet, E.Gillet, *Surf. Sci.* **367**, 221 (1996).
9. B.Ealet, E.Gillet, *Surf. Sci.* **281**, 91 (1993).
10. J.Ahn, J.W.Rabalais, *Surf. Sci.* **388**, 121 (1997).
11. I.Stará, D.Zeze, V.Matolín, J.Pavluch, B.Gruzza, *Appl. Surf. Sci.* **115**, 46 (1997).
12. M.F.Gillet, S.Channakhone, *J. Catal.* **97**, 427 (1986).
13. S.Tougaard, *J. Vac. Sci. Technol. A*, **14**, 1415 (1996).
14. *Quantitative Analysis of Surfaces by Electron Spectroscopy. User's guide* (QUASES Tougaard Aps, Odense 1999).

СТРУКТУРНІ ДОСЛІДЖЕННЯ РОСТУ ТОНКИХ ПЛІВОК Pd НА Al₂O₃ ЗА ДОПОМОГОЮ ЕЛЕКТРОННОЇ ТА ІОННОЇ СПЕКТРОСКОПІЇ

Н.Цуд, Д.Бача, К.Велтруска, В.Матолін

Кафедра електроніки і фізики вакууму, Математико-фізичний факультет,
Карлів університет, Прага, Чехія

За допомогою рентгенівської фотоелектронної спектроскопії та спектроскопії розсіювання низькоенергетичних іонів досліджено модельний каталітичний режим росту тонкої плівки у субмоноатомній області. За допомогою електронного пучка паладій поступово напилювався на різні підкладки з оксиду алюмінію. Процес росту паладію контролювався вимірюванням енергії зв'язку Pd3d_{5/2}, модифікованого параметра Оже та напівширини піка Pd3d_{5/2}. Морфологія напиленого шару визначалася за допомогою програми QUASES, що ґрунтується на аналізі форми піка Pd та фону. Порівнюються відносне покриття і товщина паладієвих плівок, отриманих на різних підкладках. Результати показали, структура оксиду та взаємодія металу з підкладкою впливають на форму й ріст частинок.