Appl. Phys. A 70, 1–4 (2000)

Applied Physics A
Materials
Science & Processing

# Surface Ostwald ripening of Pd nanoparticles on the MgO (100) surface

Á. Imre[1,*], D.L. Beke[1], E. Gontier-Moya[2], I.A. Szabó[1], E. Gillet[2]

[1] Department of Solid State Physics, University of Debrecen, 4010 Debrecen, P.O. Box 2, Hungary
[2] Laboratoire SERMEC, B61, Faculté des Sciences et Techniques de St. Jerôme, 13397-Marseille Cedex 20, France

Received: 28 November 1999/Accepted: 28 March 2000 

**Abstract.** Morphological changes of Pd nanoparticles on the (100) surface of MgO single crystal were investigated by Auger electron spectroscopy in the temperature range of 873–983 K. The size and distribution of clusters were also examined by means of atomic force microscopy. It was shown that there was practically no decrease of the effective thickness of deposited Pd during heat treatments under $6 \times 10^{-9}$ mbar. Assuming that the observed change in the Auger intensities is due to the surface Ostwald ripening the temperature dependence of the surface mass transport diffusion coefficients can be given as

$$D'_s = \left(1.6^{+8.2}_{-1.34}\right) \times 10^{-8} \exp\left\{\frac{-(136 \pm 15)\,\mathrm{kJ\,mol^{-1}}}{RT}\right\} \mathrm{m^2\,s^{-1}}\,.$$

**PACS:** 82.80.Pv; 61.46.+w; 66.30.-h

The knowledge of the surface diffusion parameters is important in the understanding of different surface-related phenomena, such as thin film growth, sintering, surface chemical reactions and stability of new-type thin film catalysts. At moderate temperatures, when there is no significant evaporation and/or dissolution into the substrate, and if the surface diffusion fields around the isolated particles are overlapping, surface Ostwald ripening process can be observed [1–4]. During this process the size of large particles increases at the expense of small ones while the mass of the discontinuous film is conserved.

The particles on the surface can be treated as spherical caps and, thus, their ensemble can be characterized by the average radius, $R$, the number of particles per unit surface, $N_s$, and the contact angle $\theta$. From the investigation of morphological changes of such discontinuous films, the surface mass transport parameters can be determined [1–4].

In our previous paper [5] we have shown that by measuring the Auger intensity the time dependence of the average radius can be obtained. Furthermore – assuming that the surface Ostwald ripening is controlled by surface diffusion – the surface diffusion coefficients of Pd on the $(10\bar{1}2)$ surface of sapphire were determined.

In this paper the results of the investigation of surface Ostwald ripening of beaded Pd films (with average radius of 19.8 nm) on the (100) surface of MgO single crystal, obtained by means of Auger electron spectroscopy (AES) and atomic force microscopy (AFM), are described. The Pd/MgO system is well known in catalysis [6] but until now there are no data on the surface diffusion [7] in this system.

## 1 Theoretical relations

The time evolution of the average radius of particles during Ostwald ripening – if the process is controlled by surface diffusion – can be expressed as [1, 2, 5]

$$R^4(t) = R^4(0) + Ct\,, \tag{1}$$

where

$$C = \frac{8 D'_s\, \omega^2\, \gamma\, n_0}{45 \ln(L)\, \varphi(\theta)\, kT}\,. \tag{2}$$

Here $\gamma$ is the surface energy, $\omega$ is the atomic volume, $k$ is the Boltzman constant and $T$ is the absolute temperature. $D'_s = D_s c_a$ where $c_a$ and $D_s$ are the atomic fraction and the diffusion coefficient of adatoms, respectively. $n_0$ is the number of sites on unit surface, $\varphi(\theta) = 1 - (3\cos(\theta)/2 + (\cos^3\theta)/2$ and $L$ is a dimensionless screening distance [1]. The value of the constant $C$ is given according to [1], where it was assumed that $L$ can be considered to be a constant (lying between 2 and 3). In general $L$ can depend on the surface diffusion length and on the cap radius [2], but we have shown in [5] that the supposition of $L = 2.5$ is a good approximation. The effective thickness of the beaded film can be given as

$$H_{\mathrm{eff}} = 2\pi\, \varphi(\theta)\, N_s\, R^3/3\,. \tag{3}$$

*Corresponding author. (Fax: +36-52/316-073, E-mail: iarpad@dragon.klte.hu)

Taking into account that the number of particles can change because the smallest beads can disappear during Ostwald ripening, we have shown in [5] that the relative Auger signal, $I(t)/I(0)$, is inversely proportional to the normalized average radius, i.e.

$$I(t)/I(0) = R(0)/R(t)\,. \tag{4}$$

In the derivation of (4), we used the fact that the change of the surface number density, $N_s$, of islands is proportional to $(R(0)/R(t))^3$ [2], and $I \sim N_s R^2$. Thus according to (1), the quantity $[I(0)/I(t)]^4$ should be a linear increasing function of $t$.

The surface mass transport diffusion coefficient, measuring $I(0)/I(t)$ by AES and determining $R(0)$ and $\theta$ from AFM image, can be calculated from

$$D'_s = \frac{45\ln(L)\,\varphi(\theta)\,kT}{8n_0\,\gamma\,\omega^2} \times \frac{\mathrm{d}\,(I(0)/I(t))^4}{\mathrm{d}t} \times R^4(0)\,. \tag{5}$$

## 2 Experimental

Polished (100) surfaces of MgO single crystals, provided by Pi-Kem., were used as substrates. First the samples were cleaned in alcohol. Afterwards the surface of the substrate was reconstructed by pre-annealing at 1273 K for 24 h in air. The final cleaning was performed by an additional heat treatment in UHV ($\cong 8 \times 10^{-9}$ mbar) for 20 min at 1073 K. Before the evaporation of Pd from the Knudsen cell the cleanness was checked by taking the Auger spectrum from this surface. As can be seen in Fig. 1a, only the peaks of O (505 eV) can be observed in the 100 eV to 550 eV energy interval. Thin Pd films were evaporated onto the substrate at room temperature just before the investigation in the vacuum chamber of the AES apparatus. The initial thickness and the deposition rate, determined by a quartz microbalance, were about 0.5 nm and 0.05 nm/min, respectively. During deposition the pressure in the chamber was never higher than $8 \times 10^{-8}$ mbar.

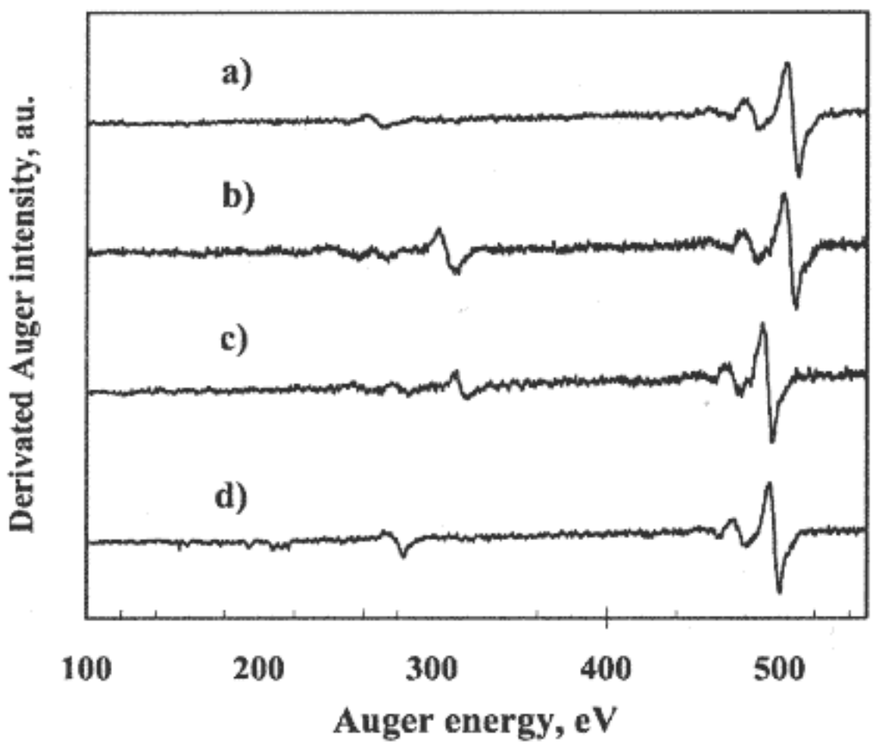


**Fig. 1.** Auger spectra of the clean surface of sapphire substrate (a), the deposited discontinuous Pd 0.5-nm-thick film (b), the film after Ostwald ripening (c), and the cleaned surface after Ostwald ripening (d)

The growth process and morphology of such Pd films on MgO substrate were discussed in [8, 9]. A few atomic monolayer thick metal film on ceramic substrate are usually discontinuous [4, 8]. Such as-produced discontinuous films were used in our experiments.

Controlled heat treatments were carried out in UHV ($8 \times 10^{-9}$ mbar) at 873 K, 898 K, 923 K, 953 K, 973 K, and 983 K by using a ceramic (Boralectric) heating element. The heat treatments and investigations were performed in the same apparatus that was described in our previous paper [5]. The morphology of the discontinuous film was examined by AFM (P4-SPM-18-MDT) in tapping mode.

## 3 Results and discussion

First the surface number density, average radius and contact angle of clusters were determined. The AFM images of the discontinuous film are shown in the Fig. 2 where the image (a) corresponds to the morphology of as-deposited film and (b) is the morphology after the Ostwald ripening. The average radius of the Pd beads at the beginning – just after the beading – was estimated from Fig. 2a. Since the direct determination of its value – due to the finite size effect of the tip – was not possible, it was determined indirectly measuring the surface number density of particles ($N_{so} = 7.3 \times 10^{13}\,\mathrm{m}^{-2}$) at the beginning and taking 0.5 nm for the effective thickness (see (3)). As a first step we assumed that $\varphi(\theta) = 1$, and thus $R = 17.4$ nm was obtained. Using this value and taking the average height of the par-

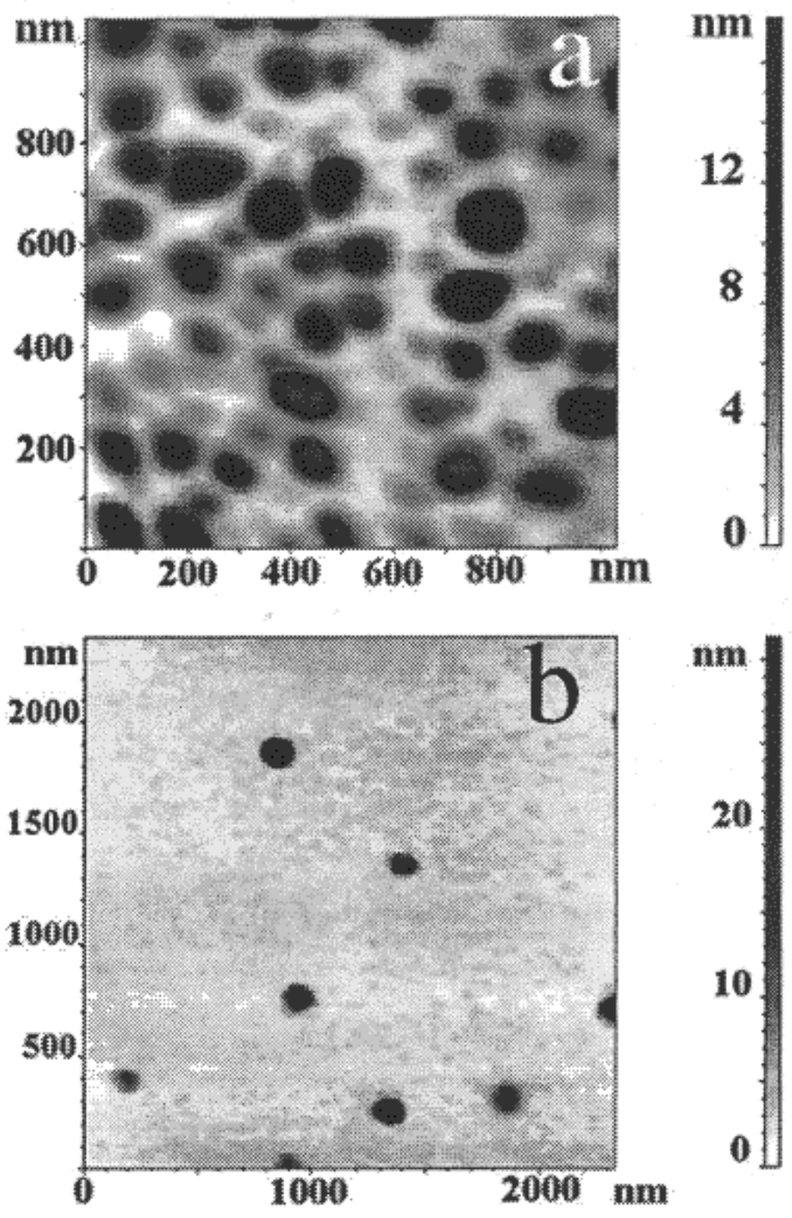


**Fig. 2a,b.** AFM images of the morphology of the Pd particles on the MgO (100) surface: as-deposited film (**a**), after one hour heat treatment at $T =$ 973 K (**b**). Note the different scale on **a** and **b**

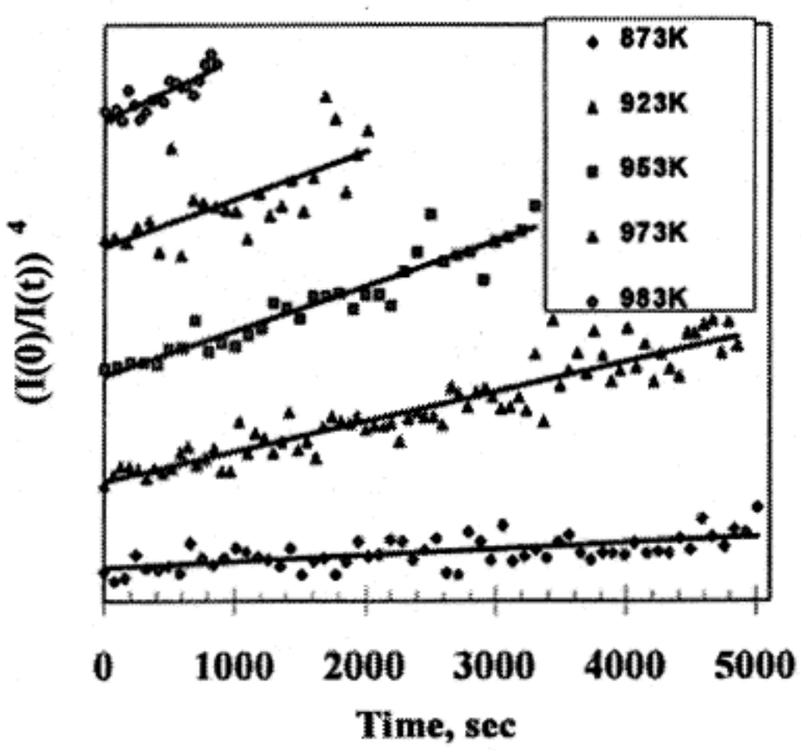


**Fig. 3.** Fourth power of the relative change of Pd Auger peak versus time at 873 K, 923 K, 953 K, 973 K, and 983 K (see the figure)

ticles, $h = 11$ nm, determined also from the AFM image, the value of the contact angle was calculated. Assuming that the particles have a shape of spherical cap, this gave $\theta = 75°$. Then the new value of $\varphi(\theta)$ was calculated and by repetition of the above process the iteration yielded $R = 20$ nm and $\theta = 66°$.

The apparent average radius of the particles, $R = 39$ nm, determined directly from Fig. 2a, allows us to estimate the size of the AFM tip, which is the difference of the apparent and real values (19 nm).

Furthermore, from Fig. 2b the surface density of the Pd particles after Ostwald ripening was determined as $N_s = 1.3 \times 10^{12}\,\mathrm{m}^{-2}$ and from (3) the real radius of the particles corresponding to this surface number density is $R = 76$ nm. If we compare this value with the value determined directly from Fig. 2b ($R = 90$ nm), we can conclude that the loss of Pd, caused by evaporation or dissolution, is negligible and at 973 K it is less then 8% after one hour heat treatment.

The Auger spectra of the initially clean substrate surface, the as-deposited film, the film after Ostwald ripening, and the cleaned surface after Ostwald ripening are shown in Figs. 1a–d, respectively. The Auger intensity of the 320-eV Pd peak was followed during in-situ heat treatments and the kinetics of ripening process was determined. As an illustration Fig. 3 shows the $[I(0)/I(t)]^4$ vs. time functions at 873 K, 923 K, 953 K, 973 K and 983 K. The experimental points can be fitted by a straight line which proves that the process is controlled by surface diffusion; for surface reaction control nonlinear time dependence would be expected [4]. Using the slopes of the above straight lines and taking $L = 2.5$ [1], $\gamma = 1.95\,\mathrm{J/m^2}$ [12] and $n_0\omega^2 = a^4/8$ where $a = 0.3879$ nm for Pd, the surface mass transport diffusion coefficient from (5) can be calculated. The temperature dependence of $D'_s$ – according to an Arrhenius-type dependence shown in Fig. 4 – can be given as

$$D'_s = \left(1.6^{+8.2}_{-1.34}\right) \times 10^{-8} \exp\left\{\frac{-(136 \pm 15)\,\mathrm{kJ\,mol^{-1}}}{RT}\right\} \mathrm{m^2\,s^{-1}}\,. \tag{6}$$

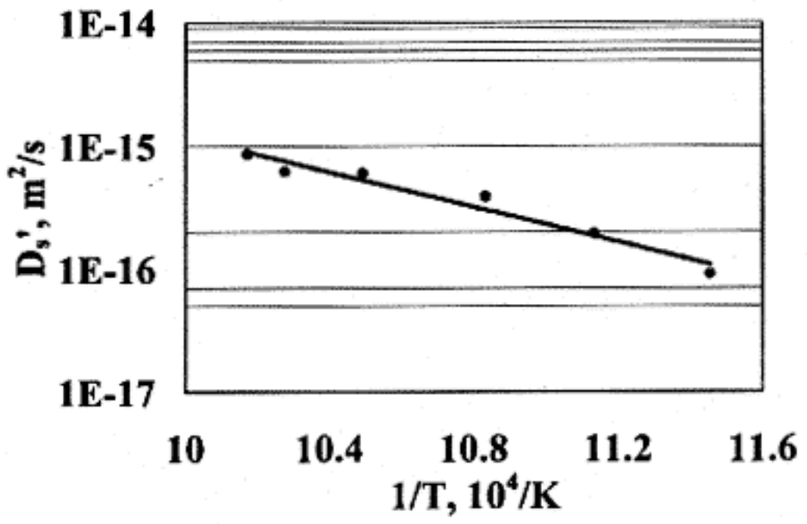


**Fig. 4.** Arrhenius curve of the surface mass-transport diffusion coefficients

Furthermore, it can be noted that coagulation of small particles caused by their Brownian migration on the surface could in principle disturb the kinetic law observed [5]. Indeed, this type of coalescence is usual during thin film growth because there is a continuous source for the formation of very small particles. Thus the coalescence of these very small clusters can be observed during a short time after the end of the deposition, but very soon a true Ostwald ripening takes place [3, 10]. Nevertheless the role of the Brownian migration of palladium particles and coagulation can be estimated similarly to how it was done in [5] by comparing the time necessary to double the average size in a true Ostwald ripening process, $\tau_s$, as well as during coalescence caused by the migration and collisions of particles, $\tau_d$ [10, 11]. If the $\tau_s/\tau_d$ ratio is much smaller than unity the effect of Brownian migration and coagulation by collision can be neglected. As it was shown in [5] this condition is equivalent to:

$$\frac{\tau_s}{\tau_d} < 675 \frac{\ln(L)\,\varphi(\theta)\,kT\zeta}{R_0^2\gamma}\,, \tag{7}$$

where $\zeta$ is the relative surface coverage and now $\zeta \cong 0.1$. Taking the numerical values for $\ln(L)$, $\varphi(\theta)$, $\gamma$, $R_0$ as above and at $T = 1000$ K the $\tau_s/\tau_d < 0.0005$. Thus in the present work the coagulation driven by Brownian migration of clusters can be really neglected.

## 4 Conclusion

We have shown that the morphological changes of discontinuous Pd films with average radius $R = 20$ nm on the magnesium oxide substrate was due to the Ostwald ripening controlled by surface diffusion. It was shown that the evaporation or dissolution into the substrate as well as effect of coagulation by Brownian motion could be neglected. Considering that the Auger signal from an ensemble of islands, during surface Ostwald ripening is proportional to the inverse of the average radius, the surface mass transport diffusion coefficients and their temperature dependence were determined.

*Acknowledgements.* The authors are very grateful to K. Masek for fruitful discussions. This work was partially supported by the ERASMUS program and by Hungarian FKFP 0453/1997 and OTKA T022995 grants.

## References


1. B.K. Chakraverty: J. Phys. Chem. Sol. **28**, 2401 (1967)
2. Y.E. Geguzin, J. Kaganovskii: *Diffuzionnije processi na poverhnosti kristalla* (Energoatomizdat, Moscow 1984)
3. I.M. Lifsitz, V.V. Slezhov: Phys. Chem. Solids **19**, 35 (1961)
4. M.Z.-Allmang, L.C. Feldman, M.H. Grabow: Surf. Sci. Rep. **16**, 377 (1992)
5. Á. Imre, E. Gontier-Moya, D.L. Beke, I.A. Szabó, G. Erdélyi: Surf. Sci. 441 (1999) TS[a]
6. C.R. Henry: Surf. Sci. Rep. **31**, 231 (1998)
7. E.G. Seebauer, Landolt-Bornstein: *Numerical Data and Functional Relationship in Science and Technology*, New Series, III/33B1, Diffusion in Non-Metallic Solids (Part 1), ed. by D.L. Beke (Springer, Berlin, Heidelberg 1999)
8. C.R. Henry, C. Chapon, C. Duriez, S. Giorgio: Surf. Sci. **253**, 177 (1991)
9. A. Renou, J.M. Penisson: J. Cryst. Growth **78**, 357 (1986)
10. R. Kern: In *Interfacial Aspects of Phase Transformations*, NATO Advanced Study Institute Series, Vol. 87, ed. by B. Mutaftschiev (Reidel 1982) p. 303
11. Y.E. Geguzin, M.A. Krivoglaz: *Studies In Soviet Science*, Migration of Macroscopic Inclusions in Solids (Consultant Bureau, New York, London 1973) p. 146
12. J.H. Alonso, N.H. March: *Electrons in Metals and Alloys* (Academic Press, London 1989) p. 436