

Ostwald ripening of Pd particles on the (10 $\bar{1}\bar{2}$) surface of sapphire

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Abstract

Morphological changes of small Pd particles on the (10 $\bar{1}\bar{2}$) surface of α -Al₂O₃ single crystal were investigated by Auger electron spectroscopy in the temperature range 833–923 K. It was shown that practically there was no decrease of the effective thickness during heat treatments under 6×10^{-9} mbar. Supposing that the observed change in the Auger intensities is due to the surface Ostwald ripening, it was established that the process was controlled by surface diffusion. It was shown that in this case, taking into account the dissolution of small particles, the normalised Auger intensity is inversely proportional to the normalised average radius. The surface mass transport diffusion coefficients were determined and they were in the range 10^{-15} – 10^{-17} m² s⁻¹ in the investigated temperature interval. Their temperature dependence can be given as $D'_s = (6^{+486}_{-5.93}) \times 10^{-5} \exp\{[-(203 \pm 30) \text{ kJ mol}^{-1}]/RT\}$ m² s⁻¹. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Very thin metal films on ceramic substrates are usually discontinuous due to the difference in the interfacial energies of the vacuum–substrate and the metal–substrate interface. The metallic particles usually have the shape of a spherical cap and thus their ensembles can be described by an average radius, density and contact angle. From the investigation of morphological changes of such discontinuous films, the surface mass transport parameters can be determined [1–7]. A knowledge of these parameters is important in the understanding of surface-related phenomena, such as thin

film growth, sintering, corrosion, surface chemical reactions and stability of thin film catalysts. At moderate temperatures there is no significant evaporation and/or dissolution into the substrate and if the surface diffusion fields around the isolated particles are overlapping, a surface Ostwald coarsening process can be observed. During this ripening process the size of large particles increases at the expense of small particles while the effective thickness of the film is constant. This phenomenon is well known in the literature and the results of some more recent experiments can be found in Refs. [8–10]

In this paper, the results of the investigation of surface Ostwald ripening [11] of beaded Pd films (with average radius of about 15.6 nm) on the (10 $\bar{1}\bar{2}$) surface of α -Al₂O₃ single crystal, carried out

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by means of Auger electron spectroscopy (AES), are described. The Pd–sapphire system is well known in catalysis [12], but until now there has been no data on the surface diffusion of Pd on a sapphire surface [13]. The only exception is our previous work [6], where — from the decrease of the effective thickness of a beaded Pd film (containing much larger particles of about $R=170$ nm) caused by evaporation — the evaporation current I_{eo} was determined and, supposing that the surface diffusion length was independent of temperature, an estimation for the activation energy of D'_s was also given. However, as is shown here, our supposition in Ref. [6] was not correct and led to an unrealistic large value for the activation energy.

2. Theoretical relations

The surface Ostwald ripening of beaded films can be controlled either by surface diffusion of adatoms, or by surface reaction at the perimeter of the small isolated particles. Models, described in Refs. [14–17], allow the determination of the surface mass transport diffusion coefficient and/or the surface reaction parameters from the morphological changes of beaded films. Thus, if the process is controlled by surface diffusion, according to Ref. [14] the time evolution of the average radius can be expressed as

$$R^4(t) = R^4(0) + Ct, \quad (1)$$

where

$$C = \frac{8D'_s\omega 2\gamma n_o}{45 \ln(L)\varphi(\theta)kT}. \quad (2)$$

Here γ is the surface energy per unit area, ω is the atomic volume, k is the Boltzmann 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_o is the number of sites on the unit surface, $\varphi(\theta) = 1 - (3 \cos \theta)/2 + (\cos^3 \theta)/2$, θ is the contact angle and L is a screening distance [14]. It is important to note that C in Eq. (2) is given according to Ref. [14], where it was supposed that L can be considered to be a constant (between

two and three). On the other hand, the same result as Eq. (1) was published in Ref. [15], and the value of C given in Refs. [14,15] is the same only if

$$\ln L = 8[\ln(\lambda_s/R_1)]/45, \quad (3)$$

where R_1 is the contact radius, $R_1 = R \sin \theta$, and the surface diffusion length of adatoms, λ_s , is defined by $\lambda_s = (D_s \tau)^{1/2}$ (τ is the residence time of adatoms on the surface).

The effective thickness of this discontinuous film can be expressed as

$$H_{\text{eff}} = 2\pi\varphi(\theta)N_s R^3/3, \quad (4)$$

where N_s is the average number of particles per unit surface.

It can be supposed that the Auger intensity $I(t)$ is proportional to the surface fraction covered by beads, $\xi(t) = \pi N_s R_1^2$ — this is strictly valid if the signal produced by adatoms is below the sensibility limit and if the beads are relatively ‘fat’ — and thus its relative value can be given as [3]

$$\frac{I(t)}{I(0)} = \frac{\xi(t)}{\xi(0)} = \frac{N_s(t)R^2(t)}{N_s(0)R^2(0)}. \quad (5)$$

Since during the surface ripening the number of particles can also change because the smallest beads can be dissolved, we need an expression for $N_s(t)$ as well. Indeed, if one supposes that the mass of the film is constant during the process, the following relation holds [15]:

$$N_s(t)/N_s(0) = R^3(0)/R^3(t). \quad (6)$$

Thus it can be seen from Eqs. (5) and (6) that the relative Auger signal is inversely proportional to the normalised average radius and, according to Eq. (1), $[I(0)/I(t)]^4$ should be a linear (increasing) function of t ; from the slope of this straight line one can determine the value

$$D'_s = \frac{45 \ln(L)\varphi(\theta)kT}{8n_o\gamma\omega^2} \frac{d[I(0)/I(t)]^4}{dt} R^4(0), \quad (7)$$

if the initial value of the average radius and the contact angle are known. The proportionality factor in Eq. (7) is constant at constant temperature and $R(0)$ can be determined for example from an atomic force microscopy (AFM) image.

Therefore, by measuring the changes of the Auger intensity at constant temperatures and taking the AFM image in the initial stage the surface mass transport diffusion coefficient can be determined.

3. Experimental

Clean, polished (10 $\bar{1}\bar{2}$) surfaces of α -Al₂O₃ single crystals, provided by Kyocera, were used as substrates. The surface of the substrate was reconstructed by pre-annealing at 1473 K for 24 h in air [18,19]. The final cleaning was performed by an additional heat treatment in ultrahigh vacuum ($\sim 8 \times 10^{-9}$ mbar) for 20 min at 1073 K. Before the evaporation of Pd the cleanness was checked by taking the Auger spectrum from this surface. As can be seen in Fig. 1a, only the peaks of Al (51 eV) and O (520 eV) can be observed. Thin Pd films were evaporated onto the substrate at 673 K from the Knudsen cell just before the investigation in the vacuum chamber of the AES apparatus. The initial thickness and the deposition rate were about 0.5 nm and 0.05 nm min⁻¹ respectively, determined by a quartz microbalance. During deposition the pressure in the chamber was never higher than 8×10^{-8} mbar.

Controlled heat treatments were carried out at 833, 853, 873, 903, and 923 K by using a ceramic

(Boralectric) heating element. The sample was carefully clipped to the front surface of the heating element with W clips to establish a good contact. First the temperature of the sample was measured with a thermocouple fixed onto the front surface of the sample. Later on, on the basis of the calibrating temperature versus heating current function, the temperature was determined from the measured value of the heating current. The pressure in the chamber during the heat treatments was about 6×10^{-9} mbar.

The evolution of the morphology of the palladium film was followed in situ by AES with a cylindrical mirror analyser (Riber, 10 kV coaxial gun) in a derivative mode. The 1300 eV primary energy of the incident electrons was used and the intensity of the 320 eV Pd Auger-peak was measured from time to time.

Different deposition–annealing cycles were performed on the same sample; after finishing the measurement of Ostwald ripening the remaining Pd was evaporated by a ‘cleaning’ heat treatment for 15 min at 1068 K before a new cycle started.

4. Results and discussion

The average radius of Pd beads at the beginning — just after the beading — was estimated from an AFM image. Since the direct determination of its value (due to the finite size effect of the tip) was not possible, it was determined indirectly from the AFM image measuring the surface density of particles $N_{so} = 5 \times 10^{14}$ m⁻² and taking the 0.5 nm value for the effective thickness [see Eq. (4)]. As a first step we supposed that $\varphi(\theta) = 1$, and thus $R = 7.8$ nm was obtained. Using this value with the help of the average height of the particles determined also from the AFM image, the value of the contact angle was determined supposing that the particles have the shape of a spherical cap. This gave $\theta = 46.5^\circ$. Then the new value of $\varphi(\theta)$ was calculated and by repetition of the above process the iteration yielded $R = 15.6$ nm and $\theta = 46^\circ$. This can be compared with the value $\theta = 68^\circ$ obtained in Ref. [6] from tilted SEM pictures of much bigger Pd particles ($R \cong 170$ nm) or with $\theta = 75^\circ$ obtained in Ref. [20]. From the comparison

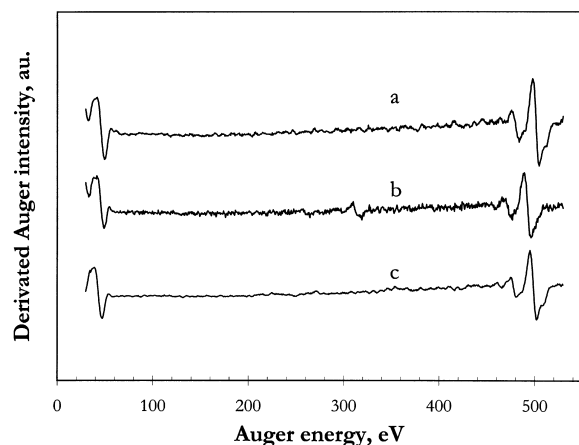


Fig. 1. Auger spectra made (a) on the clean surface of sapphire substrate, (b) on the deposited Pd film of 0.5 nm thickness and (c) on the cleaned surface after the investigation of Ostwald ripening.

of the average radius and surface density, estimated before and after the ripening process, it was checked that the loss of Pd, caused by the evaporation, was negligible and at the highest investigated temperature it was less than 4% after 1.5 h.

The Auger spectra of the initial substrate surface, the deposited area and the cleaned surface after Ostwald ripening are shown in Fig. 1a, b and c respectively.

By following the Auger intensity of the 320 eV Pd peak the kinetics of ripening were determined from in situ heat treatments. Fig. 2 shows the $[I(0)/I(t)]^4$ versus time functions at 833, 853, 873, 903 and 923 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 a non-linear time dependence would be expected [15,16]. 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. Indeed, this type of coalescence is usual during thin film growth when there is a continuous source for the adatoms on the surface, but it stops when the incoming flux of adatoms is over and then a true Ostwald ripening takes place [8,21–26]. Thus using the slope of the above straight lines, taking $L=2.5$ [14], $\gamma=1.95 \text{ J m}^{-2}$ [27] and $n_o\omega^2=a^4/8$, where $a=0.3879 \text{ nm}$ for Pd, the diffusion coefficient

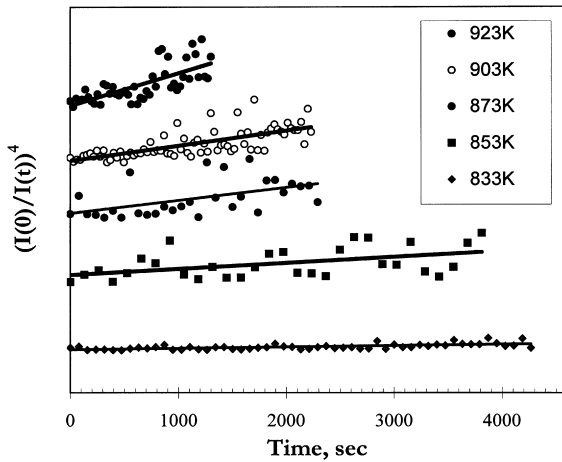


Fig. 2. Relative changes of the intensity of Pd Auger peak to the fourth power versus time.

from Eq. (7) can be determined. The temperature dependence of the surface mass transport diffusion coefficient, according to an Arrhenius-type dependence, can be given as (Fig. 3)

$$D'_s = (6^{+486}_{-5.93}) \times 10^{-5} \times \exp\{[-(203 \pm 30) \text{ kJ mol}^{-1}]/RT\} \text{ m}^2 \text{ s}^{-1}, \quad (8)$$

where the errors are given according to a least squares fitting.

As was mentioned in Section 1, in our previous paper [6] the decrease of the effective thickness of the beaded film (with much larger Pd particles), caused by evaporation, was measured under identical conditions, but at higher temperatures. The temperature dependence of the evaporation rate, given by $I_{eo} = n_o D'_s / \lambda_s^2$, was determined and

$$\frac{n_o D'_s}{\lambda_s^2} = (1.5^{+277}_{-1.492}) \times 10^{36} \times \exp\{[-(393 \pm 46) \text{ kJ mol}^{-1}]/RT\} \text{ m}^{-2} \text{ s}^{-1} \quad (9)$$

was obtained. Furthermore, in Ref. [6] an order of magnitude estimate of the averaged surface density of beads, from the breaking point of the $H_{\text{eff}}(t)/H_{\text{eff}}(0)$ curves — where the diffusion fields of particles just started to become independent from each other — was given and $\lambda_s = l/2 = 1/(2N_s)^{1/2} = 0.54 \mu\text{m}$ was obtained at about 1080 K

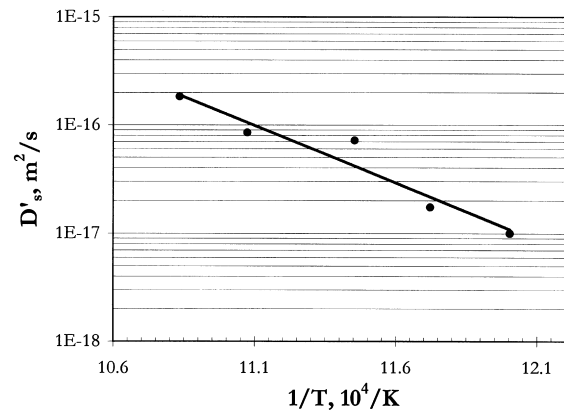


Fig. 3. Arrhenius plot of the surface mass transport diffusion coefficients.

(l is the average distance between the particles). Then, supposing that this value is independent of temperature, the Arrhenius function of D'_s was estimated as

$$D'_s = 1.2 \times 10^4 \exp[(-393 \text{ kJ mol}^{-1})/RT] \text{ m}^2 \text{ s}^{-1}, \quad (10)$$

i.e. in this case D'_s would have the same activation energy as the evaporation rate of Pd from the sapphire surface. But this energy, as has already been mentioned in Ref. [6], is too large. This is really confirmed by the present results and, instead of supposing that λ_s is independent of temperature, we can estimate it and its temperature dependence from the ratio of Eqs. (8) and (9) as

$$\lambda_s = (2^{+241}_{-1.98}) \times 10^{-11} \times \exp\{[(95 \pm 13) \text{ kJ mol}^{-1}]/RT\} \text{ m}. \quad (11)$$

Furthermore, it can be noted that, although due to the strong scatter of experimental points it was not done in Ref. [6], it is possible to obtain an estimate of the surface diffusion coefficient from the last part of the $H_{\text{eff}}(t)/H_{\text{eff}}(0)$ curve at the highest temperature ($T=1083 \text{ K}$) in fig. 4 of [6] (see Fig. 4). According to the theory [1–3,6], here an independent dissolution of particles takes place and for a slope m of the fitted straight line (see the dashed line in Fig. 4) $m = 8.7 \times 10^{-5} \text{ s}^{-1} = 2\pi n_o \omega N_s D'_s / [H_{\text{eff}}(0) \ln(\lambda_s/R_1)]$. Now, using the same values for n_o and ω as before, as well as taking $\lambda_s = 0.54 \text{ }\mu\text{m}$, $R_1 = 0.161 \text{ }\mu\text{m}$, $H_{\text{eff}}(0) = 8.2 \text{ nm}$

and $N_s = 8.7 \times 10^{11} \text{ m}^{-2}$ — as estimated in Ref. [6] — one gets $D'_s = 8.1 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$. This — taking into account the approximations used in the estimation and the experimental errors [e.g. taking $\theta = 68^\circ$ instead of $\theta = 46^\circ$, the pre-exponential factor in Eq. (8) would be about four times smaller] — is in a good agreement with the data obtained from the extrapolation of Eq. (8) to $T = 1083 \text{ K}$ ($D'_s = 9.7 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$).

It is worth mentioning that the numerical value of λ_s , as estimated at 1083 K from Eq. (11), is $\lambda_s = 0.76 \text{ }\mu\text{m}$, which is again in fair agreement with the value estimated in Ref. [6] and used before ($\lambda_s = 0.54 \text{ }\mu\text{m}$). Furthermore, at this temperature (from the data obtained here) the right-hand side of Eq. (3) is 0.69, which confirms that taking $\ln L = 0.91$ ($L = 2.5$) was not a bad supposition in calculating the numerical values of D'_s . Thus we can conclude that the two measurements made of the morphological changes (Ostwald-ripening and diminution caused by evaporation) under identical conditions, but at different temperatures, of different beaded Pd films (with $R = 15.6 \text{ nm}$ and $R = 170 \text{ nm}$ respectively) are consistent with each other and allow one to determine the correct values of the surface mass transport diffusion coefficient and surface diffusion length as well as their activation energies.

Finally, in order to make a more quantitative estimation of the possible role of the coalescence due to Brownian motion of particles [25,26], we can follow the procedure published in Refs. [15,28]. According to Refs. [15,25,26,28] the diffusion coefficient characterising the Brownian migration of small clusters D_c can be usually given as $D_c \approx (1/2\pi)D(a/R)^n$, where the value of n depends on the mechanism of this migration and D is the atomic diffusion coefficient. For example, if the motion is controlled by surface diffusion $D \equiv D'_s$ and $n=4$ in the above expression. The analytical solution of the general problem of the ripening by this type of coalescence for an ensemble of particles of finite size distribution is very difficult [28], but an estimation of the time necessary to double the average size can be relatively easily obtained:

$$\tau_d \cong A \frac{R_o^6}{\xi D'_s a^4}, \quad (12)$$

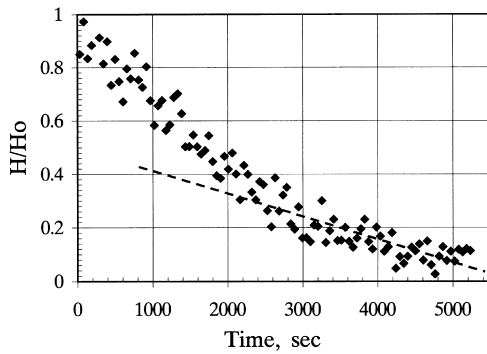


Fig. 4. Relative effective thickness versus time as determined in Ref. [6] at 1083 K.

where A is a constant of the order of unity [28].

Now, from Eqs. (1) and (2) one can also estimate the same time in the process of surface Ostwald ripening as

$$\tau_s = \frac{15R_o^4}{C} = 675 \frac{\ln(L)\varphi(\theta)kT}{8D_s'\omega^2\gamma n_o} R_o^4, \quad (13)$$

Then, if the τ_s/τ_d ratio is much smaller than unity the effect of Brownian migration and coagulation by collisions can be neglected. Indeed, using again the relations $n_o\omega^2 = a^4/8$, and $A \cong 1$:

$$\frac{\tau_s}{\tau_d} < 675 \frac{\ln(L)\varphi(\theta)kT\xi}{R_o^2\gamma}. \quad (14)$$

This — taking the numerical values for $\ln(L)$, $\varphi(\theta)$ and γ as above — gives at $T=1000$ K, with $\xi = \pi N_{so} R_{10}^2 = 0.38$

$$\frac{\tau_s}{\tau_d} < 0.001, \quad (15)$$

i.e. in our case the process is indeed a surface Ostwald ripening.

5. Conclusions

Recognising that the Auger signal from an ensemble of small islands, undergoing surface Ostwald ripening with decreasing surface density of particles, is proportional to the inverse of the average radius, a method for the measurement of the surface mass transport diffusion coefficient was established. The applicability of the method was illustrated by the example of Pd nanoparticles ($R=15.6$ nm) on sapphire and reliable surface diffusion coefficients and activation energies were obtained. It was also shown that this set of measurement was in accordance with our previous results obtained from the investigation of the diminution of the effective thickness of a beaded Pd film (but with about 10 times larger particles) caused by evaporation. The combination of the results of these two measurements allowed us to correct our previous conclusion for the activation energy of diffusion and to give an estimate for the surface diffusion length of adatoms.

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