

Coarsening of Pt clusters on amorphous carbon substrate

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Pt clusters were deposited on amorphous carbon (a-C) thin films by electron-beam vapor deposition. The cluster-size distributions at 200°C, 250°C and 300°C were investigated by transmission electron microscopy (TEM) in regular time intervals. Between 150 and 300 Pt clusters were analysed for each time interval. The cluster radii were determined by approximating the projected cluster area by a circle. Size histograms were derived and average radii at a given time t $\bar{R}(t)$ were determined.

Fig. 1 a) shows the measured $\bar{R}(t)$ values which increase strongly with time t at all investigated temperatures. The coarsening kinetics of Pt clusters during the first 1 hour of annealing at 200°C, 250°C and 300°C is very fast and can be explained by significant redistribution of the deposited Pt clusters due to cluster coalescence. An *in-situ* annealing experiment shows that, besides surface Ostwald ripening (OR), a very active coalescence of mobile Pt clusters (Smoluchowski ripening (SR)) takes place during the first hour of annealing. The SR kinetics rapidly slows down with time because the surface diffusion coefficients of Pt clusters decrease with increasing cluster sizes. Moreover, the average inter-cluster distance increases with decreasing cluster density on the a-C substrate due to the cluster coalescence. This allows us to neglect the SR process within the second ripening stage, which ranges from about 1 h until the end of our experiments.

The coarsening process during the second ripening stage is best described by a least-square fit of the experimental $\bar{R}(t)$ based on the theoretical expression $\bar{R}^4(t) = \bar{R}^4(0) + K_d t$ (t : time, K_d : constant), which corresponds to surface diffusion-limited OR with the mass transport taking place through the cluster-substrate contact perimeter [1,2]. The coarsening kinetics of the Pt-clusters accelerates with increasing annealing temperature T . A quantitative description of the OR process can be obtained by comparing the surface mass-transport-diffusion coefficient D'_s values, because a faster kinetics is described by larger D'_s . The D'_s

values can be calculated using the K_d values and the relation $D'_s = \frac{45 \ln(L) \varphi(\theta) k_B T}{4 \omega^2 \gamma n_0} K_d$ [1].

The volume of Pt atoms is denoted by $\omega = 1.51 \cdot 10^{-29} \text{ m}^3$ and the Pt-surface energy is given by $\gamma = 3.0 \text{ J m}^{-2}$ [3]. k_B is the Boltzmann constant and T the absolute temperature. $L = 2.5$ (in units of cluster radius) is the screening distance, which is taken to be constant according to Ref. [1]. The parameter $\varphi(\theta)$ is determined by the contact angle θ between cluster and substrate [1], which cannot be directly measured from the TEM images. However, the parameter $\varphi(\theta)$ derived within surface-diffusion theory is used to express the Pt-cluster volume, as given by

$V(R) = \frac{4 \pi}{3} R^3 \varphi(\theta)$. For a known cluster shape, one can estimate the cluster volume and the

corresponding value of $\varphi(\theta)$. Pt clusters with *fcc* cuboctahedral structure and a shape characterized by the average ratio $h/R = 0.82$ between the vertical facet height h and the apparent (because clusters are not spherical) cluster radius R were identified as relevant

clusters (see Fig. 1 c) and d)) [4]. The volume of Pt clusters with this geometry can be calculated and yields $\varphi(\theta)=0.56$. Moreover, for Pt clusters with an *fcc* cuboctahedral structure, the density of sites on the cluster surface is of $n_0=1.3\cdot 10^{19} \text{ m}^{-2}$. With these values, one can determine D'_s at 200°C, 250°C and 300°C. D'_s values of $(1.23\pm 0.24)\cdot 10^{-23} \text{ m}^2\text{s}^{-1}$ at 200°C and $(4.26\pm 0.85)\cdot 10^{-22} \text{ m}^2\text{s}^{-1}$ at 300°C suggest a rapid increase of the OR kinetics within this temperature interval. Moreover, an Arrhenius-type dependence assumed for the surface mass-transport diffusion coefficient D'_s on the absolute temperature T , $D'_s = D_0 \exp\left(-\frac{E_d}{k_B T}\right)$ with the pre-exponential factor D_0 , results in an activation energy E_d for the surface diffusion of Pt atoms on a-C substrate of $E_d=0.85\pm 0.09 \text{ eV/atom}$ (Fig. 1 b)).

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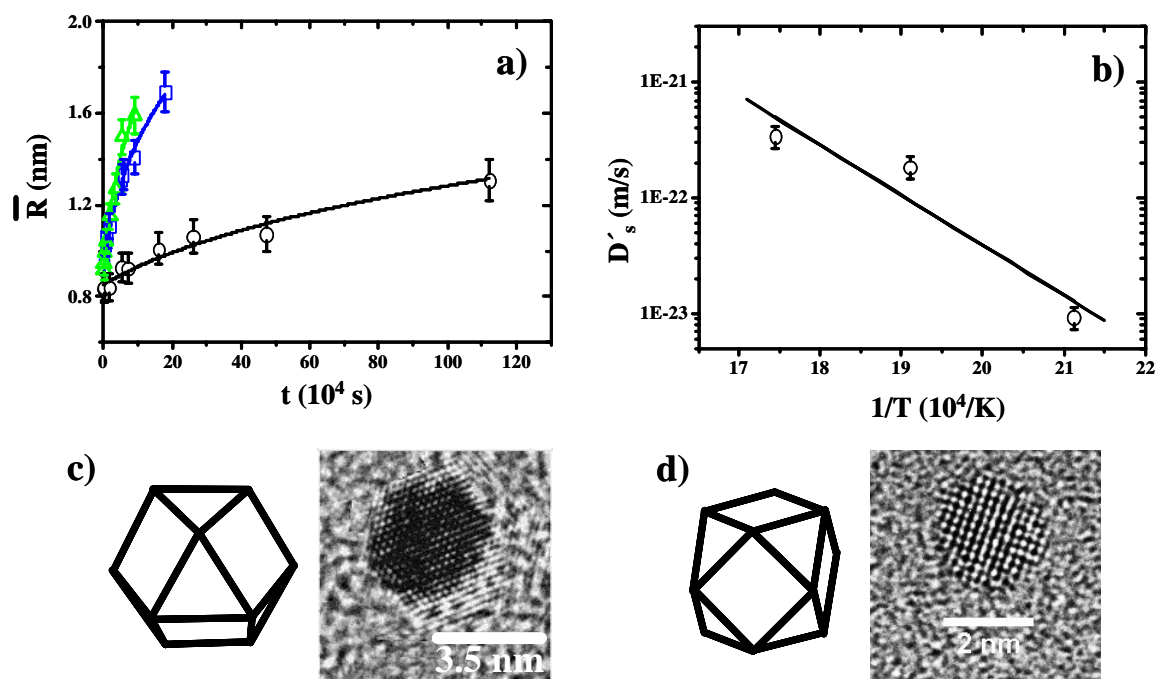


Figure 1. a) Average radii of Pt clusters $\bar{R}(t)$ as a function of annealing time t at different temperatures: at 200°C (○), 250°C (□) and 300°C (△). The solid lines with the corresponding colour represent fits of the data for diffusion-limited kinetics of surface OR under steady-state conditions with the mass transport through the cluster-substrate contact perimeter. b) Surface mass-transport diffusion coefficient D'_s as a function of $1/T$, which results in an activation energy for the surface diffusion of Pt atoms on a-C substrate of $E_d = 0.85 \text{ eV/atom}$ (see the text). c) and d) Pt clusters with *fcc* cuboctahedral structure in the [110]- and [100]-zone axis, respectively: schematic view and the corresponding TEM image.