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The impact of thermal annealing on the morphology of sputter deposited platinum clusters into anodic aluminum oxide pores

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Abstract: The influence of post deposition annealing (PDA) up to temperatures of $T_{\text{PDA}}=900^{\circ}\text{C}$ on the morphology and agglomeration behavior of ambient temperature sputter deposited platinum onto anodic aluminum oxide templates is investigated. Both cluster agglomeration and diffusion processes occur on the surface and on the inner channel walls. When the annealing temperature is less than 400°C , particles are diffusing inside the channels. Around $T_{\text{PDA}}=400^{\circ}\text{C}$, a particle agglomeration process is taking place. A diffusion process is playing an important role and the Pt particles are able to reach a depth of $12\ \mu\text{m}$. The surface morphology exhibits a remarkable change for annealing temperature above 600°C , where Pt is migrating on the outermost surface for forming flat films. When further enhancing T_{PDA} to 900°C , the particles on the surface and in the channels agglomerate together to form separated large flat islands. Moreover, the maximum channel depth where platinum is present is around $12\ \mu\text{m}$.

Keywords: Deposition; Sputtering; Nanoparticles; Porous materials; Thin films; Interfaces

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Introduction

Highly efficient catalytic systems, such as in fuel cell, photocatalysis, or gas sensors often requires noble metal catalysts supported on porous structures [1-2]. This is due to the outstanding property of high surface-volume ratio, which is helpful in enhancing the contact surface area in the catalysis reaction. Therefore, porous substrates, including porous structure, nanoarrays, nanochannels are used for gas sensors, fuel cells, photocatalysts [3-9]. Porous carbon, TiO₂ nanoarrays, ZnO nanoarrays, Anodic aluminum oxide templates (AAO) have been used as substrates to prepare these highly efficient catalysts [10]. Moreover, stability, under high temperature operation, is especially reached using AAO, as typically required for micromachined hot film, temperature sensors.

Sputtering or (plasma enhanced) chemical vapor deposition techniques are suitable for noble metal catalysts growth in porous substrates [11-13], whereas diffusion effects in the porous structure are of high interest for applications [14-16]. Due to the high resistance against oxidation and high temperature corrosion resistance, platinum is a relevant material to be deposited in a porous structure and thus has been widely investigated [17-20]. Even if there are some works on the structural, electrical properties of the thin, pure Pt films, only few publications can be found dealing with the diffusion effects of Pt in a porous structure upon annealing.

The goal of the present work is to investigate post-deposition annealing (PDA) of room temperature sputter deposited Pt nanoclusters into AAO template up to temperature of $T_{\text{PDA}} = 900$ °C on the diffusion of (Pt/AAO). A low pressure plasma deposition is applied to deposited, which has been approved to be advantageous for controlling low catalyst content and location. The morphology and agglomeration behavior of the Pt/AAO are studied as the annealing temperature increased.

Experiment

An argon plasma is created in a stainless steel deposition chamber by using an external planar antenna (TCP) powered by a radiofrequency generator operating at 13.56 MHz. The Pt target is biased with a continuous (DC) potential of $V_b = -100$ V and the deposition time is fixed to 60 min at argon pressure of $2.4 \cdot 10^{-3}$ mbar. A base pressure of $P_0 = 2.7 \cdot 10^{-7}$ mbar is achieved using a primary/turbomolecular pump combination. The AAO templates (purchased Pu-Yan Nanotechnologies, China) are made of hexagonal arrays of cylindrical pores with average pore size of 90 nm, a porosity of

25%, and pore density is $4.7 \cdot 10^9 \text{ cm}^{-2}$. The pores are perpendicular to the external surface. The AAO template is placed on a movable/rotating grounded substrate holder in front of the sputtering target with a target-substrate distance of 7 cm. After deposition, Pt deposited AAO templates were annealed in air for 60 min at five different temperatures ($T_{\text{PDA}} = 100, 200, 400, 600, \text{ and } 900^\circ\text{C}$).

The annealed Pt /AAO templates are observed by high resolution scanning electron microscopy (SEM) (SEM-ZEISS), both in plane and cross-sectional views, to determine pore size and evolution of the porosity at the surface. Rutherford Backscattering Spectroscopy), with a Van de Graaf accelerator (CEMHTI-CNRS, Orleans, France) using a 2 MeV $^4\text{He}^+$ ion beam, was used to measure the total Pt content and to quantify Pt penetration into pores.

Results and discussion

Fig. 1 displays the topography of the Pt deposits on AAO, revealing the differences of the nanostructure caused by annealing. In the “as deposited” state ($T=25^\circ\text{C}$), the sputtered Pt atoms deposited on the AAO template form clusters present on the ridges separating pores and on the inner pore walls. The morphology is the same when annealing at 200°C (Fig 1.a-c). Up to 400°C (Fig 1.d), gradual change is observed in the surface morphology of Pt/AAO. The platinum clusters evolve with larger mean grain size, and are concentrated on the ridges of the AAO. This effect is enhanced at annealing temperatures of $T_{\text{PDA}}=600^\circ\text{C}$, the migration of the Pt particles is increased and these particles connect together forming a quasi continuous Pt film. Only the pore center is not hidden (Fig 1e). This morphology is consistent with low temperature ($500\text{-}600^\circ\text{C}$) fused Pt [18-20] observations. When further increasing the temperature to 900°C , large areas (few μm) of AAO are covered with Pt films, hiding the underlying pore tops (Fig 1f).

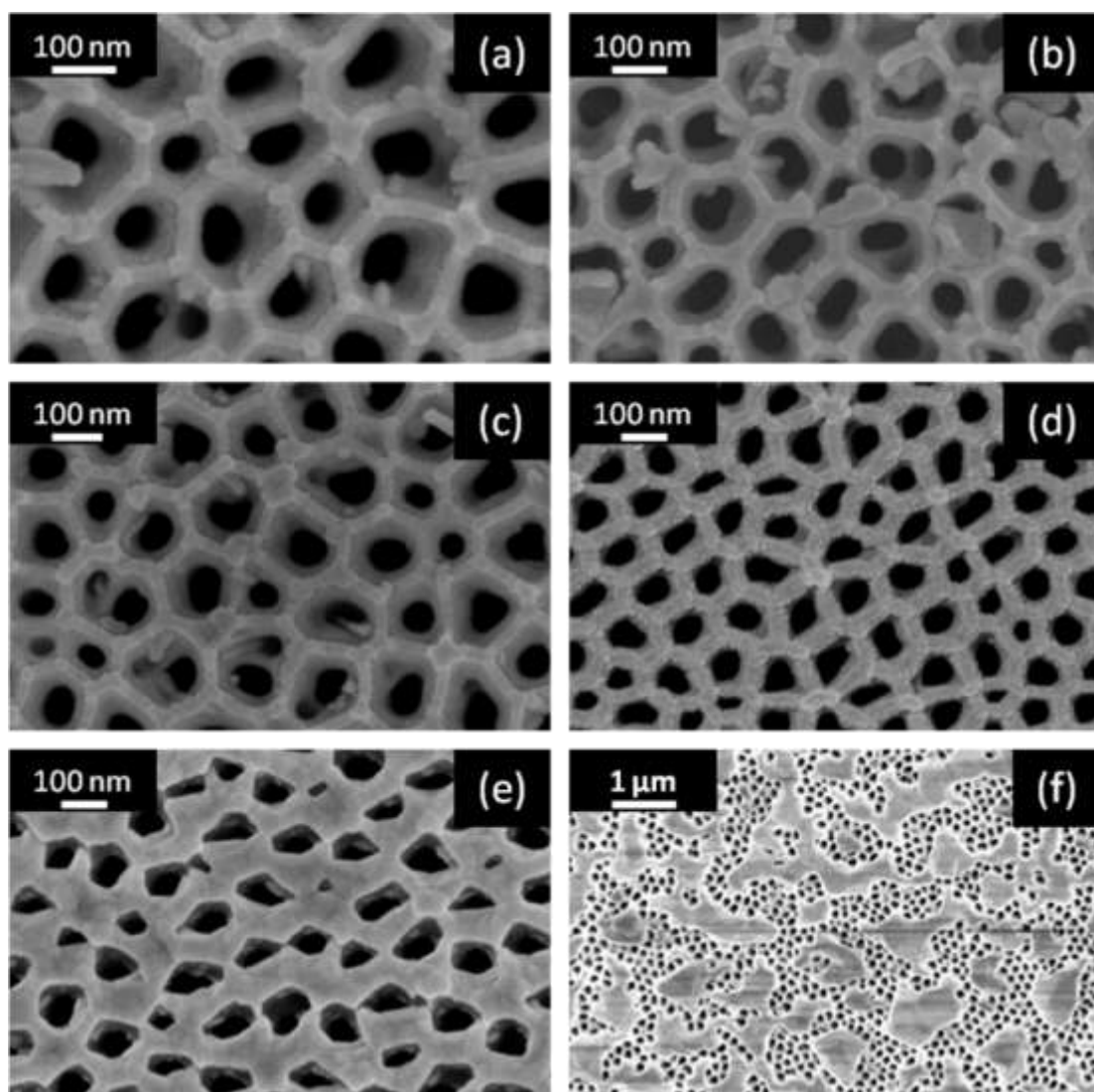


Fig. 1 Surface SEM images of the Pt deposits after annealing at different temperature (a) room temperature; (b) 100°C; (c) 200°C; (d) 400°C; (e) 600°C; (f) 900°C

Typical cross-section morphology of the Pt deposited AAO and zoom highlighting the Pt spreading inside the channels at 400°C annealing temperature, are displayed in Fig 2a. Most of the Pt particles in the channels are aggregated on the ridges delimiting pores. At this temperature, the penetration depth determined by EDS-SEM is less than 2 μm . On top elementary Pt particles have size around 10 nm while around 1 μm depth, it is reduced to 3 nm. When annealing at 900 °C, the distribution of the Pt particles is totally different (Fig. 2b). The on-top agglomerated Pt particles looks like hemisphere with a diameter around 200 nm standing on the ridges. The Pt islanding film observed on SEM top view (Fig. 1f) is peeled off from the surface in the form of a thin suspended sheet above AAO channels. In the AAO depth around 2 μm , the morphology is also meandering like a fused film, as can be observed

in the inset.

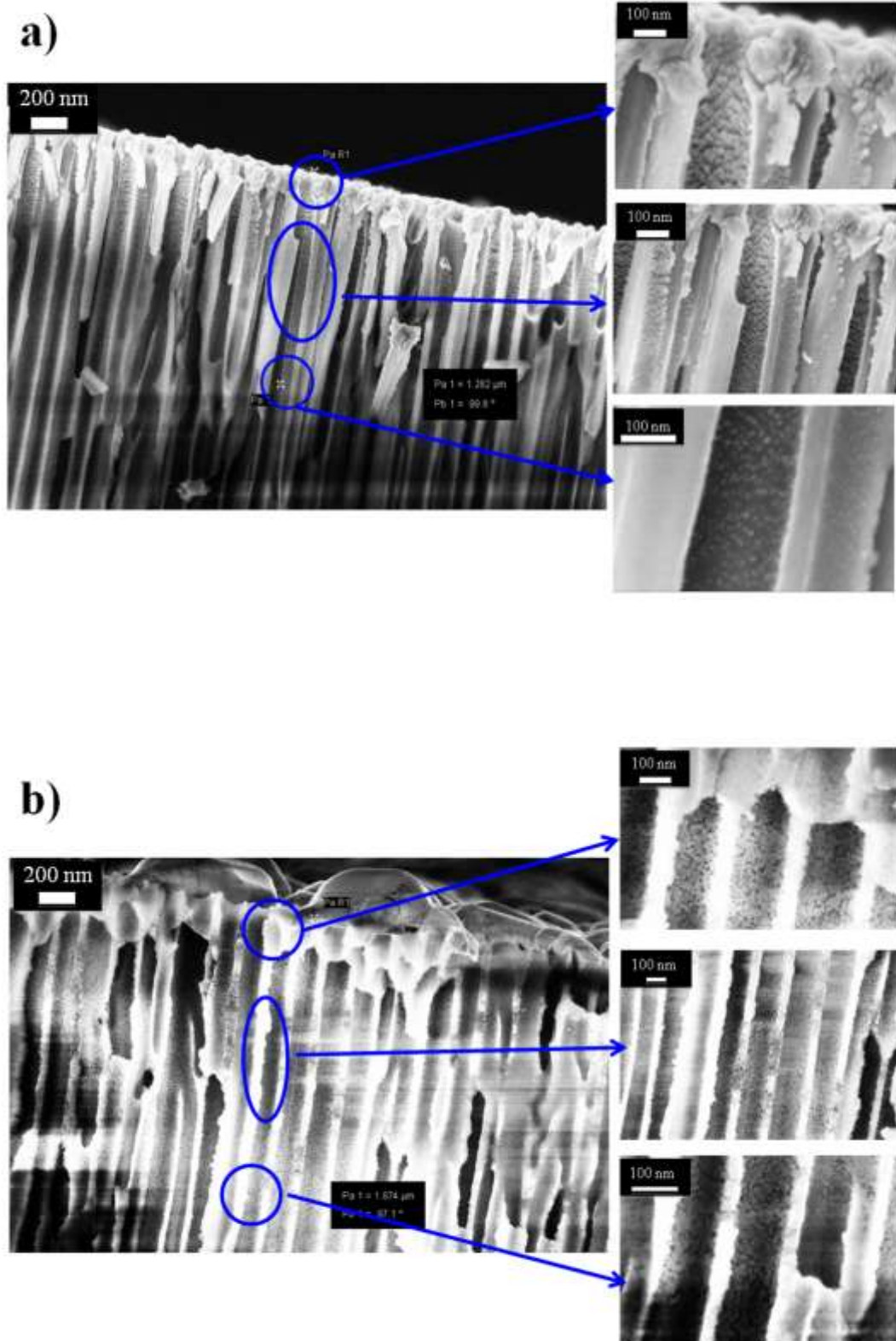


Fig. 2 SEM Cross-sectional views at different annealing temperatures. (a) annealing at 400°C; (b) annealing at 900°C.

The platinum concentration depth profiles are determined using RBS as a function of the AAO channel depth z . Figure 3a displays several typical experimental RBS spectrum of Pt/AAO annealing at 25°C, 100°C, 400°C, 600°C and 900°C. The Pt peak (channels 700 – 800) exhibits an asymmetric shape, which is the signature of the Pt spreading resulting from Pt migration into the channels. When the annealing temperature is less than 400°C, the change of the spectrum is very slight and remains similar to the spectrum at 100°C, except a little decrease the height and a broadening of Pt peak. Marked changed on RBS spectra occur around 400°C annealing and above, especially between 600°C and 900°C. The Pt peak is strongly broadened and the intensity is markedly reduced, in preserving total areal under the peak, which is proportional to the total number of Pt atoms. The broadening is attributed to the increasing Pt thickness on the ridges, while the large tail indicates that atoms are diffusing into the channels. The Pt peak intensity reduction is consistent with a density lowering.

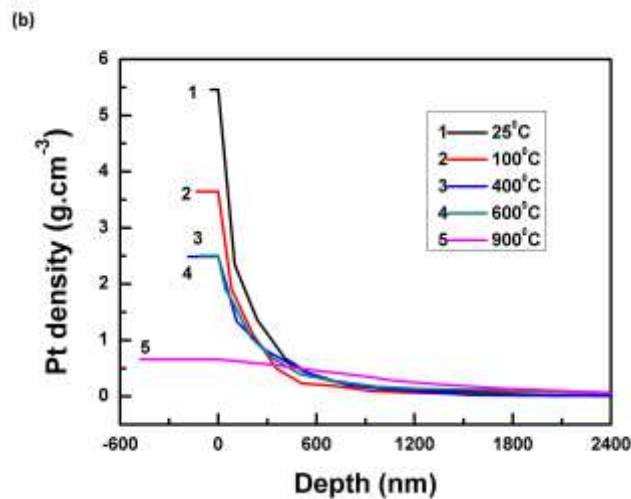
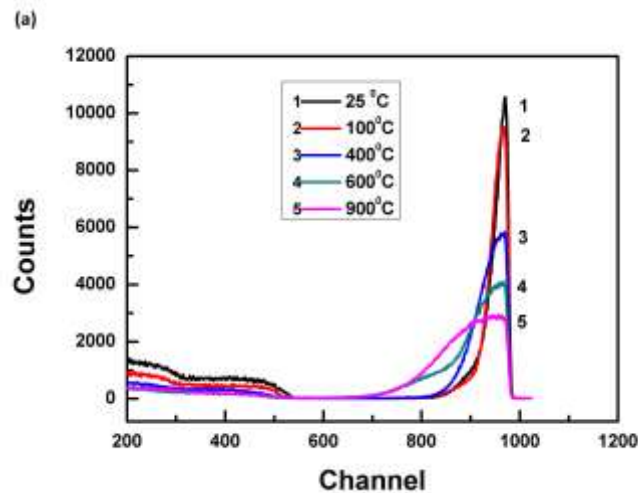


Fig 3. (a) RBS spectra of the annealed Pt deposited on the AAO at different temperatures. (b) the corresponding concentration depth profile

The concentration profiles are calculated from the RBS spectra and are presented in Fig. 3b. Basically the Pt concentration in the porous AAO at a given depth is determined by minimizing the difference between an RBS spectrum with a trial Pt content and the measured one as explained in Refs. 15 and 16. The error is thus less than 10% between the measured and the estimated RBS spectrum. It is clearly shown that increasing temperature leads an increasing Pt height above the AAO surface ($z>0$) with a reduced density. The Pt density is small compared to bulk value because it is determined as an average value in the medium composed of void, alumina and a small content of Pt. The situation at 900°C also indicates a clear increased density inside the channels even with an increasing top layer thickness.

This is clearly contrary to the Pt flat film evolution on Si substrate against annealing temperature for which film densification increases [18].

The Pt concentration profile can be fitted by a stretched Gaussian function of the form

$$\rho(z,t) = Z_1 \exp \left[- \left(\frac{z}{\lambda} \right)^{2+\theta} \right] \quad [14-16],$$

Z_1 being the density at $z=0$, λ the spreading of the profile and θ is

a an exponent characterizing the anomalous character of the diffusion. If $\theta > 0$ this is called subdiffusion, if $\theta < 0$ this is super diffusion. $\theta = 0$ describes the classical thermal diffusion. The present profile evolves from $\theta = -1.1$ at room temperature to -1.3 at 600°C indicating a superdiffusive regime. For, $T=900^\circ\text{C}$, θ is largely increased to -0.7 indicating that the diffusion process tends to become thermally driven.

During this annealing process, an agglomeration process and a diffusion process occur both on the surface and the interface of the channels simultaneously. For annealing temperature less than 400°C, the diffusion process plays the leading role and there is more Pt particles diffusion into the channels, whereas there is no observation of agglomeration areas. A significant agglomeration occurs for samples annealed above $T_{\text{PDA}}= 400^\circ\text{C}$. Examining morphology on the SEM top view (see Fig 1.d) and cross-section view (see Fig 2a), we found that this effect is more significant on the surface (ridges) than in the channels. In agreement with the observations presented in this study, Manninger and co-workers

[21] found no significant increase of the cluster size from 100°C to 300°C, whereas a fast increase of the cluster size was observed for higher temperatures. In addition, Coutanceau et al. [22] also reported that the presence of oxide species on the platinum surface lead to little aggregation of platinum and no reconstruction of cluster when the annealing temperature less than 300°C.

Increasing the T_{PDA} level to 600 °C leads larger mean grain sizes occurs. The agglomeration process and a diffusion process compete together. The maximum reached depth of Pt particles reaches is around 12 μm and with no longer increase. Film looks like a fused layer growing on the surface, starting to hide the pores. On can guess that some capillary forces, due to fused Pt state, are driving such behavior.

At $T_{\text{PDA}}=900$ °C, the film growth rate is enhanced dramatically. Film growth results in islands covering large pore areas. This growing film results from cluster fusion which starts above 600°C, consistently with the literature [20, 22]. Because part the Pt migration process occurs towards the surface, i.e. towards a higher density region, this film growth can be attributed to a capillary process. A capillary process always proceeds to rise against increasing gradients. The temperature impact on the diffusion rate is not as obvious as on the agglomeration. The maximum depth of Pt particles remains at a constant depth around 12 μm . But the local density is clearly changed. At $T_{\text{PDA}} = 900^\circ\text{C}$, the Pt density is increased in the channels while it is reduced above the surface. The agglomeration process generates areas with complex meandering patterns similar to those reported for Pt and Au films on Si substrate [19]. Pt concentration decrease dramatically due to lowered content in the probed volume.

Conclusion

The influence of post deposition annealing (PDA) up to temperatures of $T_{\text{PDA}}=900^\circ\text{C}$ on the migration/diffusion of sputter deposited platinum onto porous anodic alumina oxide (Pt/AAO) is investigated. In the “as deposited” state, a majority of Pt particles concentrate on the surface and few of the particles penetrate into the channels and stick on the inner channel walls. Up to $T_{\text{PDA}}=400^\circ\text{C}$, the morphology has no obvious change both on the surface and in the channels. However, for annealing above 400°C, a Pt film is built on the surface due to partial particle fusion. For annealing temperature between 600°C and 900°C, a capillary-driven agglomeration process plays a leading role in the concentration of the Pt particles both on the surface and the interface of the channels. The main feature is the growth of flat film on the surface which hides the pores. The maximum depth of Pt particles reached in the AAO nanochannels strongly depends on the annealing temperature. As the annealing

temperature is increased to 400°C, the reached depth is increased from 8 μm to 12 μm. However, when annealing at 600°C and 900 °C, the maximum reached depth almost remains around 12 μm.

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