Synthesis of palladium nanowire arrays with controlled diameter and length

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Abstract

Ordered palladium nanowire (NW) arrays with high aspect ratio have been synthesized using porous alumina templates and direct-current electrodeposition. The porous alumina films were prepared by double anodizing high purity aluminium foils in oxalic and sulphuric acids at 40 and 25 V, respectively. Final pore size of the processed (free-standing) alumina templates were determined to be ∼65 and 35 nm. The electrolyte consisted of 70 mM K2PdCl4 in 20 mM H2SO4 and the deposition voltage was 0.3 V (versus Ag/AgCl reference electrode). Under the employed conditions, a high filling rate (>90%) was obtained using 65 nm thick templates. The NWs synthesized in 65 nm pores were polycrystalline and textured, but those in 35 nm pores were single-crystalline. It is suggested that deposition in smaller pores proceeds under smaller overpotential due to diffusion-limitation which favors single-crystalline growth. In order to obtain self-standing Pd NWs, which may be interesting for realizing NW-array based gas sensor structures, the alumina template was dissolved away, leaving self-standing NWs supported on a conductive thin film. Such NWs were observed to form agglomerates and chemisorb O and C as surface impurities.

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1. Introduction

Recently, template synthesis of functional nanomaterials has attracted considerable attention. This is mainly owing to the possibility to control the length, diameter, and density of the synthesized nanostructures by varying template and/or deposition parameters [1,2]. In particular, porous anodic aluminium oxide (AAO) has become a common template for the production of, e.g., nanowires (NWs) and nanotubes (NTs) of metals and ceramics [3–5]. The AAO is thermally stable and contains straight and ordered nanochannels at a high density (10^9–10^11 per cm^2).

One-dimensional nanostructured Pd is considered to be a promising candidate for room temperature hydrogen sensing and storage [6]. To date, only a limited number of reports describing the synthesis of Pd NWs have appeared in the literature [7–10]. Favier et al. decorated the edge steps on a graphite surface with Pd by electrodeposition using an electrolyte containing 2 mM Pd^{4+} ions (in 0.1 M HCl or HClO_4), and attested their ability in H_2 sensing [7]. As the formed NWs were not continuous (but rather consisted of chains of non-connected Pd nanoparticles) the fabricated sensors acted, in fact, as a switch in H_2. As it was demonstrated by their in situ measurements, the Pd nanoparticles swell upon introduction of H_2 which leads to closure of the gaps between particles and so the flow of a current through the temporarily formed NWs becomes possible. More recently, Kim et al. prepared Pd NW arrays with an aspect ratio (AR) close to 10 (80 nm diameter) inside the channels of a thin-film AAO template formed on Ti/Si substrates by pulsed-current electrodeposition and utilizing a commercial electrolyte [9]. More recently, they obtained self-standing Pd NW arrays (grown using the same deposition scheme) by dissolving the alumina matrix and evaluated their performance in H_2 sensing [10]. It was realized that the resistance of their NW arrays decreased in H_2 (observable down to 0.2% H_2 concentration), which is in contrast to bulk Pd H-sensors where an increase in resistance is expected in H_2 ambient (due to the formation of PdH_x on Pd surface). It was suggested by the authors that when the sensors were exposed to H_2 the NWs swell and cause shrinkage of inter-particle gaps (near the loose
NW tips), thereby increasing the overall conduction through the NW array.

In this paper, we report on the synthesis of ordered Pd NW arrays with high AR and density using a facile and high yield method. We investigated suitable parameters (e.g., electrolyte composition, deposition voltage) for the formation of Pd NWs using dc electrodeposition inside the pores of self-standing AAO templates. Two pore diameters (65 and 35 nm) were chosen to study the dependence of growth kinetics and NW structure on different pore sizes. Structural characterizations of both embedded and self-standing NW arrays are exposed in some detail.

2. Experimental details

The templates were prepared by double anodization method [11] using high purity (99.999%) Al foils. Briefly, Al foils were first cleaned in acetone, annealed in N2 at 500 °C for 4 h, and then electropolished at 48 V in a perchloric acid:ethanol (1:5, v/v, ratio) mixture. Anodization was performed potentiostatically in 0.3 M oxalic acid at 40 V or in 0.3 M sulphuric acid at 25 V. The electrolyte temperature was kept constant at 15 °C and the anodization time was 8 h in all cases. After the first anodization, the oxide film with a low pore ordering was removed in 5 wt.% phosphoric acid:1.8 wt.% chromic acid at 70 °C. Second anodization resulted in the formation of a highly ordered porous alumina film. Self-standing AAO templates were obtained by dissolving first the non-oxidized Al in 5.2 wt.% mercury chloride and then the barrier layer (i.e., unopened side of the porous alumina tubes) in 5 wt.% phosphoric acid at 35 °C. Pores were rounded and further widened by dipping the membranes in 5 wt.% phosphoric acid for a few min.

Prior to NW deposition, one face of the membrane was sputter-coated with a thin Au film and subsequently reinforced with a ~1 μm electrodepositied Pd film. The template was then sealed and its non-coated part was exposed to the electrolyte compartment of the electrodeposition cell. The template was then sealed and its non-coated part was exposed to the electrolyte compartment of the electrodeposition cell. The empty pores were then wetted with de-ionized water by ultrasonic agitation to facilitate electrodeposition of Pd NWs. Finally, the water in the cell was removed and replaced immediately with the deposition electrolyte such that 70 mM K2PdCl4 in 20 mM H2SO4. Pd electrodeposition was carried out at 0.3 V Ag/AgCl in all cases. We note that a similar electrolyte with up to 1 mM K2PdCl4 was previously used by Naohara et al. to grow ultrathin Pd films on Au single-crystals [12]. In some cases, the alumina template was removed by soaking the sample in a 0.1 M NaOH solution for 24 h, in order to obtain and study the characteristics of liberated Pd NWs.

The morphology of the embedded and free-standing Pd NW arrays was studied mainly by scanning electron microscopy (SEM). For this purpose, either a Philips XL30 microscope or a Hitachi S4800 system with a cold field emission gun was employed. The template with smaller pores (produced using sulphuric acid) was imaged using an atomic force microscope (AFM, Nanostation II) in non-contact mode. Further structural characterizations were performed by powder X-ray diffraction (XRD, Cu Kα, λ = 0.154 nm), energy dispersive X-ray (EDX) analysis, and X-ray photoemission spectroscopy (XPS, ESCA). Peak energies in the XPS spectra were corrected for charging effect using the internal C 1s peak (285.0 eV).

3. Results and discussion

Fig. 1. (a) A typical SEM image of oxalic acid AAO produced at 40 V (dp ≈ 65 nm). The image bar denotes 0.5 μm. (b) An AFM micrograph of sulphuric acid AAO produced at 25 V (dp ≈ 35 nm).

Typical micrographs taken from the bottom part of the produced AAO filters are shown in Fig. 1. The pores in the oxalic acid AAO produced at 40 V seem to be more ordered and the film surface is more homogeneous (Fig. 1a) compared to sulphuric acid AAO formed at 25 V, which presents a number of additional pore defects (Fig. 1b). The average center-to-center pore distance and pore sizes (dp) of the corresponding membranes are determined to be approximately 110 and 65 nm for the oxalic acid AAO and 65 and 35 nm for the sulphuric acid AAO. The pore distances are in agreement with an expected pore growth rate of 2.5 nm V−1 in anodic alumina [13].

Fig. 2 provides typical current density versus time (J–t) curves for the deposition of Pd into AAO templates with dp ≈ 35 and 65 nm. It is noticeable that the current density decreases
sharply within seconds at the beginning of the deposition and then becomes saturated. For the template with \( d_p \approx 65 \text{ nm} \) the current density remains at around 1.2 mA cm\(^{-2} \) until 30 min and then starts to gradually increase. SEM analysis of a number of samples produced using different deposition times (\( t_{\text{dep}} \)) indicated that a small fraction of pores in this template become quickly filled at \( t_{\text{dep}} \approx 30 \text{ min} \), and that the increase in current density after this time coincides with the formation of hemispherical Pd caps at the end of these pores. Finally, the caps grow in size with increasing \( t_{\text{dep}} \) and start to form a continuous Pd film on AAO surface before the remaining pores get filled completely. If the NW growth took place very homogeneously having the same growth rate for all the pores, then current density would be expected to increase rather sharply as soon as NWs reach the AAO surface collectively. In the case of \( d_p \approx 35 \text{ nm} \), the current density at first decreases monotonically from 0.4 to 0.3 mA cm\(^{-2} \) in 10 min, then remains constant until \( t_{\text{dep}} \approx 40 \text{ min} \). Although the reason for this observation is not clear at present it is believed that deposition in 35 nm pores is diffusion controlled (vide infra). After \( t_{\text{dep}} \approx 40 \text{ min} \) the current density starts to increase slowly again; this period is believed to be governed by the same mechanism observed in 65 nm pores, namely a rapid overfilling of a small fraction of pores and subsequent growth of a Pd film on the AAO surface.

The cross-sectional SEM image in Fig. 3a shows that AAO pores are filled with very long NWs (AR \( \approx 400 \)) and the pore filling rate is very high. Although, the average dispersion in the NW length is \( \sim 15\% \), additionally, a few overgrown NWs can also be spotted. Fig. 3b and c provides high resolution SEM images of Pd NWs grown in 65 and 35 nm pores, respectively. It appears that average NW diameters deducible from these images do not correlate with the measured \( d_p \) values for the corresponding AAO membranes. For example, a NW diameter of \( \sim 50 \text{ nm} \) can be estimated from Fig. 3c while \( d_p \) was measured by AFM to be \( \sim 35 \text{ nm} \) for this template. An exaggeration of NW diameter by the SEM technique was reported previously (e.g., see ref. [14]).

Fig. 4 provides XRD scans of Pd NWs embedded in templates with \( d_p \approx 35 \text{ and 65 nm} \) in comparison to that of polycrystalline Pd (JCPDS 46-1043). It can be inferred that both NW arrays are pure-phased and can be indexed following face-centered cubic (fcc) Pd. Moreover, the NWs in 35 nm pores show a single main peak at \( 2\Theta = 68.3^\circ \) (Fig. 4a) which corresponds to the (2 2 0) reflection of fcc Pd. This means that the [1 1 0]-direction is parallel to the long NW-axis in this sample. On the other hand, NWs in 65 nm pores are textured having both [1 1 0]- and [1 0 0]-directions parallel to the growth direction (Fig. 4b). Meanwhile, several other low-intensity Pd peaks are also observable, e.g., (1 1 1) and (3 1 1) reflections at \( 2\Theta = 40.4^\circ \) and 82.3\(^\circ \), respectively, in these spectra which probably arise from the electroplated Pd film at the bottom of templates.

As for the occurrence of (1 1 0)-dominant texturing it is not possible to provide a concrete explanation. The crystallinity of metallic NWs grown by nanoporous templates is in fact governed by numerous factors. In other words, for a given porous template, composition [15], temperature [15] and pH [16] of the electrolyte as well as the type (ac or dc) [17] and overpotential value [18] of the deposition bias can alone determine the phase and texture of the NWs. Consequently, for fcc metal NWs a variety of textures and growth mechanisms have been reported so far [19–22]. For example, Au NWs with \( \sim 40 \text{ nm diameter} \) grown in nanoporous templates were found to be either (1 1 0)- or (1 1 1)-textured (i.e., along their long axis) [15,20]. Moreover, though seldomly reported in the literature [19–22], for a given electrolyte and bias parameters, texture of NWs may be dependent on \( d_p \) and/or AR of the pore channels (as observed in Fig. 4). It has been suggested that deposition in narrow and high AR channels may drive the deposition to become diffusion-
limited [20]. In this case, a lower current density associated with a reduced effective overpotential is expected. Lower overpotentials are known to favor single crystalline growth [20]. Indeed, even though a higher effective electrode area (EEA) is supposed to be in contact with the electrolyte through the template with \( d_p \approx 35 \, \text{nm} \), a lower current density was observed for the Pd NW deposition in this template (see Fig. 2). The AR and EEA are estimated to be approximately 2.9 and 1.9 times higher in the 35 nm template compared to that with \( d_p \approx 65 \, \text{nm} \). Consequently, it can be asserted that the single-crystalline character observed for the thinner NWs in Fig. 4 is related to diffusion-limited growth in this template.

Self-standing Pd NW arrays with \( L \approx 3 \, \mu\text{m} \) obtained by dissolving the AAO matrix in 0.1 M NaOH are shown in Fig. 5a. The residue of etching was carefully removed by washing the sample with de-ionized water several times. The NWs are self-standing as supported on a Au/Pd film and a certain degree of agglomeration can be observed. The EDX spectra of such NW arrays indicated the presence of only C along with Pd (not shown), which means that NWs are mostly free from oxygen and etch residues, but covered by C impurity. An XPS spectrum of such free-standing NWs aged for 2 months is given in Fig. 5b, in comparison with that of AAO-embedded Pd NWs. The embedded XPS sample was prepared by grinding and polishing the surface of an AAO/Pd NWs composite sample (\( d_p \approx 65 \, \text{nm} \)). In the XPS spectrum of embedded NWs, along with dominant Pd- and Al\(_2\)O\(_3\)-related bands, a relatively small C band can also be seen. On the other hand, in the spectrum of free NWs, apart from metallic Pd 3d\(_{5/2}\) and 3d\(_{3/2}\) bands, respectively, at 334.9 and 340.1 eV strong O and C 1S bands can also be seen. As pointed out above, the presence of oxygen in this sample is not due to alumina (Al\(_2\)O\(_3\)) which is also confirmed by the EDX spectrum of free NWs. The appearance of oxygen and carbon impurities in free NWs can therefore be attributed to aging effects. The composition of the final product on aged NW surface is yet to be determined.

The deposition method presented in this report can be very promising for hydrogen gas sensing applications of Pd NW arrays with controlled diameter and ARs. As indicated by the experience with NW and NT-based gas sensors [23,24] both diameter and length of the NWs are expected to affect the performance of gas sensors based on Pd NW arrays. A bottom electrode needed for gas sensing measurements (to contact the NW arrays) is readily available as the free NWs were grown and supported on a metal film/substrate (see Fig. 5a). Contacting the top of array surface using a macro-electrode would ultimately be dependent on the robustness presented by agglomerated NWs in self-standing arrays. Finally, further tailoring and optimization of the crystallinity, length dispersion and surface chemistry of the NW arrays may become possible if different deposition and sample storage conditions were attested.

4. Summary

Palladium nanowire arrays with controlled diameter and aspect ratios were grown using a facile direct-current electrode-
position method and ordered porous alumina templates. While the length can be controlled by tuning synthesis parameters such as the deposition time, electrolyte concentration and the deposition bias, the diameter can be varied by changing the template (AAO templates can be fabricated with regular pores of diameter 5–500 nm). Differences in deposition characteristics and crystallinity of NW arrays grown in templates with 35 and 65 nm sized pores were observed. In particular the NWs grown in 35 nm templates are shown to be single crystalline. It is suggested that this could be related to diffusion-limited growth in 35 nm pores. Self-standing Pd NWs supported on a metal film were obtained after the removal of alumina host. Surface chemistry of fresh and aged NW arrays were investigated and it was found that carbon impurities are formed faster than oxygen impurities. The presented material preparation conditions are promising for gas sensing applications of Pd NW arrays.

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