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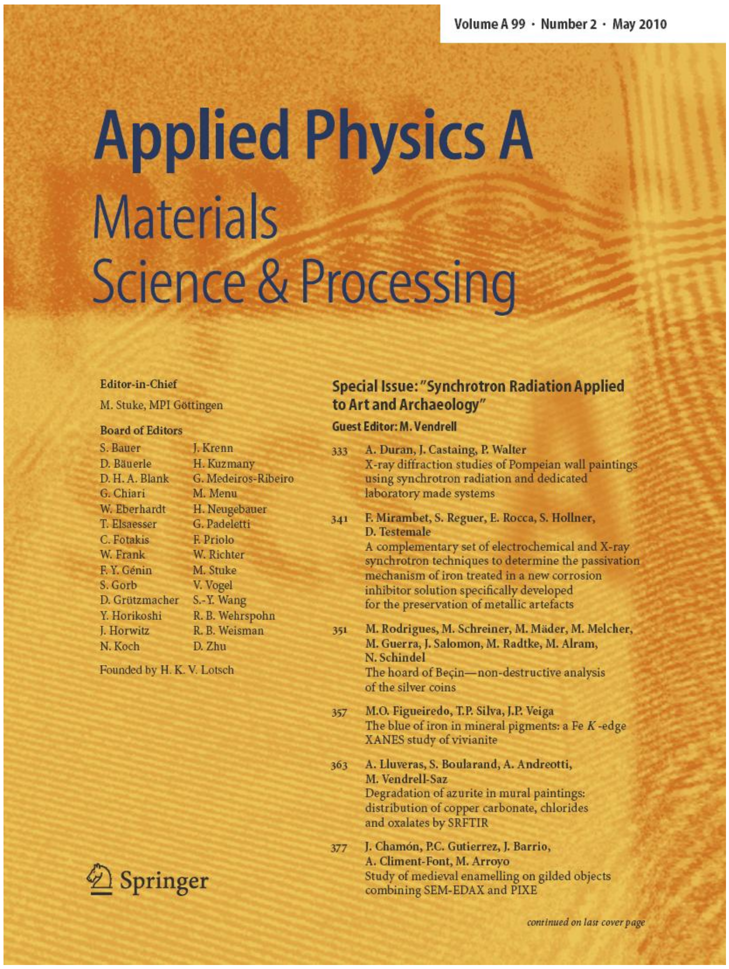

Volume A 99 · Number 2 · May 2010

Applied Physics A
Materials Science & Processing

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Special Issue: "Synchrotron Radiation Applied to Art and Archaeology"
Guest Editor: M. Vendrell

333 A. Duran, J. Castaing, P. Walter
X-ray diffraction studies of Pompeian wall paintings using synchrotron radiation and dedicated laboratory made systems

341 F. Mirambet, S. Reguer, E. Rocca, S. Hollner, D. Testemale
A complementary set of electrochemical and X-ray synchrotron techniques to determine the passivation mechanism of iron treated in a new corrosion inhibitor solution specifically developed for the preservation of metallic artefacts

351 M. Rodrigues, M. Schreiner, M. Mäder, M. Melcher, M. Guerra, J. Salomon, M. Radtke, M. Alram, N. Schindel
The hoard of Beçin—non-destructive analysis of the silver coins

357 M.O. Figueiredo, T.P. Silva, J.P. Veiga
The blue of iron in mineral pigments: a Fe *K*-edge XANES study of vivianite

363 A. Lluveras, S. Boularand, A. Andreotti, M. Vendrell-Saz
Degradation of azurite in mural paintings: distribution of copper carbonate, chlorides and oxalates by SRFTIR

377 J. Chamón, P.C. Gutierrez, J. Barrio, A. Climent-Font, M. Arroyo
Study of medieval enamelling on gilded objects combining SEM-EDAX and PIXE

continued on last cover page

Appl Phys A (2010) 99: 505–509
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Deposition behavior on the barrier layer of porous anodic alumina

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Abstract This work is trying to fabricate nanostructure, for the first time, on the porous anodic alumina's (PAA) barrier layer, which has smooth half-sphere structure. The deposition of indium oxide confirms that the materials can completely cover the surface area of the barrier layer. Both chemical dissolving the PAA or mechanical peel-off can bring free-standing indium oxide thin layer. Morphology study on both sides of deposited layer verifies that the ordered indium oxide nanorods can self-arrange well and form a half-sphere front surface and nanohole-array rear surface. This work confirms that we can get some special nanostructures with the help of the barrier layer of PAAs.

1 Introduction

Porous anodic aluminas (PAAs) have been very important templates for nanostructured materials [1, 2], especially for fabricating nanodot, nanorod, nanowire, nanotube and nanopore arrays. Nanodots and nanorods were deposited onto various substrates, where free-standing thin (100–500 nm) PAAs [3] with throughout nanopore arrays were adhered before deposition as templates [4–7]. Nanowires and nanotubes were fabricated in thick (>500 nm) PAAs through electrochemical ways [8, 9]. Polymer materials melted into liquids and went into the nanopores, and then PAA templates were removed in acidic solutions to realize ordered polymer nanowires and nanotubes [10].

These works utilize the nanochannels of PAAs, and we have done some works to make the benefit from the PAA surface topology, i.e., to obtain some special nanostructures on top of PAAs by the aid of surface charges which were introduced into the wall of PAAs during anodizations. Well ordered zinc oxide nanopores [11] with hexagonal grain units and indium oxide nanopores [5] with nanowire units were realized by carefully controlling the deposition parameters. Zheng et al. also employed modified PAA surface to fabricate ordered carbon nanodots [12].

Except for the nanochannel-array and porous surface, PAAs have another microstructure feature for its barrier layer at the bottom of the nanochannels. Figure 1(a) and (b) shows typical field emission scanning microscopy (FESEM) images of periodic half-sphere arrays of the PAAs' barrier layer. There were many works on how to remove or open this barrier layer to get throughout PAAs [13–16], but no one realize that the half-sphere topology is also useful for nanotechnology. It is interesting that this half-sphere array has no outstanding parts, so: what happens if depositing onto this surface?

We propose three possible deposition behaviors, as demonstrated in Fig. 1(c), (d) and (e). The deposited materials may prefer to grow at the top of the half-sphere structure, or at the connecting point of two cells, or prefer to cover the overall surface area. Here we deposited indium oxide on the PAAs' barrier layers to experimentally demonstrate the preferred deposition behaviors since indium oxide is a versatile material for broad applications. The experimental result was that a deposited layer had a nanorod microstructure, and that these nanorods covered the whole PAA barrier layer surface and arrange into half-sphere structure. Furthermore,

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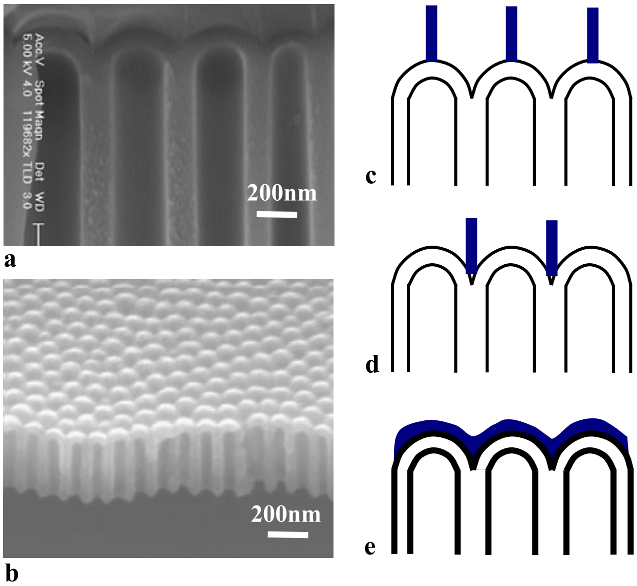

Fig. 1 Typical cross-section view (**a**) and oblique view (**b**) FESEM images of the PAAs' barrier layer. The deposited materials may prefer to grow at the top of the half-sphere structure (**c**), or the connecting point of two cells (**d**), or cover the overall surface area (**e**)

the free-standing indium oxide layer with 50 nm thickness was realized by chemically dissolving PAAs or mechanically peeling off the deposited layer by adhesive tape. These two ways have different effects on the morphology of free-standing indium oxide layer.

2 Experimental details

PAAs were fabricated through two-step anodization process in oxalic acid and phosphoric acid, and detailed fabrication method can be found in Refs. [2] and [3]. Indium oxide layer was deposited onto the PAA barrier layer though a parallel plate radio frequency magnetron sputtering system. Hot pressed indium oxide ceramic with purity of 99.99% was employed as the sputtering target. The space from the target to the substrate was fixed at 2.60 cm, and the working chamber was pumped lower than 1.0×10^{-3} Pa before sputtering. The sputtering power was 60 W with the frequency of 13.56 MHz and sputtering gas of 99.999% argon. The substrate temperature was kept at 170 to 190°C, and the argon pressure from 0.4–0.6 Pa during the deposition. The average deposition rate was about 2 to 5 nm/minute. The morphology of samples was studied by FESEM (XL30FEG from Philips).

3 Results and discussion

Figure 2a and b are the top view FESEM images of the deposited indium oxide on the PAAs' barrier layer. There are many grain-like parts in each hexagonal cell, and the cell arrangement is similar to that of the PAA barrier layer. By making some cracks on the sample surface, we can directly confirm the two layers with similar half-sphere structure, as shown in the inset of Fig. 2b. Figure 2c further verifies that there are many indium oxide nanorods with the same height of about 50 nm and same diameter around 10 nm, and these nanorods are parallel to each other and self-arranged into ordered half-sphere structure by the aid of PAAs' barrier layer. These images confirm that the preferred deposition behavior is to cover the whole PAAs' surface area, not just a part of it. As a result, the indium oxide layer is a continuous and ordered thin layer, as the sketch map Fig. 1(e).

Since it is possible to get free-standing PAAs with ~100 nm thickness [3], we also try to take away the ultrathin indium oxide layer from PAAs. Considering that alumina, as PAAs' main component, is amphoteric oxide, and that indium oxide cannot react with alkali, PAA with the indium oxide layer was immerged into 1 wt% NaOH solution at 10°C. It is interesting that the indium oxide layer automatically detached from PAAs and floated in the solution when the main part of PAAs remained undissolved, which may be caused by that a small amount of NaOH solution went through the indium oxide layer onto the interface of PAA and indium oxide. We also tried to dissolve PAAs in the mixture of phosphoric acid and chrome acid, but the indium oxide layer breaks into pieces soon.

Figure 2d shows the free-standing indium oxide layer transferred onto silicon substrate. The half-sphere array remains, but on each half-sphere cell a small hole on the top area can be found, which indicates that the indium oxide nanorods have a loose arrangement, and tend to drop when operating in the NaOH solution and water-washing process. This result is also consistent with above deduction that liquid can go through the deposited indium oxide layer. To characterize the cross section of the indium oxide layer on Si substrate, we just artificially made some damage to this thin layer to reveal more parts of this film, as shown in Fig. 2e. It can be seen that the arrangement of the nanorods is not as good as that in Fig. 2c, and that some nanorods are lost. Figure 2f is the oblique view FESEM image confirming that each cell actually is a hollow half-sphere.

There is another simple way to take the whole indium oxide layer away from PAA. Stick the general office adhesive tape or conductive tape onto the sample surface, then peel off the tape to take the indium oxide layer away. Since the thin film was adhered to the tap, its front surface (Fig. 2a and b) cannot be observed any more. However, its reverse side morphology can be revealed in its integrity, as shown in the oblique view FESEM images of Fig. 3(a) and (b). There are many indium oxide nanorods, and these nanorods have same size and shape with that in Fig. 2c. These nanorods' arrangement on PAAs' barrier layer brings taper-like pore

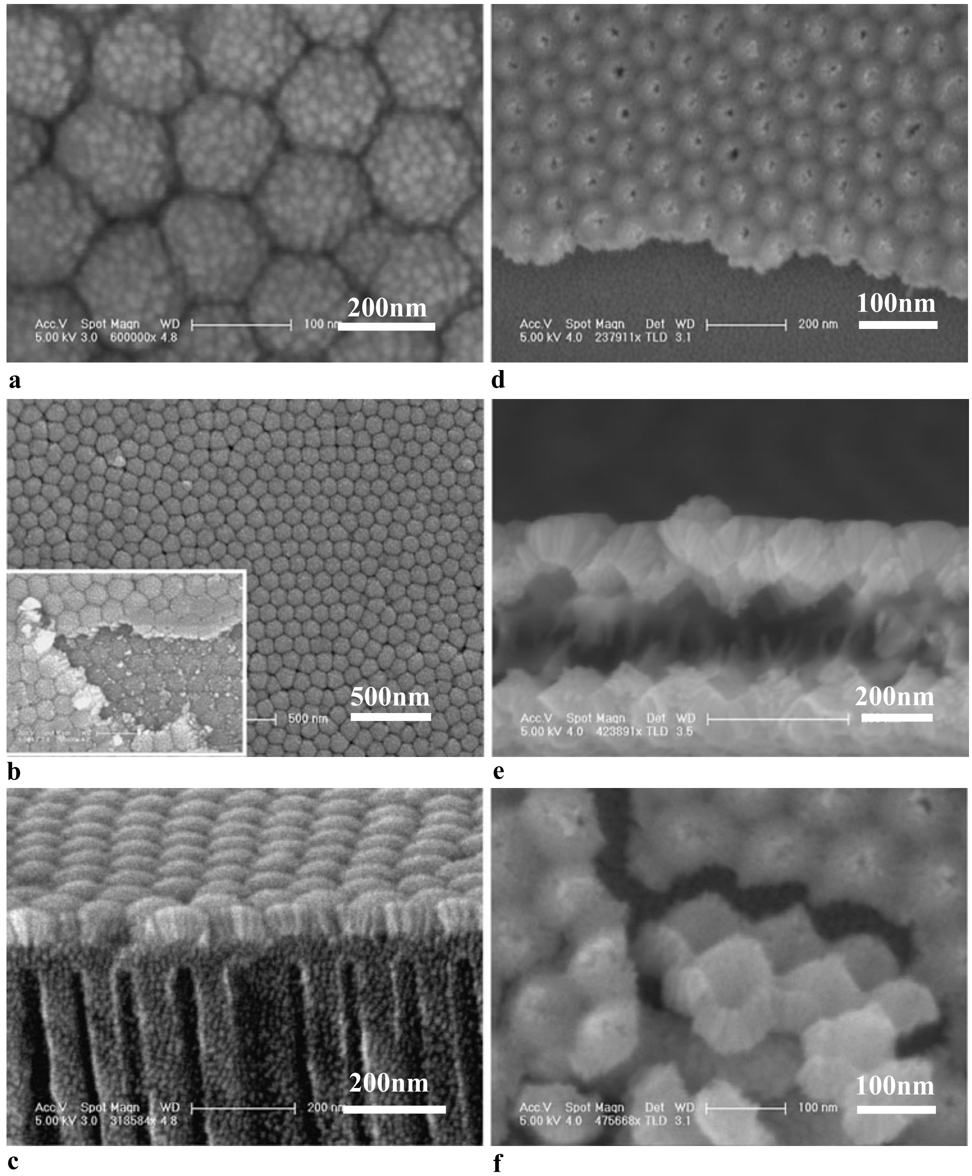

Fig. 2 **a**, **b** and **c** are the top view and cross-section view FESEM images of the indium oxide deposited on the PAAs' barrier layer, **d**, **e** and **f** are FESEM images of the free-standing indium oxide layer obtained through chemical dissolution

array. Figure 3(c) and (d) show the top view FESEM image with different magnification. There are also hexagonal cells with one nanohole in each cell, which is similar to the structure of PAA surface. But the nanoholes have different shapes due to the arrangement of nanorods, and the defects during the peel-off process may contribute to these irregular hole arrays.

We also separately tried higher temperature under 200 and 240°C and higher argon pressure of 1.0 and 2.0 Pa while other depositing conditions were the same. As the temperature and argon increased, the indium oxide microstructure transferred into irregular grains with increased grain size. The typically cross-sectional view FESEM image can verify that the large disordered indium oxide grains, deposited under 240°C, cannot be arranged well into a regular nanoscale pattern on the PAA barrier layer, as shown in the inset of Fig. 3(d). According to these experimental results, The nanorods' formation mainly relies on the depositing technique. The role of PAAs is to control the arrangement of indium oxide nanorods. Since PAA's pore diameter is adjustable from 10 to 500 nm, another role of PAA is its capability to tune the topology of indium oxide nanorods. From materials science point of view, the anion contaminations distributed in the barrier layer will attract materials during the deposition and effect the nucleation and growth of the indium oxide nanorods.

The present indium oxide nanorods on PAA have a high sheet density of $\sim 1 \times 10^{16}$ per m^2, and can be free-standing and transferred onto various substrates. It can be used for nanostructured devices, such as gas sensors and light-absorbing windows. Indium oxide is just an example for the deposition on PAA barrier layer, and other materials

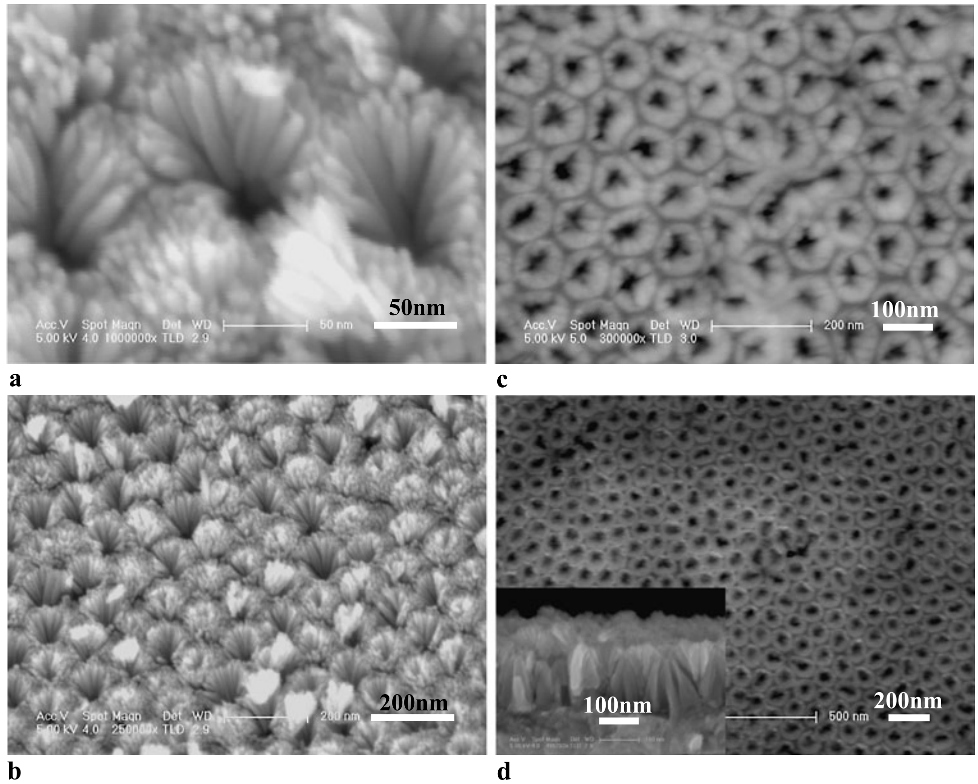

Fig. 3 The oblique view, (**a**) and (**b**), and top view, (**c**) and (**d**), FESEM images of the morphology of the back side after mechanical peeling off the indium oxide layer. The *inset* in (**d**) shows pyramid grains and an irregular arrangement

can also be deposited on this half-sphere surface to form new nanostructures. For example, zinc oxide nanorod arrays could easily form on PAA barrier layer since zinc oxide prefers to grow alone the [0001] direction under various fabricating conditions to form high aspect ratio nanostructures. Based on the current study, we further propose to study how the nanostructured materials deposit on PAA barrier layer through electrochemical or hydrothermal approaches in liquids.

4 Conclusions

In summary, PAAs' half-sphere barrier layers were employed to fabricate indium oxide nanostructures. The deposition of indium oxide confirms that the materials can cover the overall surface area of the barrier layer, so deposited layer can copy the nanoscale half-sphere structure. Both chemical dissolving or mechanically peeling off PAAs can bring about a free-standing ultrathin indium oxide layer. Morphology study on both sides of deposited layer verifies that the ordered indium oxide nanorods can arrange well and form half-sphere front surface and nanohole-array rear surface. The present indium oxide nanorods on PAA have high sheet density, and can be free-standing and transferred onto various substrates. It can be used for nanostructured devices, such as gas sensors and light-absorbing windows. This work also indicates that we can get some special nanostructures of other materials by the aid of the PAA barrier layers through different deposition techniques.

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