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Three-dimensional micro- and nanometre composite aluminium patterns*

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Three-dimensional micro- and nanometre composite aluminium patterns are constructed on Al substrate by using photolithography, reactive ion etching and anodization. A layer of patterned SiO_2 mask is introduced as resist on the surface of Al foil, and during anodization the tilted nanopores and remaining Al microstructure are formed underneath the SiO_2 mask. The existence of SiO_2 mask leads to the deflection of electric field and effect on the transportation of ions, which results in the formation of laterally tilted nanopores, while the nanopores go down directly when being far from the boundaries of SiO_2. The vertical and lateral anodization processes proceeding simultaneously construct the Al microstructure under the patterned SiO_2 mask.

Keywords: anodization, micro-machine, pattern
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1. Introduction

The fabrication of three-dimensional (3D) micro- and nanometre structures is one of the key elements in modern technologies for creating novel materials and functional devices. They have potential applications in microelectronic devices with new architectures,[1] photonic materials,[2] microchip reactors,[3] microfluidic systems,[4] more efficient and low-cost catalytic surface[5] or miniaturized sensors.[6] In this regard, the development of novel methods of building large-scaled patterned microstructures, especially 3D microstructures by use of easy and low-cost implementing have been attracting many attentions.

Patterned metallic micro-/nano-structures are particularly attractive because of their potential applications in printed wiring boards, magnetic recording materials, microwave conductors, contact materials, display devices, optical discs etc.[7] At present the commonly adopted route for constructing 2D or 3D metallic patterns is using self-assembly monolayers (SAMs)[8,9] as resist mask to construct ordered patterns on a metallic film by microcontact printing. Jackman *et al*[10] investigated the possibility of transforming 2D patterns into 3D metallic microstructures. Geissler *et al*[11] fabricated Au, Ag, Cu, Pd, Al metallic nanowires on oxidized Si substrates by combining microcontact printing techniques, chemical etching and electroplating processes. This method is very useful for patterning the surface of a thin metallic film because the metallic film can be selectively deposited on the SAMs by chemical vapor deposition or physical vapor deposition, electrodeposition and electroless deposition in the fabrication process. However, with this approach it is obviously difficult to conduct deep lithography to construct a 3D pattern on a metallic surface. Recently, the highly anisotropic bulk micromachining of titanium has been reported by using the metallic anisotropic reactive ion etching with oxidation process. Arbitrarily high aspect-ratio structures with straight sidewalls and micrometre scale features have been micromachined into tita-

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nium substrates.[12] In addition, electrochemical micromachining is also an effective method of fabrication of the oxide,[13] metallic[14]or semiconducting[15] microstructures. By controlling electrochemical reactions between electrolyte and specimens, local etching on a metallic surface is realized to obtain certain microstructures. In this paper, we report the construction of 3D micro-/nano-patterns on the surface of an aluminium (Al) foil by using an electrochemical anodization method, which allows us easily constructing large-scaled micro-/nano-patterns on a metallic Al surface with low-cost and nondestructive process.

2. Experimental procedures

The experiment was carried out in the following steps and a schematic illustration of fabricating process is given in Fig.1.

2.1. Pretreatment of Al foil

High-purity Al foil (99.999%, 0.30mm thick) was pretreated before patterning and anodizing. The Al foil was degreased in acetone and ethanol for several minutes under the ultrasonic condition, followed by annealing at 500°C for 5h to increase Al grain size, and then the Al foil was dipped into dilute HNO_3 solution for 2h, and electropolished afterwards in a mixed solution of perchloric acid and ethanol (1:4 in volume) to remove impurities and contaminants from the surface of Al foil.

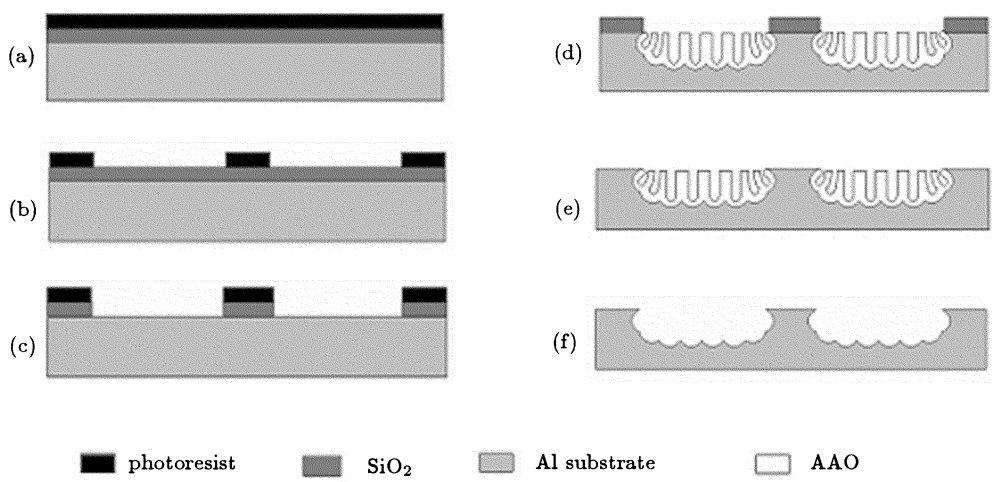


Fig.1. Schematic illustration of the fabrication process of micro- and nano- patterns on Al substrate. (a) SiO_2 sol and photoresist are spin-coated on the Al substrate. (b) The patterns are firstly formed on the photoresist layer by UV lithography. (c) The patterns are transferred to SiO_2 layer by plasma etching. (d) Washing off the photoresist and anodizing the Al substrate. (e) After anodization, the SiO_2 pattern is removed by plasma. (f) The AAO is dissolved and finally the micro- and nano- patterns on the Al substrate are obtained.

2.2. Coating SiO_2 resist mask on Al foil

A sol–gel process as described before[16] was introduced to prepare SiO_2 sol. Then the sol was spin-coated on the surface of Al foil which had been pretreated to form a layer of thin SiO_2 resist film. During the coating, rotation lasted 60s at a rotating speed of 1000rpm, and the thickness of SiO_2 film was about 400nm. Furthermore, the specimen was baked at 150°C in an oven for several hours in order to obtain a solid silica film.

2.3. Formation of patterns

To realize patterned structures, a standard photolithography technique was adopted. In the process of pattern preparation, the positive photoresist S9918 was firstly deposited onto the SiO_2-coated Al foil by spin-coating. After pre-baking at 95°C for 60s, the sample was exposed to the UV (λ=365nm) radiation (MA6 Germany) through a photomask. After exposing the specimen was immersed in a development solution to remove photoresist in the exposed regions to reveal SiO_2 layer. After the UV photolithography the pattern of photoresist was transferred to the underlying layer of SiO_2 by plasma etching (Plasmalab 80 plus Oxford). The samples were etched by CHF_3 (25sccm) and Ar (25sccm) plasma with a chamber pressure of 400Pa and R F power of 150W. The remaining photoresist on the SiO_2 pattern were washed off by acetone or ethanol.

2.4. Obtainment of micro-/nano-patterns on metallic Al foil

The anodizing of the Al foil with SiO_2 patterned layer on the surface was performed in 0.3M oxalic acid at 40V and 1°C. After finishing the first anodization, we once again utilized plasma to remove the patterned SiO_2 mask and then dissolved the porous alumina in a mixture of 5wt% H_3PO_4 and 1.8wt% H_2CrO_4 at 60°C to reveal the underlying Al substrate.

The morphologies of samples were characterized by scanning electron microscopy (SEM) (S-5200 Hitachi, Japan) and atomic force microscopy (AFM) (Nanoscope IIIa, USA).

3. Results and discussion

We chose Al as a sacrificial material because of its unique property that Al anodization can form porous alumina,[13,17−20] usually called anodic aluminium oxide (AAO), which exhibits the self-organization of hexagonal cells with cylindrical pores in the centre. Due to the special structure, AAO is extensively used as template to fabricate various one-dimensional (1D) nanoscaled materials.[21−25] We took advantage of the anodization behaviour of Al and combined with photolithographic technology to construct patterned nano-/microstructures on the Al substrate. In the experiment, SiO_2 was introduced as a resist mask because SiO_2 exhibits good adhesion to Al and enough inertness to acidic electrolyte.[26,27] Figures 2(a)–2(c) show SEM images of the specimens corresponding to different stages of the fabricating process respectively. Figure 2(a) is the SEM image of the cross-section of the specimen anodized for 40min. The existence of SiO_2 mask surely affected the anodization of Al foil. At the boundary of SiO_2 strips, tilted pores formed and grew laterally from two boundary sides inwards and gradually consumed Al under the SiO_2 mask. We can take advantage of this anodizing behaviour to construct a 3D microstructure on an Al substrate. The SiO_2 mask pattern was removed by CHF_3 plasma after anodization. Figure 2(b) shows the surface image of the specimen after removing the SiO_2. The right part of the inset in Fig.2(b) is the AAO and the left part is the revealed surface of Al, which was originally underneath the SiO_2 mask. Energy-dispersive x-ray spectroscopy (EDS) detection (not shown here) confirmed that there existed Al, F, O and Si in the left region. The appearance of bumpiness on the surface was possibly due to the formation of fluoride of Al in the process of CHF_3 plasma etching. At last the AAO

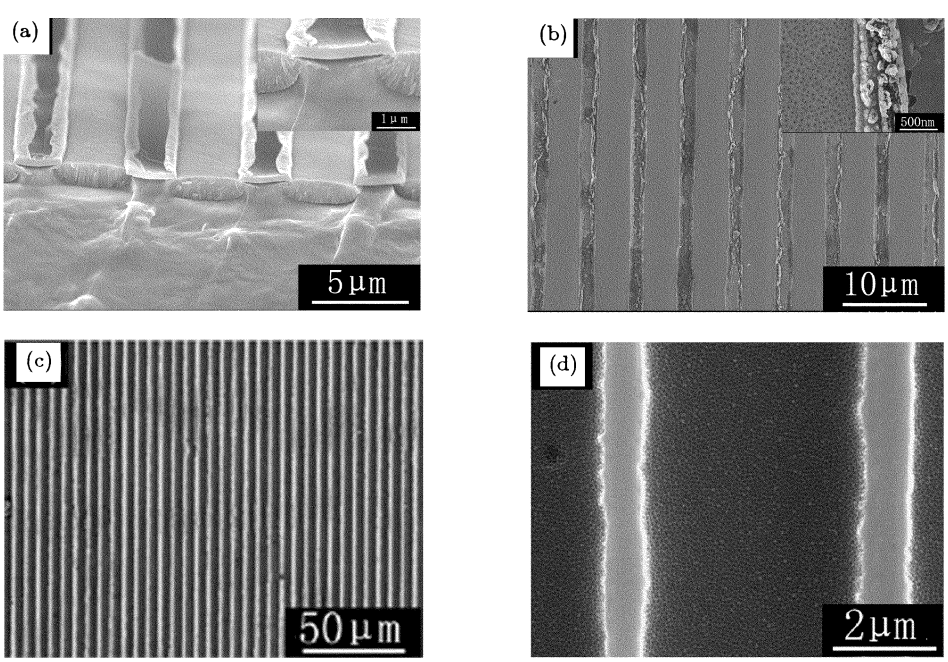


Fig.2. SEM images of samples at different periods of fabricating process. (a) Cross-sectional image of Al foil with SiO_2 patterned mask on the surface is anodized for 40min. (b) After anodization, the SiO_2 mask (corresponding to the left part in the inset) is removed. (c) The porous alumina is dissolved and microstripes and concave nano-texture are constructed on Al substrate. (d) Magnified image of (c), the concave nano-texture can be clearly observed.

film was dissolved in a mixture of 5wt% H_3PO_4 and 1.8wt% H_2CrO_4 at 60°. Because the bottom part of each nanopore is ended with a scalloped barrier oxide layer, a concave nano-texture is self-formed on the Al substrate after removal of the AAO film. At the same time the bumpiness that once existed on the surface of Al was dissolved too. We finally obtained a patterned nano-/microstructure on the Al substrate, as shown in Figs.2(c)–2(d).

We performed the first anodization for 40min, 65min, 90min, 2h and 6h respectively. After removing the SiO_2 and AAO, the metallic Al nano-/microstructures were obtained. Figures 3(a)–3(d) show the AFM images and cross-sectional analysis of the specimens. In fact, the formation of Al microstripes under the SiO_2 layer was due to a vertical and lateral anodization process proceeding simultaneously. The shape (including height and width) of Al microstripes changed continuously with the anodization time. The heights were about 1.2μm (40min), 1.5μm (65min), 2.1μm (90min), 1.0μm (2h), 0.4μm (6h) (see cross-sectional analysis in Figs.3(a)–3(d)). To obtain a high aspect-ratio structure by use of the method the initial mask pattern had to be large enough. With the proceeding of lateral etching, the Al microstripes continuously changed into ridge-like structure. When tilted pores from two sides met together in the centre the height of the microstripes began to decrease, it took about 90min to reach the extent in our experiment. If anodization time was long enough the ridges would disappear finally.

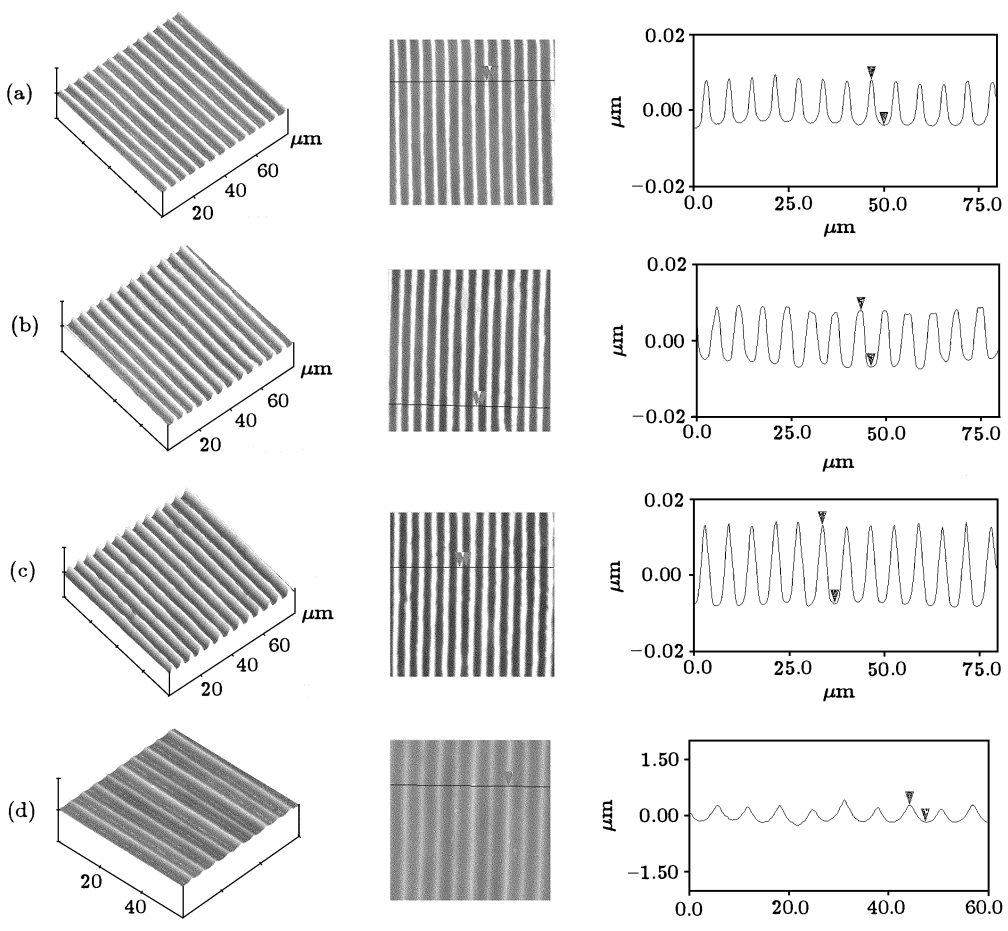


Fig.3. AFM images of samples. 3D schematic map and cross-sectional analysis (a) for the sample anodized for 40min. (b) for the sample anodized for 65min. (c) for the sample anodized for 90min. (d) for the sample anodized for 6h. For all the 3D map X: 20μm/div and Z: 8μm/div.

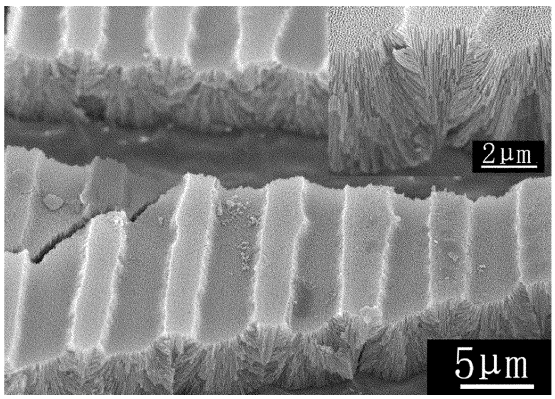


Fig.4. SEM image of AAO formed on Al substrate with microstripes on the surface formed during the first anodization. Inset gives the magnification of cross view.

The mechanism of the lateral anodization and the formation of ridge structure on Al substrate is possibly the change of the distribution of electric field due to the existence of SiO_2 mask. The local SiO_2-coated regions can break down the contact between electrolyte and metallic Al, which caused the deflection of electric field and the effect on the transportation of ions. Furthermore, with the proceeding of anodization, the continuously changing contour of the Al surface further affected the direction of electric field, which determined the direction of pore growth. The two factors may possibly explain the formation of tilted pores and remaining microstructures on the Al substrate. We utilized the substrate with metallic Al 3D microstructures formed on the Al foil surface during the first anodization (65min), to perform the second anodization under the same condition. Figure 4 shows the typical SEM image of the obtained structure. As observed, when the SiO_2 mask was removed, the direction of electric field was only affected by the surface contour of Al. Because the surface was at equal potential, the direction of the electric field was perpendicular to the metallic surface everywhere. We can also see the tilted pores propagating along the direction of electric field on lateral sides, as shown in the insert of Fig.4. Rabin *et al*[28] also reported laterally grown pores from the side wall inward and observed ridge-like Al structure when vertically and horizontally grown pores met each other.

4. Conclusions

We have reported a simple, nondestructive and low-costed method, which involves electrochemical anodization and photolithography, to construct large-scaled metallic groove micro-patterns on an Al surface. The depth and width of the grooves can be effectively adjusted by controlling the anodization time and pattern size. A possible anodization mechanism based on the deflection of electric field has been suggested to explain the occurrence of tilted pores and formation of Al microstripes. In addition, the Al texture surface with nano-concave can be naturally formed at the bottoms and on the walls of the grooves after the AAO film is removed. The micro- and nano-scaled composite patterns can be expected to serve as masters to mold other metallic or organic pattern films or metallic micro-channels for advanced micro-fluid systems.

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