Topographical studies of electrochemical anodized metal surfaces

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Abstract. An electrochemical anodization technique associated with wet surface cleansing processes was applied for fabrication of surface nanoscale structures on Al plates. Dynamic force microscopy (DFM) measurements clarifies that different wet cleansing processes create different initial surface structures on Al such as a linked-crater pattern and a groove-pattern on Al surfaces and induce finer and well-ordered characteristic surface nanoscale patterns. Based upon those structures, anodization proceeds in the fabrication of well-ordered characteristic nanoscale patterns on Al surface such as a well-oriented row-aligned pattern and a well-fined lattice pattern. Deposition of copper phthalocyanine (CuPc) molecules upon anodized crater-arrayed Al surface is conducted by casting CuPc resolved toluene. DFM and X-ray photoemission spectroscopy (XPS) measurements clarify that an organic-inorganic nanoscale patterned material is fabricated.

1. Introduction

Fabrication of templates for creating nanoscale structures becomes an important subject for innovation of nanoscale devices such as quantum dots, nanoscale array and nanoscale imprinted devices [1,2,3,4]. Submicron to nanometer scale devices, especially in the field of inorganic-organic hybrid devices [5,6] and molecular devices [7] as a nano-pattern template. One of those templates is a nano-porous alumina fabricated by anodization. Creation of nanoscale honeycomb structures in anodized alumina substrates were reported by Masuda et al [3] for nano-hole arrays. The application of nano-porous alumina for creation of hybrid optical devices were also suggested [8,9,10].

In the present study, the authors propose new types of nanoscale structures on Al surface by wet processes. An electrochemical anodization technique combined with wet processes was applied for fabrication of surface nanoscale structure on Al. Wet techniques under different conditions create different nanoscale patterns on Al surfaces, which are investigated by DFM. Furthermore, the authors tried on grafting molecular layers on nano-patterned Al surfaces by casting CuPc molecules on Al surface for fabricating an inorganic-organic nanoscale device.
2. Experimental details

In the present work, the surface of Al was cleaned with several stages of wet cleansing processes before applying anodization techniques to 5 mm square Al plates (Al 99.999%, Nilako Co. Ltd.). The surface cleansing was conducted by two different cleansing measures. One is cleansing using Semi Clean (LGL, Yokohama Oils and Fats Industry Co. Ltd.), acetone and pure water under ultrasonic waves. Semi Clean is an inorganic alkali cleansing agent which contains surfactants. The other is cleansing acetone and pure water under ultrasonic waves. The process of anodization was conducted by applying a DC positive voltage (20-40 V) to Al plates as an anode in H_2SO_4 solution with 0.015-0.30 mole % concentration.

The anodized Al surfaces processed under different conditions were investigated by dynamic force microscopy (DFM) employing SPI4000 (SII Nanotechnology Co. Ltd.). Mechanical-cut Si cantilever and closed-loop scanner was used for the DFM observation. DFM measurements were performed under atmospheric conditions. The molecular deposition of copper phthalocyanine (CuPc) was prepared by casting CuPc resolved in toluene on nanoscale patterned Al and was investigated by DFM and X-ray photoemission spectroscopy (XPS) employing a ESCA AXIS ULTRA DLD (Kratos Co. Ltd.) in order to clarify the topographical image and the deposition states of the CuPc pattern created on nanoscale patterned Al surface. Monochromatic Al K_α was used for the X-ray radiation. Pass energy was 160 eV.

3. Results and discussion

At the cleansing stage before anodization process, DFM measurements clarified that different topographical shapes were created on Al surfaces between samples prepared by two different cleansing measures. In the case of Semi Clean processed Al surface, craters were linked up forming a scaled-pattern (see Fig. 1(a)). Various-sized craters with 200-500 nm in diameter were randomly created. The scaled-pattern is supposed to be created by surface chemical reaction with Semi Clean which induces the surface erosion. In contrast to the Semi Clean treated Al surface, no craters were observed in Al surface treated with acetone and pure water (see Fig. 1(b)). Instead, line-shaped grooves with various widths were observed. Major role of acetone cleansing process is supposed to remove surface contamination and react differently with the surface aluminum oxide.

In the case of Semi Clean treated Al surface, anodization creates finer and more ordered nanoscale structures on Al surface under the intermediate anodization condition: applied voltage was around 25 V and average current was around 5 mA. Excessive high voltage caused too rapid anodization reaction to create ordered structures. Figure 1(c) shows that a fine-scale pattern was created overall 5 micrometer square area. In Fig. 1(c), small pores were created in a crater indicates that the secondary structures were fabricated. In the scaled-pattern, the linked craters with 60-100 nm in diameter covered up-and-down hills with several tens nanometer height differences. Focusing on a crater, small pores with 14 nm diameter were created in the large crater as shown in Fig. 1(c). The secondary structure in the crater-array pattern was a quite unique pattern as a nanoscale template. In the case of Al surface treated with acetone and pure water, the anodization created different pattern. Hut-shaped structures were observed. A nanoscale pattern was observed on each hut structure. Figure 1(d) shows well-oriented groove pattern with homogeneous width on a hut-shaped structure.

The other characteristic pattern was a highly-oriented nanoscale row-aligned pattern spread over large area, the distance of which rows was 50nm and the width of the dark line was 20 nm, as shown in Fig. 2(a). The pattern was created from crater-array pattern, which was induced from strip-shaped crater array fabricated by applying anodization to Semi Clean treated Al surface under the anodization condition: applied voltage was 25 V for 130 min and average current was 4.5 mA. Long anodization time assisted in fabrication of the highly ordered nanoscale structure. Anodization process in Semi Clean treated Al surface generates various types of crater shapes such as circle, ellipse and strip shapes. In the case of Al surface treated with acetone and pure water, further anodization in the hut-shaped structure created the fine lattice pattern with the dark spot diameter of 20 nm, as shown in Fig. 2(b) possibly induced by the hut-shaped secondary structure shown in Fig. 1(d).
Grafting CuPc molecules on nano-structured Al surface was implemented by casting CuPc resolved toluene on anodized crater-arrayed Al surface. Figs 3(a) and 3(b) show the DFM image of CuPc pre-deposited and deposited Al surfaces. If we compare the two cross sections in the same sized crater of pre-deposited and deposited patterns, the contours of the craters become thick in the case of CuPc deposited Al surface while the contours were clear-cut in the case of pre-deposited Al surface. The depth profile shows the depth of the crater becomes shallow and smooth, which indicates CuPc layers are deposited along the crater surface.

Figure 4 shows the XPS core-level spectra of CuPc deposited nanoscaled Al surface. The spectrum of Al 2p was composed of several peak components, which reflects the Al surface states. The Cu 2p spectra of the deposited CuPc molecule split, which indicates the charge transfer between Cu and substrate Al. C1s spectrum was also composed of several peak components due to the deposited CuPc molecule. Main peak and the neighboring lower energy component corresponding to different C sites

Figure 1. DFM images of pre-anodized and anodized Al surfaces treated with cleansing processes. (a) Pre-anodized Al surface treated with Semi Clean, acetone and pure water under ultrasonic waves. Linked-crater forms a scaled pattern. (b) Pre-anodized Al surface treated with acetone and pure water under ultrasonic waves. Groove-pattern. (c) DFM images of anodized Semi Clean treated Al surface. Ordered crater-array forms a finer scaled structure. Solution: 0.04 mol%; Anodization voltage: 25 V; Current: 5.0 mA; Time: 30 min. (d) DFM images of anodized Al surface treated with acetone and pure water. Well-oriented groove structure was observed in each hut-shaped structure. Solution: 0.3 mol%; Anodization voltage: 25 V; Current: 4.0 mA; Time: 40 min.
of CuPc. Higher binding peaks reflect the interaction of CuPc with nanoscaled Al surface. CuPc molecules deposited on nanoscale-patterned Al surface creates organic-inorganic hybrid nanoscale pattern.

**Figure 2.** DFM images of further anodized Al surfaces. (a) Well-oriented row-aligned pattern created from a linked-crater pattern. Solution: 0.03 mol%; Anodization voltage: 25 V; Current: 4.5 mA; Time: 130 min. (b) Fine lattice pattern created from a groove-pattern. Successive anodization applied to the hut-shaped structure. Solution: 0.3 mol%; Anodization voltage: 25 V; Current: 6.0 mA; Time: 15 min.

**Figure 3.** DFM images of CuPc deposited nanoscale Al surfaces. (a) Pre-deposited crater-array pattern. (b) Deposited pattern.
4. Conclusions
Cleansing process of Al surface creates the initial unique structures on the surface and anodization process induces characteristic nanoscale pattern on the surface. The crater-array pattern possibly creates a well-ordered crater-array structure and a fine ordered row-aligned structures, which can be important candidates for nanoscale hybrid devices, while a groove-pattern possibly creates a fine lattice pattern. XPS measurements clarifies the patterning deposition of CuPc is possible and various states of deposited CuPc exist on nanoscale Al surface.

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Figure 4. XPS core-level spectra of CuPc deposited Al surface. (a) Al 2p. (b) Cu 2p (c) C 1s.