Nanoscale molecular patterning on artificially fabricated nanoscale structured Al surfaces

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Abstract. The surface of an Al plate was treated with a combination of chemical and electrochemical processes for fabrication of surface nanoscale structures on Al plates. Chemical treatments by using acetone and pure water under supersonic waves were conducted on an Al surface. Additional electrochemical process in H2SO4 solution created a finer and oriented nanoscale structure on the Al surface. DFM measurement clarified that the nanoscale highly oriented line-structure was successfully created on Al surface. The line distance was estimated approximately 30-40 nm. Molecular patterning on the highly oriented line-structure by copper phthalocyanine (CuPc) was also conducted. The CuPc molecules were put on the nanoscale structure by casting a toluene droplet containing CuPc. DFM and X-ray photoemission spectroscopy (XPS) measurements demonstrated that a molecular pattern that the groove channels were filled with CuPc molecules was fabricated.

1. Introduction

Fabrication of templates for creating nanoscale structures becomes an important subject for innovation of nanoscale devices [1,2,3,4,5]. 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 and memory devices were also suggested [6,7,8,9]. The authors proposed new types of nanoscale structures such as a linked-crater structure and a hut-shaped structure on Al surface by unique combination of chemical and electrochemical processes [10]. Both nanoscale patterns possessed higher order structures [10]. In the present study, the authors have developed the fabrication techniques to create a nanoscale highly-oriented line structure, which are homogeneously extended in a large area. Furthermore, the authors tried on grafting molecular layers on the line-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 electrochemical techniques to 5 mm square Al plates (Al 99.999%, Nilako Co. Ltd.). The surface chemical treatment was conducted by using acetone and pure water under ultrasonic waves with several stages. The additional electrochemical process was conducted by applying a positive dc voltage (20-30V) to Al plates as an anode in H$_2$SO$_4$ solution with 0.015-0.30N concentration.

The electrochemically treated 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 a toluene droplet containing CuPc on a nanoscale patterned Al surface. The toluene liquid was extended on the Al surface with toluene gradually evaporating from the surface. The Al surface 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$_\alpha$ was used for the X-ray radiation. Pass energy was 160 eV.

3. Results and discussion

At the chemical treatment stage before an electrochemical process, DFM measurements clarified that line-shaped grooves with random widths and depths were observed on the Al surface. Successive electrochemical process created finer and more ordered nanoscale structures on Al surface under the intermediate electrochemical conditions: applied voltage was around 25 V and average current was around 5 mA. DFM measurement clarified that the nanoscale highly oriented line-structure was created on Al surface by the successive electrochemical process as shown in Fig. 1. The line distance was estimated approximately 30-40 nm by the cross section analysis of the Al surface. The depth of each groove was estimated approximately as 5-6 nm in the flat region. The highly-oriented line-pattern was homogeneously extended in a large area, which is remarkably prospective for fabrication of feasible nanoscale devices. High applied voltage caused too rapid anodization reaction to create ordered structures. Excessive electrochemical reaction with a high speed caused the aluminum plate to become thinner, which indicates that this phenomenon is electrochemical etching to create a nanopattern. Long anodization time with a small current assisted in fabrication of the highly ordered nanoscale structure.

Grafting CuPc molecules on nano-structured Al surface was implemented by casting CuPc resolved toluene on the highly oriented line structure on the Al surface. Figures 2(a) and 2(b) show the DFM images of CuPc pre-deposited and deposited Al surfaces in 1 $\mu$m x 1 $\mu$m area. Figures 2(c) and 2(d) show the DFM images of CuPc pre-deposited and deposited Al surfaces in 500nm x 500nm area. If we compare the two cross sections between pre-deposited and deposited patterns, the contours of the grooves 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 groove becomes shallow and smooth, which indicates CuPc layers are put in the groove. Finer topographical periodicity was found in the cross section in Fig. 2(b) suggested that the groove channels were filled with CuPc molecules.

Figure 3 shows the XPS core-level spectra of CuPc deposited nanoscaled Al surface. N 1s and Cu 2p core-level lines appeared after CuPc deposition. C 1s spectrum was composed of two peaks which was characteristic to CuPc. A lower binding energy component at 285 eV is attributed to C 1s from benzene ring and higher binding energy components at 288 eV and at 286.5 eV are attributed to C1s and shake-up from pyrrole ring [11]. Much lower binding energy components around 283 eV and the highest component at 290 eV might reflect the interaction of CuPc with nanoscaled Al surface. Spectral profiles of Al 2p peak differed between pre-deposited and deposited samples which reflected the molecular-surface binding states as shown in Figs 3(a) and 3(b). In the case of CuPc deposited Al
surface, the spectrum of Al 2p was composed of lower 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 as shown in Fig. 3(e). CuPc molecules deposited on nanoscale-patterned Al surface creates organic-inorganic hybrid nanoscale pattern.

4. Conclusions
The surface of an Al plate was treated with a combination of chemical and electrochemical processes. Chemical treatment were conducted by using acetone and pure water under supersonic with several stages of processes. Additional electrochemical process in H₂SO₄ solution created successfully a highly oriented line-structure homogeneously extending on a large scale area of the Al surface. The line distance was estimated approximately 30-40 nm. Molecular patterning on the highly oriented line-structure by using CuPc was also conducted by cast method. DFM and XPS measurements demonstrated that the groove channels were filled with CuPc. XPS measurements clarified that various states of deposited CuPc exist on the nanoscale patterned Al surface.

Figure 1. DFM images and cross section analysis of additional electrochemically processed Al surface after acetone treatment.

Figure 2. DFM images and cross section analysis of CuPc pre-deposited and deposited line-structured Al surfaces. (a) Pre-deposited image. (b) Deposited image. (c) Pre-deposited image. (d) Deposited image.
Figure 3. XPS core level spectra of CuPc deposited line-structured Al surface.
(a) Pre-deposited Al 2p (b) Al 2p (c) C1s (d) N 1s (e) Cu 2p

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References
[1] Leonard D, Krishnamurthy M, Reaves C M, Denbarrs S P and Petroff P M 1993 Appl. Phys. Lett. 63 3203
[2] Park G, Shchekin O B, Huffaker D L and Deppe D 2000 IEEE Photon. Tech. Lett. 13 230
[3] Masuda H, Yamada H, Satoh M, Asoh H, Nakao M and Tamamura T 1997 Appl. Phys. Lett. 71 2770
[4] Martini I, Kuhn S, Kamp M, Worschech L, Forchel A, Eiserdt D, Koeth J, and Sijbesma R 2000 J. Vac. Sci. Technol. B 18 3561
[5] Naito K, Hieda H, Sakurai M, Kamata Y and Asakawa K 2002 IEEE Trans. Magn. 38 1949
[6] Masuda H, Kanezawa K and Nishio K 2002 Chem. Lett. 12 1218
[7] Nishio K, Nakao M, Yokoo A and Masuda H 2003 Jpn. J. Appl. Phys. 42 L83
[8] Matsumoto F, Nishio K and Masuda H 2004 Jpn. J. Appl. Phys. 43 L640
[9] Dieny B, Superiosu V S, Parkin S S P, Gurney B A, Wilhoit D R and Mauri D 1991 Phys. Rev. B 43 1297
[10] Kato H, Takemura S, Sugiyama T, Watanabe Y, Matsunami H, Takarai Y, Izumiyanay M, Ishii A, Hiramatsu T, Nanba N, Nishikawa O and Taniguchi M 2007 J. Phys: Conference Series 61 518
[11] Berena B, Luo Y, Nyberg M, Carniato S, Nilson K, Alfredsson Y, Ahlund J, Martensson N, Siegbahn H and Puglia C 2004 Phys. Rev. B 70 195214