Dynamic force microscopy and X-ray photoemission spectroscopy studies of nanowire fabrication on a highly oriented line-structure of Al surface

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Abstract. Nanowire fabrication was implemented on the nanoscale highly-oriented line-structure of Al surface. An Al plate was chemically and successively electrochemically processed by applying dc voltage in H₂SO₄ solution in order to fabricate a nanoscale highly-oriented line structure on the surface. The line width was estimated under 50 nm. As a nanowire polymerization process, aniline monomer solved in pure water and oxidizing agent APS solved in HCl successively dropped on the nanostructured Al surface. The Dynamic force microscopy (DFM) measurements and cross section analysis clarified that the line-structure still remained and the depth of the row became shallow after the polymerization process was applied. Since N 1s core-level lines appeared after the aniline polymerization by X-ray photoemission spectroscopy (XPS) measurements, the aniline monomers were polymerized along the line and filled in the row channel.

1. Introduction

Conducting polymers with π conjugate system are supposed to be prospective for nanowire fabrication because of variety of monomer selectivity and of side chain selectivity such as oligomers, oligothiophene, and porphyrin [1,2,3,4]. Organic nanowires have been chemically synthesized. In contrast to organic nanowire fabrication method, in fabrication of metal and inorganic semiconductor nanowires, substrate surface for template have been used by using non-lithography techniques [5,6]. In the present study, the authors intend to fabricate organic nanowires using nanoscale pattern templates. The authors fabricated new types of nanoscale structures such as a linked-crater and hut-shaped structures on Al surface by unique combination of chemical and electrochemical processes [7]. In the present study, the authors develop the method to fabricate a highly-oriented nanoscale line structure on Al surface and intend to fabricate conducting polymer polyaniline nanowire using the highly-oriented nanopattern template.
2. Experimental details

In the present work, 5 mm square Al plates (Al 99.999%, Nilako Co. Ltd.) were used. The Al surface was chemically processed with several stages by using acetone and pure water under supersonic waves. The electrochemical process was conducted by applying a positive dc voltage (20-30V) to Al plates as an anode for 40 min in H₂SO₄ solution with 0.30N concentration. The average current was around 5 mA.

The electrochemically processed Al surfaces 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. After ensuring that a highly-oriented nanoscale structure was formed on the Al surface by DFM, as-grown polymerization process of polyaniline nanowire on the nanopatterned Al surface was conducted. Pure water droplet containing 0.005M aniline monomer dropped on the nanopatterned surface and was extended on the surface. A pure water droplet containing 0.05M HCl was successively dropped on the surface. Finally, a pure water droplet containing 0.05M ammonium peroxodisulfate (APS) was dropped on the surface in order to polymerize aniline on the nanopatterned Al surface. Concentrations of the chemical agents were pre-tested in a test tube to ensure that polyaniline was polymerized. Four types of polyaniline are known, namely, leucoemeraldine (LE), pernigraniline (PE), emeraldine base (EB) and emeraldine salt (ES). Under the above mentioned concentrations, the liquid color turned blue which indicated that EB was synthesized.

DFM measurements and cross section analysis were conducted on the polymerization processed Al surface. X-ray photoemission spectroscopy (XPS) measurement was also conducted employing a ESCA AXIS ULTRA DLD (Kratos Co. Ltd.) in order to clarify the polymeriizaion states of polyaniline on the nanoscale patterned Al surface. Monochromatic Al Kα was used for the X-ray radiation. Pass energy was 160 eV.

Atomic force microscopy-current imaging tunneling spectroscopy (AFM-CITS) measurements were also conducted on two types of samples as follows in order to investigate local conductivity on the Al surface. First sample was as-grown polyaniline on the nanopatterned Al surface. The second sample was the nanopatterned Al surface dropped by a pure water droplet containing aniline monomer, HCl, APS.

3. Results and discussion

After the chemical treatment by using acetone and pure water under supersonic waves, successive electrochemical process created finer and ordered nanoscale structures on Al surface under the intermediate electrochemical conditions: applied voltage was 25 V and average current was around 5 mA. DFM measurements clarified that the nanoscale highly oriented line-structure was created on Al surface by the successive electrochemical process as shown in Fig. 1(a). The line distance was estimated under 50 nm by the cross section analysis of the Al surface, see Fig. 1(c). The depth of each groove was estimated approximately as 3-17 nm. The highly-oriented line-pattern was homogeneously extended in a large area, which is remarkably prospective for fabrication of feasible nanoscale devices.

Figures 1(b) and (d) show the DFM images of the Al surface after the as-grown polymerization process of polyaniline nanowire was conducted. A pure water droplet containing 0.005M aniline monomer dropped on the nanopatterned surface and was extended on the surface. A pure water droplet containing 0.05M HCl was successively dropped on the surface. Finally, a pure water droplet containing 0.05M APS was dropped on the surface in order to polymerize aniline on the nanopatterned Al surface. Figures 1(b) and (d) shows the DFM images of as-grown polymerization processed Al surface by using small quantity of the liquid. The liquid was homogeneously extended on the nanopatterned Al surface. Different regions could not be observed. The Al line-structure remained on the surface. The depth of the groove was estimated 2-10 nm in the flat region, see Fig. 1(d). The depth of the groove became shallow and the ripple became finer compared with the pre-processed Al surface. Thus, the channel of the groove was filled with as-grown polyaniline.
Figure 2 shows the XPS spectra of preprocessed and processed Al surfaces. N 1s and C 1s lines appeared in the XPS spectra of processed Al surface, see Figs. 2(c) and (d), which suggested that polyaniline was polymerized on the nanopatterned Al surface. In the C 1s spectrum, higher binding energy component was observed. In Al 2p spectrum of the processed surface, a lower binding energy component was observed. The higher binding energy component of C 1s spectrum and the lower binding energy component of Al 2p suggested the polyaniline-Al interaction.

AFM-CITS measurements showed that metallic and semiconductive IV curves were measured. In the case of as-grown polyaniline on Al surface, the tunneling current was so small that the current image could not be obtained. The tunneling characteristic was observed spatially different as semiconductive and metallic in the case of nanopatterned Al surface dropped by droplet containing aniline monomer, HCl and APS as shown in Fig. 3. In this case, two samples were measured. One case was that the droplet was put on the Al surface before the liquid color turned light blue. The other case was that the droplet was put on the Al surface after the liquid color turned light blue. In the former case, the Al surface nanopattern was observed while surface roughness increased in the latter case. In those cases, the channel of the groove on the Al surface was filled with polyaniline. Three types of IV characteristics were found, namely, semiconductive with a large gap, semiconductive with a small gap, and metallic. Three types of IV characteristics might reflect the various local density of polyaniline on the nanopatterned Al surface. Conductive area in the current image was abundant in the topographically dent area. In this case, polyaniline was supposed to be accumulated in the groove channels.

4. Conclusions
Nanowire fabrication was implemented on the nanoscale highly-oriented line-structure of Al surface. The line width was estimated under 50 nm by the cross section analysis. As a nanowire polymerization process, aniline monomer solved in pure water and oxidizing agent APS solved in HCl successively dropped on the nanostructure as a droplet. The DFM measurements and cross section analysis clarified that the line-structure still remained and the depth of the row became shallow after the polymerization process was applied. Since N 1s core-level lines appeared after the aniline polymerization by XPS measurements, the aniline monomers were polymerized along the line and filled in the row channel. AFM-CITS measurements showed that the tunneling IV characteristic was observed spatially different as semiconductive and metallic in the case of droplet containing aniline monomer, HCl and APS cast on Al surface.
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