Supplementary Material (ESI) for Journal of Materials Chemistry
This journal is (c) The Royal Society of Chemistry 2010

Nanolithographic patterning via electrochemical oxidation of stable poly(nitroxide radical)s to poly(oxoammonium salt)s

Tsuyoshi Hyakutake,[a,b‡] Jin Young Park,[b] Yasunori Yonekuta,[a] Kenichi Oyaizu,[a] Rigoberto Advincula[b*] and Hiroyuki Nishide[a*]

[a] *Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan. Fax: +81-3-3209-5522; Tel: +81-3-3200-2669; E-mail: nishide@waseda.jp*

[b] *Department chemistry and Department Chemical Engineering, University of Houston, Houston, TX77204, USA. E-mail: radvincula@uh.edu*

‡ Current address: Advanced Materials Research Team, Public Works Research Institute, Tsukuba 305-8516

1. Experimental

1.1 Material

1.2 Film fabrication

1.3 Nanolithography

2. PTMA nanopatterning (Fig. S1)

1. Experimental

1.1 Materials.

Poly(2,2,6,6-tetramethylpiperidine-1-oxyl methacrylate) (PTMA) and poly(2,2,6,6-tetramethylpiperidine-1-oxyl vinylether) (PTVE) were synthesized in Nishide group.[1] The detail information on synthesis was described in the literatures. Freshly distilled toluene and THF were used as solvents.

1.2 Film fabrication.

The mixture solution of toluene and THF (4.89 wt %) was used to dissolve each polymer. The prepared solution was filtered using PTFE filters (pore size: 0.22 μm) prior to usage. Ultra-thin films were prepared as follows: gold (thickness: 100nm) sputtered Si wafers were prepared and rinsed with H_2O and C_2H_5OH several times, finally oxygen plasma cleaning was performed for 1 min to remove residual dust on the surface. A solution of the polymer was carefully dropped on the substrates and spin-casted at 4000 rpm for 2 min two times. The thickness of the poly(nitroxide radical)s film was determined by ellipsometric measurements.

1.3 Nanolithography.

Nanolithographically electrochemical oxidation was performed by using current-sensing atomic force microscopy (CS-AFM; Agilent Technologies, Agilent 5500 AFM/SPM System). For the CS-AFM nanopatterning, conductive tips (Pt-Ir coated tips; Agilent) were used to make patterns on the film. The free frequency was 10-17 kHz and driving force was 0.07-0.4 N/m (N+-silicon, resistivity: 0.01-0.02 Ωcm). The patterning process was conducted under ambient conditions at ~42-47 % relative humidity and 22-23 °C. Tip velocity was set to 1.5-2.0 lines/sec. The particular patterns can be driven by the conductive AFM tip and controlled in a programmed manner by use of “Picolith” (Agilent) software. Subsequent images after patterning were performed at lower bias voltage under the same conditions to obtain current images. All the 2D/3D images and *I-V* curves were shown by SPIP software (scanning probe image processor, Imagemet.com) after flattening and filtering.

The organic radical polymer layer was fabricated to test the PTVE-based MIM-diode type device. The preparation of the device is as follows; firstly, the bottom substrate [ITO (150 nm)] was degreased with solvents and cleaned in a UV-ozone Cleaner. PTVE and $PTVE^+BF_4^-$ were then dissolved in acetonitrile (75 g/L and 25 g/L, respectively), spin-coated on the bottom substrate, followed by baking at 80 °C for 90 min and drying in vacuum at 6×10^{-7} Torr. Lastly, an aluminum layer as a top electrode was deposited onto PTVE layer through a shadow mask. Both the top and the bottom electrodes had a linewidth of 5 mm, so that the device had a surface area of 25 mm^2. The thickness of the PTVE and Al layer were 100 nm and 150 nm, respectively. Agilent 4155 semiconductor parameter analyzer or Keithley 2400-C digital source meter were employed to study the performance of the radical polymer-based MIM-diode type devices. All electrical measurements were conducted at room temperature under ambient atmosphere.

Reference

1. (a) H. Nishide and T. Suga, *Electrochem. Soc. Interface*, 2005, **14**, 32. (b) H. Nishide, N. Yoshioka, T. Kaneko and E. Tsuchida, *Macromolecules*, 1990, **23**, 4487. (c) Y. Yonekuta, K. Susuki, K. Oyaizu, K. Honda and H. Nishide, *J. Am. Chem. Soc.*, 2007, **129**, 14128. (d) T. Suga, S. Takeuchi, T. Ozaki, K. Oyaizu and H. Nishide, *Chem. Lett.*, 2009, **12**, 1160.

2. PTMA nanopattening

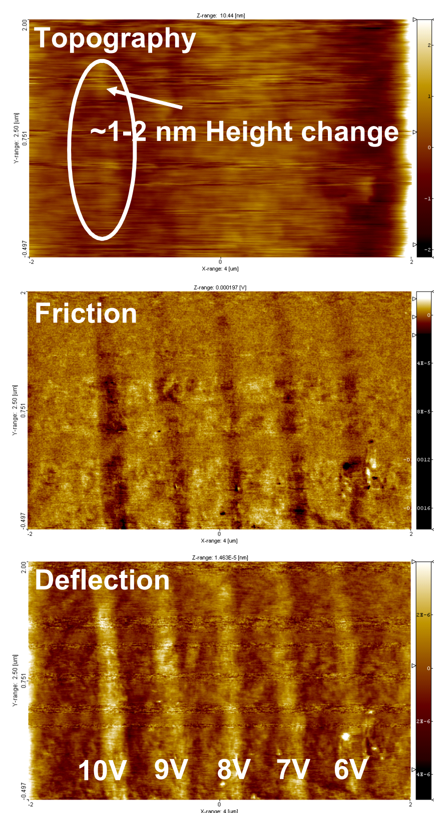

Fig. S1 Topography, friction and deflection image of the patterned lines in PTMA solid film after applying various sample bias voltages (between 10 and 6 V) at a scan rate of 0.1µm/s.

Surface morphology of the PTMA film was affected in the nano-scale area where the bias voltage was applied. The topography features are shown in Fig. S1. The height on the patterned line formed at an applied voltage of 9 V or 10 V (positive sample bias) was slightly raised in 1-2 nm when compared to the relatively unpatterned film. However, it is clear that all the patterned lines have friction and deflection change in voltage range investigated. Unfortunately, these changes can not imply that electrochemical oxidation was accomplished on the patterned lines. To obtain more obvious clues, current image and *I-V* measurements were carried out, but significant change from those experiments did not appear.