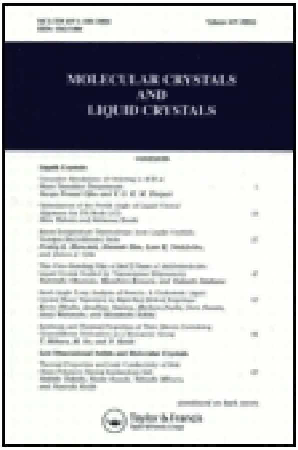

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 1999, Vol. 337, pp. 7-12
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Atomic Force Microscope Lithography with Octadecyldimethyl-Methoxysilane Monolayer Resist

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Nanometer-scale patterning of thin films was performed by using the atomic force microscope (AFM) as the exposing tool. The octadecyldimethyl-methoxysilane (ODMS) films were prepared on a silicon (Si) substrate by self-assembled monolayer. Patterning was accomplished through the local degradation of the monolayer as a result of anodic reaction induced by an AFM tip. When the voltage applied to the ODMS monolayer on the silicon substrate, the protruding lines appeared in the exposed regions. After etching probe-scanned substrate, we obtained fine grooves as narrow as 80 nm.

Keywords: scanning probe anodization; nanolithography; organosilane; self-assembled monolayer; atomic force microscope

INTRODUCTION

Scanning probe microscope (SPM) such as the scanning tunneling microscope (STM) and the atomic force microscope (AFM) have been used to modify the surface on a nanometer-scale utilizing various interactions between a tip and substrate.[1-2]

For lithography, the AFM has a distinct advantage over the STM because AFM can be used for insulating as well as conducting materials. And patterning by the AFM tip can be used for nanometer scale lithography with narrower than those obtained by the use of photon[3],electron[4]and scanning probe lithography.[5-8]

Resist films must be prepared in a thin and uniform layer in order to attain high spatial resolution nanometer scale. These organic molecules are spontaneously chemically bind to solid substrates such as silicon and gold. In addition to forming a highly ordered layer, resist films should be chemically resistant to many common acids and solvents and must be stable at moderately high temperature.

In this paper, we report the preparation of self-assembled octadecyl-dimethylmethoxysilane (ODMS) monolayer and then we fabricate the submicrometer scale on a organosilane films using the AFM as a mechanical tool. In the regions where the AFM tip had been passed while positively biasing the substrate, the monolayer was locally degraded. The monolayer can be used as a mask for pattern transfer into substrate by their self-degradation caused by the tip-scanning.

EXPERIMENTAL

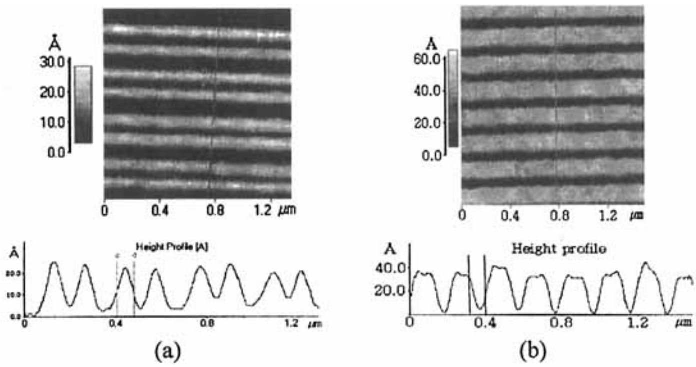
The silicon substrate was cleaned in Teflon container filled with Piranha solution(H_2SO_4 : H_2O_2 = 3 : 1) for 30~60 min. After the substrate was cleaned, was rinsed with deionized (DI) water and then blown with dried N_2 gas to remove any moisture. The cleaned silicon substrate became completely hydrophilic because a thin oxide layer was grown. The cleaned substrate was developed for 16 hours with a 0.1 M solution of the ODMS in hexane at 60~70 °C. The alkyl groups provide a hydrophobic surface and resistance to etching solution. The thickness of the ODMS monolayer estimated by

Rudolph Auto EL 2 ellipsometer. Silicon substrate formed with ODMS monolayer was mounted on the AFM operating in the air. We measured with contact mode AFM of imaging provided a Park Scientific Instrument (Autoprobe CP). While maintaining a constant tip-substrate force of 5-15 nN by a feedback control of the piezoelectric actuator, the tip was atomic resolution capability. The silicon cantilever with a force constant of 0.24 N/m was used. To chemically modify a material at nanometer scales using the AFM, it is necessary to provide enough energy either by mechanical forces or by electron bombardment. The sample was attached to the sample holder with conducting colloidal graphite and the sample holder was insulated from the piezoscanner. Patterning of the ultrathin films on Si substrate was performed with a AFM using a 100 μm range piezoelectric scanner. For AFM lithography, a power supply (2400 SourceMeter, Keithley) was installed in the AFM to control the electric current and the voltage. Prior to modifying silicon substrate, we examined the film quality with the AFM , for example, pinhole and roughness. When the tip of the AFM was applied with a negative DC bias voltage, the protruded patterns of the ODMS monolayer were made. The patterned sample was etched for 1-5 min in buffered oxide etch (BOE) solution. BOE solution was prepared by diluting the concentrated HF (45wt%) with water at 1:50 ratio. The probe scanned regions were selectively etched by the BOE solution while the unscanned regions were protected from the etching by the ODMS monolayer. The etched samples were investigated with the same AFM as used for the lithography. All the experiments were carried out in an ambient air atmosphere.

RESULTS AND DISCUSSION

The thickness of the ODMS monolayer was approximately 16~18 Å as estimated by ellipsometry. The ODMS monolayer films were chemisorbed uniformly. While maintaining a constant attractive force of 5~15 nN between the tip and surface, the tip was scanned over the surface of the self-assembled ODMS monolayer films to obtain topographical image. Due to the anodic reaction, local degradation of the monolayer occurred at the place where the probe-tip of the AFM scanned with the applied voltage. Sugimura et al. have reported the degradation mechanism of scanning probe anodization.[9] The regions of self-assembled ODMS monolayer on the silicon substrate became hydrophobic while the degraded regions on the substrate became hydrophilic again. Because the alkyl groups were removed and probably replaced with –OH groups. The differential interference contrast (DIC) confirmed these modified surface before and after anodization.[10] Crooks et al. also proposed the same mechanism of electrochemistry in the anodization of alkanethiol SAMs in air.[11] We also obtained AFM image showing that the tip scanning regions on the substrate slightly protruded from the surrounding undegraded regions. This phenomenon was due to the silicon volume expansion in the degraded regions. The formation of protruded lines due to scanning probe anodization depends on the scan rate, applied voltage and humidity in the laboratory. Figure 1(a) shows the AFM image of anodized surface. The condition of scanning probe annodization was the voltage of –27 V, scan speed of 120 μm/s and current of 13 nA. The nanopattern was fabricated with a resolution of 75 nm by scanning probe anodization.

To etch the protruding patterns fabricated on the silicon substrate, probe-scanned substrate was etched in the BOE solution for 1 min. The etching process required a lower level of damage to the monolayer to allow selective etching. The etching of the substrate in solution proceeded isotropically, so the etched groove widened due to side etching as the etching time increased. After the substrate was etched, rinsed with a deionized (DI) water and then blown with nitrogen. The scanned region was selectively etched, while the unscanned region was protected from etching. In other words, ODMS monolayer resist played a role as an etching mask. Figure 1(b) shows AFM image of some etched lines. The AFM image was about 80 nm in width .



(a) (b)

FIGURE 1 AFM images of anodization and the etched on silicon substrate. (a) An AFM image of the protruding lines formed at the condition of –27 V, scan speed of 120μm/s and current of 13 nA. (b) Grooves of 80 nm were fabricated by using ODMS monolayer resist.

CONCLUSIONS

We have successfully demonstrated the nano-scale patterning by using AFM. The self-assembled ODMS monolayer was used as a resist for SPM lithography. The self-assembled ODMS monolayers have been used to pattern and etch nano-structures into silicon. The AFM negative image of the protruding lines created by scanning the silicon with AFM tip under a –27 bias. The scan speed was 120 μm and the average of line width was about 75 nm. And then groove as narrow as 80 nm were formed after the chemical etching.

Acknowledgements

This work was supported by the Ministry of Education (998-016-E00030) and We would like to thank Prof. Sunwoo Park and Mr. Yongwoo Shin for helpful discussion.

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