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Nanolithography of Self-Assembled Zirconium N,N′-Bis(Ethyl Dihydrogen Phosphate)-3,4,9,10-Perylene(Dicarboximide) (Eppi) Layer on Silicon Surface

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Nanometer-scale patterning of self-assembled zirconium N,N′-bis(ethyldihydrogen phosphate)-3,4,9,10-perylene(dicarboximide) (EPPI) films has been performed by using the atomic force microscope (AFM). The formation of Zr-EPPI monolayer was obtained by sequential adsorption of organobisphosphonic acids and metal ions (Zr^{4+}) on modified silicon surface. After AFM anodization, the protruding lines appeared in the exposed regions. From these results, we report the effects of positive charges and of difference of thickness on silicon surface.

Keywords: self-assembled film; perylene; AFM anodization; metal ions

INTRODUCTION

Scanning probe microscopes (SPMs) have attracted the attention of many researchers as potential tools for nanolithography. Nanometer-scale patterning of organic thin films has been performed by using AFM as the exposing tool[1]. Especially, self-assembled monolayer (SAM) films have been patterned through the electron irradiation emitted from the tips of AFM. The EPPI molecules have been known as one of photoconducting and photoinduced electron transporting materials[2]. The Zr-EPPI monolayer was prepared on silicon substrate

by self-assembly. In this paper, we report the differences of protruding lines as the effect of charge and thickness on modified surface through AFM anodization.

EXPERIMENTAL

The silicon wafers were cleaned in a piranha solution (H_2O_2 : H_2SO_4, 1 : 3 by volume) for 30~60 min. The cleaned silicon surface was phosphorylated with 10 mM $POCl_3$ and 10 mM 2,4,6-collidine in acetonitrile solution for 12 hours at 70℃. These substrates were dipped in 5 mM $ZrOCl_2$ solution and 1 mM EPPI solution at room temperature, alternatively[3,4]. The synthetic scheme for the formation of Zr-EPPI monolayer on silicon surfaces is shown in Figure 1. Patterning of Zr-EPPI on Si substrate was performed with an AFM using 100 μm range piezoelectric scanner. The morphology of anodized surface was observed by AFM.

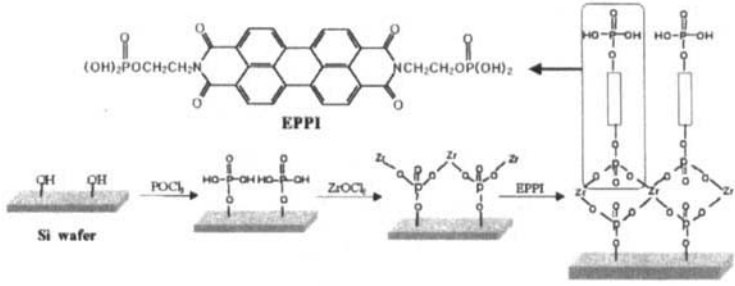

FIGURE 1. The synthetic scheme for the formation of Zr-EPPI layer on silicon surface.

RESULTS AND DISCUSSION

The thickness of the layer for each step was estimated by ellipsometry.

The thickness of phosphorylated, zirconated and Zr-EPPI layers was 4, 7 and 23 Å, respectively. The uniformity of these films was confirmed by using ellipsometry and UV-vis spectroscopy. Patterning was accomplished through the localized degradation of the monolayer as a result of anodization induced by an AFM tip. When the voltage was applied to Zr-EPPI layers on silicon substrates, the protruding lines appeared in the exposed regions. Figure 2 shows the AFM images of anodized patterns in air. The image of protruding lines formed on surfaces terminated with zirconium ions (Zr^{4+}) is shown in Figure 2 (a). Figure 2 (b) shows the image of patterns of anodized Zr-EPPI monolayer. These results indicate that the charge of surface has an effect on the AFM anodization. The protruding patterns formed on Zr^{4+}-terminated surface were more fine compared to those of anodized

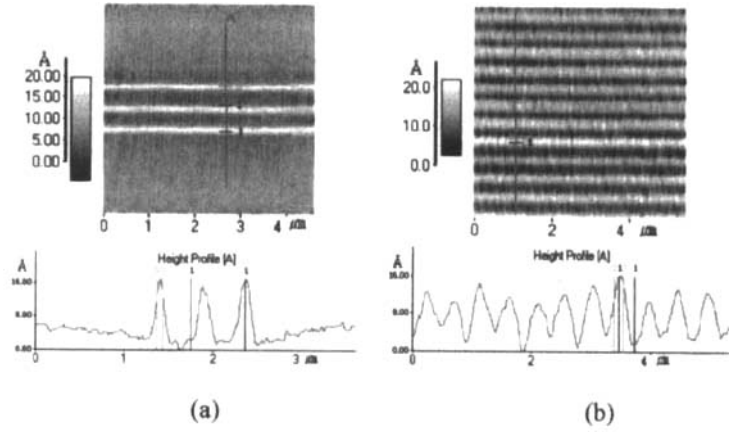

FIGURE 2. The AFM images of anodized patterns. The condition of anodization is that the induced voltage was -12 V and the scan speed was 30 μm/s. The average of line-width is about (a) 54 nm and (b) 170 nm : (a) The image of patterns anodized on Zr^{4+}-terminated surface. (b) The image of anodized Zr-EPPI patterns.

Zr-EPPI monolayer. When the electron emitted from the AFM tip descends on the surface of the Zr^{4+}-terminated monolayers, the AFM anodization can be enhanced by the effect of positively charged Zr^{4+} ions of the monolayers. Also, the protruding lines anodized on Zr-EPPI layers were more clear and narrow compared to those of phosphorylated surface. The line width of Zr-EPPI layer is 170 nm. The width of lines formed on anodized phosphorylated surface is 210 nm. Because the phosphorylated and Zr-EPPI layers have same terminal groups but have different thickness, the protruding patterns of different width are observed. These results describe that the localized force effectively acts on Zr-EPPI and the thickness of layers has an effect on AFM anodization.

CONCLUSION

AFM anodization of self-assembled Zr-EPPI layer shows that the formation of protruding patterns is affected by the surface charge and the layer thickness.

Acknowledgment

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