

Surface Functional Group Effect on Atomic Force Microscope Anodization Lithography

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The lithographic effect of surface chemical functional groups of organic resists on atomic force microscope (AFM) anodization lithography is investigated using mixed self-assembled monolayers (SAMs). The SAM resist films were prepared with 1,12-diaminododecane dihydrochloride (DAD·2HCl), *n*-tridecylamine hydrochloride (TDA·HCl), and 1,12-diaminododecane hydrochloride (DAD·HCl), and their film characteristics were evaluated by ellipsometry, zeta-potential measurements, and AFM. The lithographic results indicate that the most dominant factor of the surface functional group effect is the electrochemical property of the surface groups as an anode surface in the anodization reaction, and the dimensions of the protruded patterns are critically determined by the wetting property of the resist surface. By controlling the surface chemical groups with considerations of their effects, high-speed patterning at 2 mm/s was achieved successfully using the mixed SAM resist of DAD·2HCl and TDA·HCl.

Introduction

The technological aspects of optical lithography with photoresists has been developed to keep pace with recent growth up to present-day technological limits. Thus, several kinds of next-generation lithographic technologies such as electron beam lithography,¹ imprint lithography,² and scanning probe lithography,^{3–18} have been developed and suggested in the past 10 years. Atomic force microscope (AFM) based lithographic technologies have gained interest because the operation of AFM has a wider freedom

to select substrates and environmental conditions for operation even with only simple instrument settings. Thus, various AFM-based lithographic technologies have been investigated by Sugimura,³ Dagata,⁶ Garcia,^{6,9} Mirkin,¹⁵ Liu,¹⁶ Gorman,¹⁷ and Sagiv¹⁸ in the past 10 years. Especially AFM-based lithography using organic films has been recently investigated intensively.^{7–8,10–14}

Although AFM lithographic techniques have advantages in the resolution of the resultant patterns and their easy process, most AFM-based lithographic techniques have a limit for their low lithographic speed of only several tens per second. Moreover, some techniques such as nano-grafting and current sensing have an environmental restriction; i.e., they need a liquid–solid interface. In this sense, AFM anodization lithography is an excellent solution to fabricate highly resolved nanopatterns at high speed without environmental restrictions. Most of the physical principles and the effects of experimental parameters on AFM anodization lithography have already been reported by the constant activities of researchers elsewhere.^{3–9} In particular, we reported the effect of the surface chemical group on AFM anodization using well-defined self-assembled monolayers (SAMs).^{7,8} The main works for elucidating the origin of the surface chemical group effect were achieved by using the SAMs of 1,12-diaminododecane dihydrochloride (DAD·2HCl) and *n*-tridecylamine hydrochloride (TDA·HCl) resist molecules.⁷ Through these previous reports, two kinds of important elements of the surface chemical groups on anodization lithography have been discussed: first, the electrochemical property of the surface functional group as an anode surface to affect the lithographic applied voltage for the anodization reaction; second, the effect of wetting property of the surface group to water on the width of protruding patterns. Additionally, concerning the speed of lithography, there is much room to break through the limit of lithographic speed by developing molecular resists through chemical approaches. Because the sensitivity of SAM resists for anodization lithography depends on the characteristics of the surface chemical groups, the well-defined mixed SAMs of DAD·2HCl and TDA·HCl are excellent

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resist films for fabricating nanopatterns at high lithographic speed. In our previous report, several kinds of nanostructures were successfully fabricated at the lithographic speed of several hundreds per second.⁷

In this paper, there are two main goals to be achieved with SAM resists. The first is to determine the predominant factor of the effect of surface chemical group for AFM anodization by investigation of the resultant lithographic patterns. Then, from the technical point of view, the enhancement of lithographic speed of writing by considering the surface group effect would be presented. 1,12-Diaminododecane hydrochloride (DAD·HCl) molecular resist was newly synthesized to extend the resist system for the detailed investigation of the surface group effect.

Experimental Section

Chemicals and Materials. 1,12-Diaminododecane (DAD), *n*-tridecylamine (TDA), hydrochloric acid (HCl), and HPLC-grade methanol were commercially obtained from Aldrich and used as received. DAD·2HCl and TDA·HCl were synthesized by the same method used in our previous report.⁶ The additional monosalt adsorbate DAD·HCl was synthesized from DAD solution in ethanol and the stoichiometric amount of HCl. Then the precipitates were separated using filter paper and washed thoroughly with ethanol to remove the remaining DAD. Prime grade p-doped silicon wafer (<100, 5–10 Ω·cm) was purchased from Reticon Enterprises.

Preparation of Self-Assembled Monolayers. The negatively charged silicon substrates were prepared using boladication solution as reported by Decher.¹⁹ Four kinds of SAM resist films were prepared with various chemical compositions at the surfaces; TDA·HCl SAM, DAD·2HCl SAM, mixed SAM of TDA·HCl and DAD·2HCl, and DAD·HCl SAM. The SAMs of TDA·HCl, DAD·2HCl, and DAD·HCl were prepared by immersing the negatively charged substrates into 1 mM solutions of corresponding adsorbates, respectively. The mixed SAM of DAD·2HCl and TDA·HCl was prepared using the mixed solution of DAD·2HCl and TDA·HCl at the mixing ratio of 6:4 (D6 mixed SAM, 1 mM of DAD·2HCl solution:1 mM of TDA·HCl solution, v/v). To obtain the kinetics diagram of the DAD·HCl SAM on negatively charged substrate, a series of molecular films of DAD·HCl were prepared at the various adsorption times of 3, 5, 10, and 15 min.

Characterization of Self-Assembled Monolayers. The film thickness measurement of the DAD·HCl SAM resist was carried out using an AutoEL ellipsometer (Rudolph Technologies, New Jersey). Five individual points on each sample were measured by an ex situ method at the various exposure times, and the thicknesses were determined. Static contact angles of TDA·HCl, DAD·2HCl, DAD·HCl, and D6 mixed SAM resists were measured by the use of a G-1 contact angle goniometer (Erma, Japan) at room temperature. AFM images for the surfaces of those SAM resists and patterned SAMs were obtained by a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) with rectangular-type cantilevers, which have 0.6 N/m force constants, from Mikro-Masch USA (Oregon). The zeta (ζ) potentials of TDA·HCl SAM, DAD·2HCl SAM, and D6 mixed SAM were obtained by an ELS-800 (Otsuka Electronics, Japan) ζ-potentiometer using the cell kit for rigid surfaces. The measurements were carried out twice in 10 and 1 mM NaCl solutions at room temperature. The pH values of those solutions were 5.30 and 5.33, respectively.

Atomic Force Microscope Anodization Lithography. The nanopatternings on the SAM resists were carried out using a Nanoscope IIIa with a homemade voltage amplifier and a pulse generator for obtaining the anodization patterns. In this system, the pathway of tips and the applied voltage between a tip and a sample were artificially controlled using Nanoscript software of the Nanoscope IIIa from Digital Instruments.

Results and Discussion

Material and Self-Assembled DAD·HCl Monolayer. Figure 2 shows the Fourier transform infrared

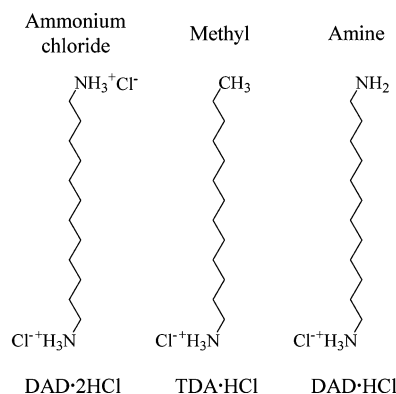


Figure 1. Chemical structures of DAD·2HCl, TDA·HCl, and DAD·HCl.

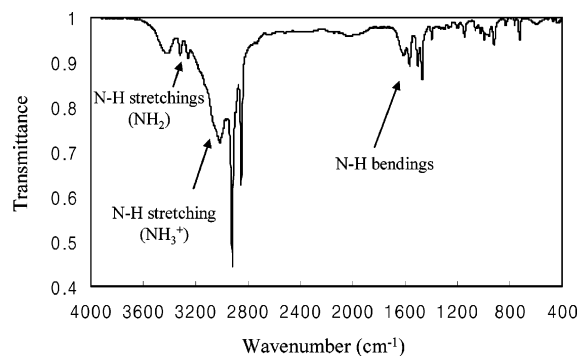


Figure 2. FTIR spectrum of DAD·HCl.

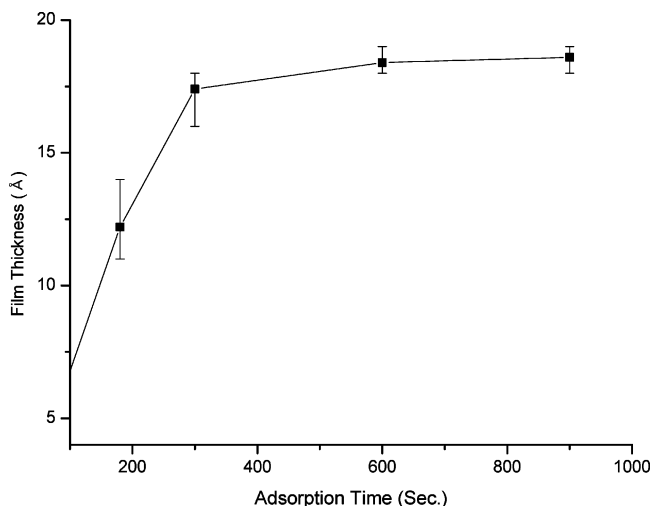


Figure 3. Adsorption behavior of DAD·HCl SAM on negatively charged silicon surface.

(FTIR) spectrum of DAD·HCl in a KBr pellet. The broad and strong N–H stretching in the region of 3200–2900 cm^{-1} is observed with stretching peaks near 3300 cm^{-1} for amine moieties.²⁰ The bending modes of N–H are also observed in the region of 1610 and 1505 cm^{-1} . This result is matched well with the suggested structure of DAD·HCl in Figure 1.

As shown in Figure 3, the SAM of DAD·HCl was prepared on the negatively charged silicon surface with adsorption behavior similar to those of DAD·2HCl, TDA·HCl, and mixed SAMs in previous reports.⁷ The saturated film thickness was estimated as 19 Å by ellipsometry,

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Table 1. ζ Potentials and Surface Charge Densities of DAD·2HCl SAM, D6 Mixed SAM, and TDA·HCl SAM

	1 mM NaCl			10 mM NaCl		
	ζ potential (mV)	surface charge density		ζ potential (mV)	surface charge density	
		ions/cm ²	normalized value		ions/cm ²	normalized value
TDA·HCl SAM	-1.3	6.00×10^{10}	1	-0.5	6.75×10^{10}	1
D6 mixed SAM	-7.8	3.58×10^{11}	6	-0.8	1.16×10^{11}	2
DAD·2HCl SAM	-12.9	5.96×10^{11}	10	-1.9	2.69×10^{11}	4
negatively charged surface	-34.9	1.73×10^{12}	29	-20.5	3.05×10^{12}	45

and the static water contact angle (θ_s) was measured as $59 \pm 3^\circ$. These measured values are well matched with theoretically calculated film thicknesses and the reported θ_s value of amine-modified surface.²¹

Surface Potentials and Charge Densities of Self-Assembled Monolayer Resists. Because the newly formed surfaces of SAM resists are prepared on negatively charged substrate and the DAD·2HCl adsorbate includes ammonium chloride salt as its surface group, both the surface potential and the surface charge density are very important for considering the electrostatic characterization of the SAM resist films. The electrical potential at a surface is an important property for obtaining the charge density, which comes from the distribution of the ionic chemical groups at the surfaces of the SAMs. Since the ζ potential allows us to apply the surface potential ψ_s , then electrostatic properties of the surfaces of the SAM resists can be examined by measuring the ζ potential. The potential field near a plane wall against a reservoir of monovalent electrolyte solution can yield an exact solution of a well-known Poisson–Boltzmann equation²²

$$\psi = 2 \left(\frac{kT}{e} \right) \ln \left[\frac{1 + \exp(-\kappa x) \tanh\left(\frac{e\psi_s}{4kT}\right)}{1 - \exp(-\kappa x) \tanh\left(\frac{e\psi_s}{4kT}\right)} \right] \quad (1)$$

where kT is the Boltzmann thermal energy, e is the elementary charge ($=1.6 \times 10^{-19}$ coulomb), and x is the separation distance from the surface. The Debye double layer thickness κ^{-1} provides a measure of the range of the electrostatic interactions. With the basis of the Gouy–Chapman model²² under the assumption of uniform charge distribution, the surface charge density σ_s can be obtained from the surface potential, given as

$$\sigma = 2 \left(\frac{\epsilon \kappa kT}{e} \right) \sinh\left(\frac{e\psi_s}{2kT}\right) \quad (2)$$

where the dielectric constant is taken as $\epsilon = (80)(8.854 \times 10^{-12})$ coulomb²/(J·m) at room temperature.

As given in Table 1, for the negatively charged Si wafer surface, the ζ potential was measured as -34.9 and -20.5 mV at 1.0 and 10 mM NaCl concentrations, respectively. We can easily understand the screening effect with the surrounding electrolytes, where the ζ potential increases with decreasing NaCl concentration. From these results the expected ionic charge density on the negatively charged surface by boladication was calculated by eq 2 as 1.73×10^{12} and 3.05×10^{12} ions/cm², respectively.

The magnitude of ζ potentials of DAD·2HCl SAM, D6 mixed SAM, and TDA·HCl SAM decreases dramatically by the amount of charged ammonium chloride functional

group on the surface as -12.9 , -7.8 , and -1.3 mV for the case in 1 mM NaCl solution, and as -1.9 , -0.8 , and -0.5 mV for the case in 10 mM NaCl solution, respectively. In the case of molecular films, the estimated surface charge density decreases to several tens of times from the case of negatively charged surface and the normalized values of the surface charge densities were 1:6:10 in 1.0 mM NaCl solution. These results agreed with the suggested model to fabricate the set of SAM resists: TDA·HCl SAM, D6 mixed SAM, and DAD·2HCl SAM. The abnormal behavior in 10 mM NaCl solution results from the disturbance of the relatively higher screening effect.²²

Dominant Effect of Surface Group for AFM Anodization Lithography. The AFM lithographic results using the DAD·HCl SAM resist compared to other SAMs at the constant applied voltage of 14 V and ambient relative humidity of 32% are presented in Figures 4 and 5, and are summarized in Table 2. The regular five-dot patterns in spacing of 0.5 were prepared by AFM anodization lithography on various resist surfaces: DAD·HCl SAM for amine surface, TDA·HCl SAM for methyl surface, DAD·2HCl SAM for ammonium chloride surface, and D6 mixed SAM for well-controlled mixing surface of methyl and ammonium chloride.

As shown in Figure 4, the full width at half-maximums (fwhm's) of the protruded silicon oxide dots on a methyl-modified surface of TDA·HCl SAM and ammonium chloride modified surface of DAD·2HCl SAM at the presented conditions were 50 ± 3 and 67 ± 3 nm, respectively, and these results are well matched with those

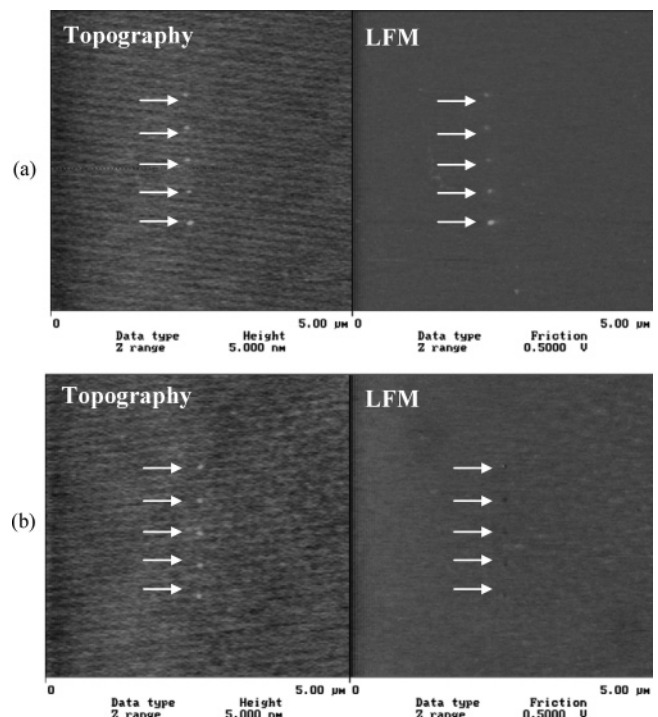


Figure 4. Dot patterns on (a) TDA·HCl SAM and (b) DAD·2HCl SAM at applied voltage of 14 V in 32% relative humidity.

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Table 2. Summary of Lithographic Results on Various Surfaces Using DAD·2HCl, TDA·HCl, and DAD·HCl

SAM resist	surface functional group	static water contact angle, θ_s (deg)	dot width (diameter) (nm)
TDA·HCl	-CH ₃	107 ± 3	50 ± 3
DAD·HCl	-NH ₂	59 ± 3	
mixed SAM	mixed (D6)	57 ± 3	56 ± 3
DAD·2HCl	-NH ₃ ⁺ Cl ⁻	37 ± 3	67 ± 3

of previous reports.⁷ The other important thing is that the lateral force microscope (LFM) image of DAD·2HCl shows the protruded patterns as dark dots, but in contrast, the result of TDA·HCl shows the protruded patterns as bright ones. This is because the *z*-scale of the lateral force image by the employed tip depends on the relative adhesion forces of the tip to the varied samples; i.e., the adhesion of the tip to the surface of the newly protruded silicon oxide dots is smaller than the adhesion of the tip to the ammonium chloride surface of DAD·2HCl SAM and larger than the adhesion of the tip to the methyl-modified surface of TDA·HCl SAM.

As shown in Figure 5, there are no observed protruding patterns on both the AFM image and the LFM image for the lithographic result using amine-modified DAD·HCl SAM resist. By contrast, at the same anodization conditions of applied voltage and relative humidity, the anodization lithography using D6 mixed SAM with a controlled surface provides discrete dot patterns with

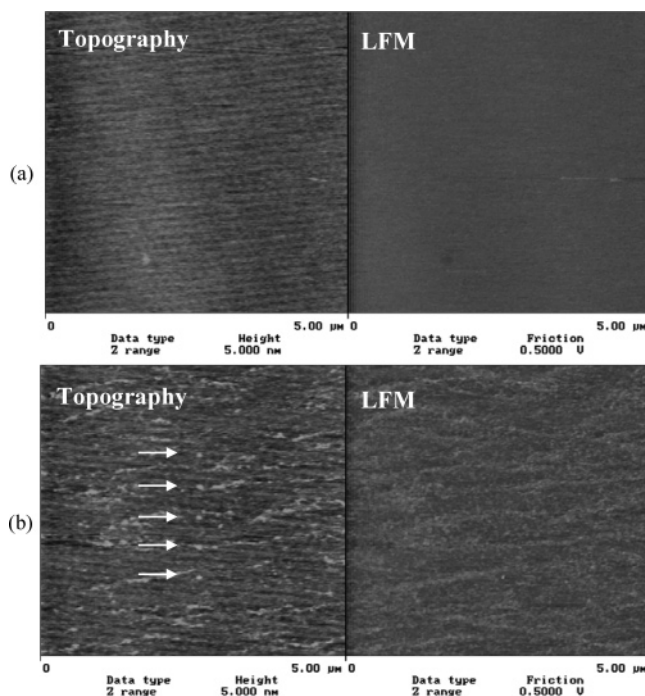


Figure 5. Dot patterns on (a) DAD·HCl SAM and (b) mixed SAM (D6) at applied voltage of 14 V in 32% relative humidity.

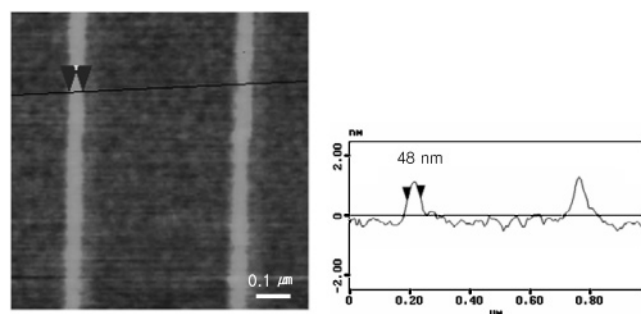


Figure 6. AFM image of line patterns at high lithographic speed of 2 mm/s.

regular dot widths of 56 ± 3 nm (fwhm). The static water contact angle for the D6 mixed SAM was controlled as 57 ± 3°, which is almost the same as the intrinsic value for amine surfaces such as DAD·HCl SAM resist (59 ± 3°), even though the chemical identities of the D6 mixed SAM and the DAD·HCl SAM are contrastingly different. Thus, the influence of a water column would be negligible for protruding the anodization patterns, and the contrasting results of the AFM anodization on those two different resist films are due to the electrochemical effect of the chemical groups at the surface of the resists; i.e., the requirement of applied voltage for anodization with the electron donating amine functionality is higher than those of the electrically neutral methyl functionality or the salt ammonium chloride functionality. Accordingly, the electrochemical property of the resist surface is the most dominant factor for determining the lithographic voltage. Then other factors such as the water contact angle, the lithographic speed, and the applied voltage determine the dimensions of the protruded patterns.^{3–9} Additionally, the water contact angle also depends on the characteristics of the chemical groups at the sample surface. Thus, the effect of chemical groups at the resist surface plays an important role to control both the electrochemical property of anode surface and the wetting property of the surface for controlling the AFM anodization. The LFM images of the dot patterns on these two resists show interesting results, such as the LFM images of DAD·2HCl SAM and TDA·HCl SAM as shown in Figure 4. The LFM image of mixed SAM shows no distinguishable dot patterns even though the protrusion of the dot patterns is confirmed by the topographic AFM image as shown in Figure 5b. This observation is easily understood based on the relative differences of adhesions of the employed tip to the various surfaces: DAD·HCl SAM, D6 mixed SAM, and the local dots of silicon oxide. The adhesions of the tip to both protruded local oxide and D6 mixed SAM have almost the same values between DAD·2HCl and TDA·HCl.⁷

Figure 6 shows the anodization line patterns at the high lithographic speed of 2 mm/s. The optimum condition for achieving the high speed of anodization lithography was found at an applied voltage of 12 V and the relative humidity of 62%. Subsequently, the reliable pattern of anodization was successfully fabricated at those lithographic conditions using the mixed SAM resist by considering the effect of surface chemical groups. The fwhm of the pattern was 48 nm.

Conclusions

Well-defined resist films were prepared by self-assembling processes using DAD·2HCl, TDA·HCl, and DAD·HCl resist molecules for AFM anodization lithography. The surface chemical functional groups of the SAM resists played important roles in controlling AFM anodization. The most dominant one is the electrochemical property of the surface functional group as an anode surface in the anodization reaction to determine the threshold applied voltage for protruding patterns. Then, by the second factors including the water contact angle of the resist film, which could be optimized by controlling the surface chemical functional group, the protruding dimensions of the pat-

terns are determined. By controlling the mixing ratio of surface groups in the mixed SAM of DAD·2HCl and TDA·HCl, the high speed of patterning was successfully achieved at 2 mm/s.

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