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SCANNING PROBE NANOPROCESSING

Hiroyuki Sugimura and Nobuyuki Nakagiri

Tsukuba Research Laboratory, Nikon Corporation, 5-9-1 Tokodai, Tsukuba 300-26, Japan

ABSTRACT

Scanning probe microscopes (SPMs) such as the scanning tunneling microscope (STM) and the atomic force microscope (AFM) were used for surface modification tools at the nanometer scale. Material surfaces, i. e., titanium, hydrogen-terminated silicon and trimethylsilyl organosilane monolayer on silicon, were locally oxidized with the best lateral spatial resolution of 20nm. The principle behind this proximal probe oxidation method is scanning probe anodization, that is, the SPM tip-sample junction connected through a water column acting as a minute electrochemical cell. An SPM-nanolithogrphy process was demonstrated using the organosilane monolayer as a resist. Area-selective chemical modifications, i. e., etching, electroless plating with gold, monolayer deposition and immobilization of latex nanoparticles, were achieved in nano-scale resolution. The area-selectivity was based on the differences in chemical properties between the SPM-modified and unmodified regions.

INTRODUCTION

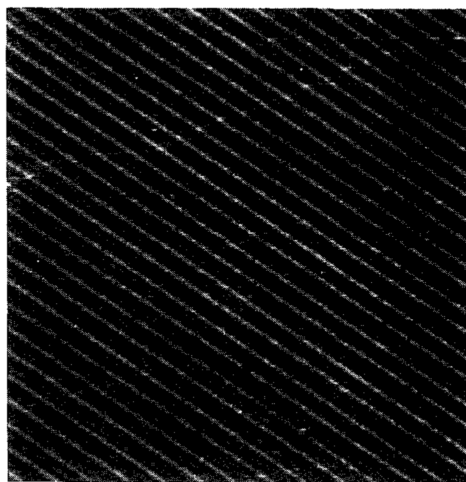
Scanning probe microscopes (SPMs) have become powerful instruments in the investigation of material surfaces. Besides surface imaging, many attrmpts have been made to use the SPM as a surface modification tool at the nanometer~atomic scale. Nanofbrication based on SPM has potential application to various technologies such as high-density data storage, high-resolution lithography, and the production of novel nano-structured materials. Among the numerous approaches towards nanofabrication, surface oxidation induced by an SPM-probe tip is one of the most promising, since it is applicable to a wide variety of materials, e. g., metals, semiconductors and organic thin films[1-4]. Furthermore, such oxidation nanoprocessing is compatible with various nanolithographic processes including pattern transfer transfer and device fabrication[5].

Here we report our recent progress in research on scanning probe nanoprocessing. First, we show the local oxidation of metal[e. g., titanium(Ti)] and semiconductor [e. g., silicon(Si)] surfaaces on the basis of SPM tip-induced anodic oxidation using adsorbed water as a chemical reagent. Next, we demonstrate the patterning of an organosilane monolayer using the same principle and a nanolithgraphy process in which this monolayer serves as a resist ptternable by SPM. Third, we present the chemical synthesis of nanostructures on templates prepared by scanning probe lithography. Finally, we discuss the utility of scanning probe nanoprocessing and its future applications.

SCANNING PROBE ANODIZATION OF METALS AND SEMI CONDUCTORS

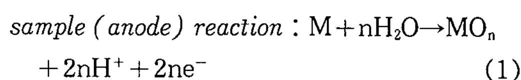
The nanoprocessing of conductive materials on the basis of tip-induced oxidation in scanning tunneling microscopy (STM) was first reported in 1990[1, 2]. Dagata et al. have modified hydrogen-terminated silicon (Si-H) surfaces using an STM operated in an atmosphere containing oxygen[1]. Nagahara et al. have conducted STM-oxidation of Si and gallium arsenide (GaAs) in a dilute hydrofluoric acid solution[2]. In their experiments, an STM tip was biased positively with respect to a sample substrate and, thus, the substrate worked as a cathode. Therefore, as pointed out by Nagahara et al[4]., the oxidation chemistry is not idntified as the normal electrochemical oxidation, i. e., anodization, which occurs on an anode[6].. Field-enhanced chemistry was proposed as its mechanism[1, 2]. We have reported that oxide patterns in nanometer scale were successfully fabricated on Ti and Si-H surfaces using an STM with a positive sample bias. An example is shown in Fig. 1. We have identified that the electrochemical oxidation reaction locally induced beneath the tip, i. e. *scanning probe anodization*, is the true oxidation mechanism[3, 7-9].

In air or other humid atmospheres, both the surface of the sample and the SPM-tip are covered with a thin layer of adsorbed water. When the tip approaches the sample close enough for these adsorbed water layer of adsorbed water. When the tip approaches the sample close enough for these adsorbed water layers to come in contact with each other, a water column is formed around the tip-sample junction due to capillarity. By applying an appropriate bias voltage across this junction, electrochmical reactions both between the water and the sample material and of the wateritself are induced at both the tip and the sample electrodes. If the sample is polarized positively, the tip and the sample work electrochemically as anode and cathode, respectively, as illustrated in Fig. 2. Anodic oxide is formed on the sample surface at the point beneath the tip. The net electrochemical reaction at the anode is shown in eq. (1).



0 2 4 6 µm

Fig. 1 AFM image of anodic oxide lines fabri-canted on a Si-H surface. An STM was used for patterning at a sample bias(Vs) of +5.0 V, a reference current(i) of 0.2 nA and a tip scan rate(ν) of 0.1µm/s in nitrogen atmosphere with a relative humidity (RH) of 20%. The region where the tip had scanned protruded 1~2 nm from the surrounding unscanned region due to volume expansion accompanying the anodization of the substrate Si.



sample (anode) reaction : $M + nH_2O \rightarrow MO_n + 2nH^+ + 2ne^-$ (1)

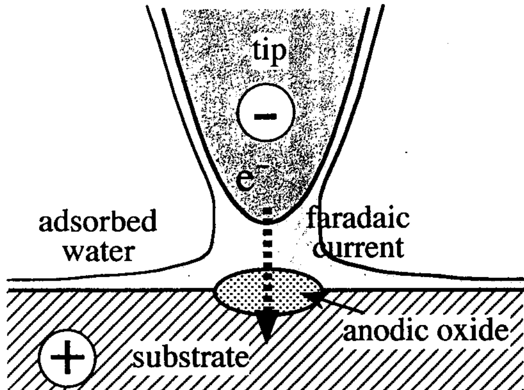
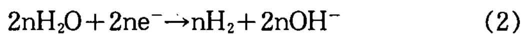


Fig. 2 Schematic illustration of scanning probe anodization. When an STM was used, both V_S and i were kept constant. In all of the STM-based experiments, a conductive-diamond STM-tip was used due to its durability. When an AFM was used, the tip contacted the substrate surface and only V_S was kept constant. Metal-coated (20nm thick NiCr) conducting pro-bes were used to allow electrical condu-ctance.

Hydrogen generation most certainly occurs at the tip as the counter electrochemical reaction eq. (2).

tip (*cathode*) reaction :



$$2nH_2O + 2ne^- \rightarrow nH_2 + 2nOH^- \quad (2)$$

A part or all of the current flowing thro-ㅌ ㅌㅌugh the tip-sample junction is responsible for the faradaic current accompanying these electrochemical reactions.

Detailed study of STM-based scanning probe anodization was conducted by examining the effects of humidity and bias on the anodization[7-9]. The process strongly depends on the amount of adsorbed water and, therefore, atmospheric humidity. Since the thickness of the water column formed around the tip-sample junction increases with an increase in humidity, the spatial resolution of scanning probe anodization worsens as humidity increases. Under low humidity conditions, the water column is confined to just under the tip. Therefore, the size of the anodized area is rimarily governed by the size of the tip end. However, under high humidity (relative humidity (RH)=90%), the anodized area is no longer restricted to only that beneath the tip. In our experiments, under such a highly humid atmosphere, the sample surface was anodized in a broadened area of 4㎛ in diameter when the STM tip was kept located at a single point for 40min[9]. We concluded that the lateral diffusion of the ionic species carrying faradaic current was significant under such a high humidity condition since the adsorbed water layer on the sample surface was relatively thick. This humidity effect is clear evidence that the oxidation is primarily governed by an electrochemical rection, i. e., anodization.

Scanning probe anodization is simple but very advantageous since it requires no intentional solvents or chemical reagents for electrochemical reactions and is applicable to a wide variety of materials, e. g., chromium, aluminum and silicon nitride[10-12].
In particular, Si has been the focus of interest due to its importance as an electronic material[1, 2, 7, 13-16]. It is possible to added an active reagent to adsorbed water for SPM tip-ainㅌduced electrochemical nanofabrication. An oxide superconductor surface was electrochemically etched by using an STM with acidic adsorbed water formed in a humid atmosphere with a high concentration of carbon dioxide[17]. Such control of the acidic/basic condition of the adsorbed water might be useful for the electrochemical nanofabrication of various materials.

SCANNING PROBE NANOPROCE SSING OF ORGANIC THIN FILMS

The patterning of organic then films is of special importance due to their application as lithographic resists. There have been many reports describing the SPM-based patterning of organic molecular films. For example, spin-coated polymer films and Langmuir-Blodgett films have been patterned using STMs operated in vacuum[18-20] as well as by using STMs or AFMs operated in air[21, 22]. Resist films for scanning probe microscope lithography must be prepared in a thin and uniform layer in order to attain high spatial resolution. Furthermore, these films must be compatible with pattern transfer processes such as chemical etching. Self-assembled monolavers (SAMs) of organosilane molecules spontaneously chemisorbed on certain substrates, such as oxides of Si or Ti, have attracted attention due to their excellent uniformity in molecular order and their resisti-vity to various of solvents and chemical reagents[23]. Therefore, such monolayers have been employed as resists for a variety of lithographic methods employing photon, electron and ion beams[24-26]. An STM operated in a vacuum has been applied to the patterning of organosilane SAM films[27]. SPMs operated in air can serve as patterning tools for organic thin films on the basis of scanning probe anodization as described in the previous section. We have succeeded in fabricating nano-scale patterns on an alkylsilane monolayer on si and a fluoroalkylsilane monolayer on Ti[3, 29-30]. Both STM and AFM were compatible with patterning of these monolayers. There have been reports that alkylthiol SAM s prepared on Au and GaAs surfaces were patterned using STM in air, and very recently, it was proven that the patterning mechanism in these experiments was electrochemistry between organic molecules and the adsorbed water[31-33]. This is the same electrochemistry which we earlier demonstrated as occurring in organosilane monolayer patterning[4].

In this section, we describe scanning probe lithography in which an organosilane moolayer served as a self-developing resist (Fig. 3).

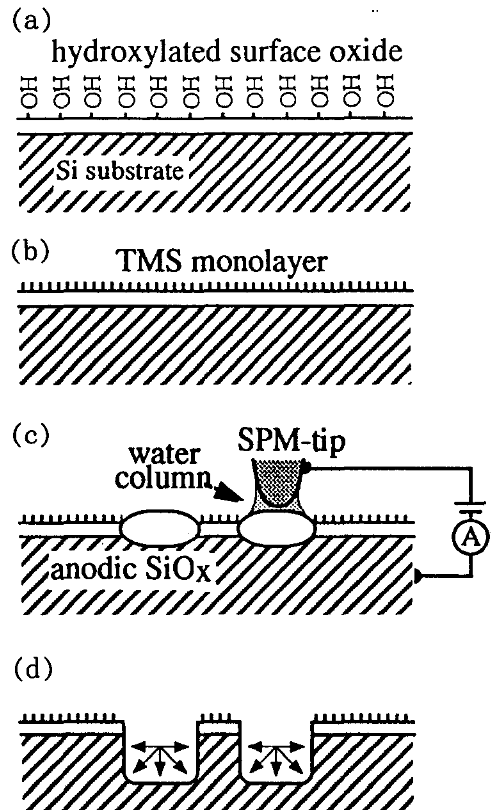
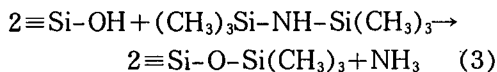


Fig. 3 Schematic diagram of SPM lithography.
(a) Cleaning of Si substrates.
(b) formation of the TMS monolayer resist.
(c) Patterning. Either an STM of an AFM was used.
(d) Pattern transfer to the Si substrates by chemical etching.

An organosilane monolayer was formed on a Si substrate by chemical vapor deposition (Fig. 3b). The Si substrate was first cleaned by ultraviolet light-generated ozone cleaning using an excimer lamp of $\lambda=172$ nm. By this cleaning, organic contamina tion on the substrate was removed and a clean surface oxide was chemically prepared (Fig. 3a). The oxide surface was hydroxy-lated and, there fore, completely hydrophilic. The cleaned substrate was then exposed to hexa-methyldisilazane [$(CH_3)_3Si-NH-Si(CH_3)_3$ HMDSN] vapor at 150℃ for more than 5hours. The hydroxyl groups on the substrate surface reacted with the HMDSN molecules, resulting in the formation of a monolayer of trimethylsilyl (TMS) groups [eq.(3)][34]. Its thickness was less than 1 nm as estimated by AFM and ellipsometry.



$$2\equiv Si\text{-}OH+(CH_3)_3Si\text{-}NH\text{-}Si(CH_3)_3 \rightarrow 2\equiv Si\text{-}O\text{-}Si(CH_3)_3+NH_3 \quad (3)$$

The sample surface became hydrophobic after the deposition of this monolayer. Since this CVD method depends on the spontaneous chemical reaction between the -OH groups and the HMDSN molecules, hydroxylation of the substrate surface is crucial for the film deposition.

Next, the Si-TMS sample was patterned by scanning probe anodization in a N_2 atmosphere under controlled humidity. Each sample was patterned by either an STM or AFM. Local degradation of the TMS layer occurred due to the anodic reactions under the path of the SPM-tip scan (Fig. 3c). The degraded region on the sample became hydrophilic again, indicating that, as a result of the tip-scan, TMS groups were removed and probably replaced with -OH groups. We also confirmed using the AFM that the tip-scanned region slightly protruded ($\sim$0.5 nm) from the surrounding undegraded area as shown in Fig. 4a. This protrusion was due to volume expansion accompanying the anodization of the substrate Si, which followed the monolayer degradation. The degradation rate of the TMS monolayer was governed by several parameters[29, 30]. The degradation rate increased with an increase in humidity showing that the reaction is primarily governed by the amount of adsorbed water. THe presence of oxygen in the atmoaphere also resulted in an acceleration of the degradation rate. Therefore, it is crucial to control the patterning atmosphere to obtain the best results. The degree of the TMS degradation in the tip-scanned region decreased with an increase in the probe scan rate. That is to say, the degradation rate is governed by the amount of injected current per unjt area. Therefore, the patterning became incomplete at a high patterning speed of hundreds of m/s due to insufficent degradation of the monolayer. On the other hand, the current at the tip-sample junction increase in the bkas voltage applied to the junction. By applying a relatively high bias voltage of 20V, we have obtained sufficient current density even with a high-rate probe-scan and have succeeded in patterning at 500 ums which is the limit of our AFM instrument[30].

Finally, the patterned sample was immersed in an etching solution ($NH_4F/H_2O_2/H_2O=10/3/100$, weight ratio). A Si nanostru-cture was fabricated by this chemical etching rusing the patterned TMS resist as an etching mask (Fig. 3d). An AFM image of the etched Si grooves is shown in Fig. 4b. The results clearly show that the region where the

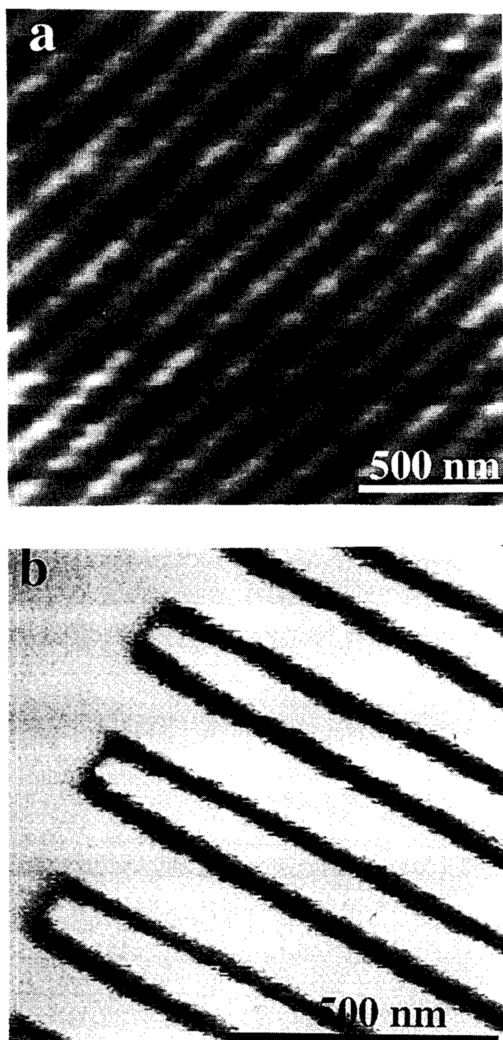


Fig. 4 (a) AFM image of the patterned Si-TMS sample surface. AFM-probe scan was conducted with $V_S = +10.0V$ at $v = 0.4 \mu m/s$ in air with RH=18%. Line pitch of the pattern is about 150nm. The scanned region slightly protrudes due to anodization of the substrate Si. (b) AFM image of the etched Si-TMS sample surface. AFM-probe scan was conducted with $V_S = +10.0V$ at $\nu = 0.3 \mu m/s$ in air with RH=20%. The patterning current was not meas-ured but based on results from other experiments, it is supposed to be approximately 0.1nA at this bias voltage[30]. Etching was conducted for 5min. The scan-ned region was selectively etched resul-ting in the formation of fine grooves. The width and depth of the grooves are 30 and 15nm, respectively.

TMS layer had been degraded by scanning probe anodization became an etching window, while the surrounding area was blocked from etching by the TMS monolayer. Thus, it is demonstrated that the TMS layer can successfully serve as a resist in scanning probe lithography. This TMS monolayer resist patterning was entirely accomplished through scanning probe anodization without the need for any further develooping processes. This resist can thus be regarded as a self-developing resist. Both STM-and AFM-based scanning probe anodization were effective in patterning the TMS resist. At present, the spatial resolution of 20nm has been the best obtained.

Electron irradiation has been proposed as the mechanism of the organosilane monolayer degradation induced by an STM in vacuum[35]. However, we found that, under our experimental conditions, water adsorption on the surfaces of both the tip and the sample was inevitable. A voltage of 4V, which was reported as the minimum for the STM-exposure in vacuum of an organosilane SAM resist prepared from 4-chloromethylphenyltrichlorosilane[35], is high enough to induce the electrolysis of water. In addition, we found that at RH=60% the TMS monolayer became degraded even below the reported threshold voltage of 4V[28]. It is unlikely that electrons emitted from the SPM-tip propagate through the water layer and directly degrade the organosilane layer. Water electrolysis and the related electrochemical reactions induced beneath the tip are responsible for the degradation mechanism of the organosilane layers under the atmospheric conditions of our experiments.

CHEMICAL SYNTHESIS OF NANOSTRUCTURES

If a substance with cemical or physical properties different from those of the substrate material can be area-selectively deposited on patterns on patterns predefined by scanning probe lithography, nano-scale patterns of various functionalities can be fabricated. In this section, we describe examples of the chemical synthesis of nanostructures through such an approach.

The chemical and physical properties of a silicon oxide (SiO_X) surface are quite different from those of a Si-H surface. Owing to these differences, a variety of area-selective chemical modifications of Si-H sample with patterned SiO_X become feasible. Dagata et al. have demonstrated the area-selective deposition of GaAs onto a Si-H surface by molecular beam epitaxy[36]. We have deposited an organosilane monolayer by chemical vapor deposition area-selectively onto anodic SiO_X surfaces[37, 38]. We have also made reports of area-selectrve electroless plating, where the plating proceeded selectively on a Si-H surface while a SiO_X surface remained free of deposits[39, 40]. Accordingly, through this area-selective electroless plating, a negative pattern of Au, that is, opposite to that of the SPM-tip scanning pattern, was formed as shown in Fig. 5

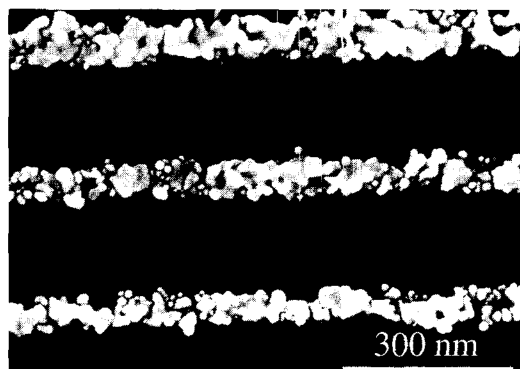


Fig. 5 SEM image of Au nanostructures fabricated on a Si-H sample. The oxide lines shown by the dark regions in the image were generated by STM-based scanning probe anodization with $V_S=+5.0V$, $i=0.2nA$ and $V=0.6\mu m/s$. Plating was performed for 7 min at 50℃. We have succeeded in plating Si-H surfaces using two commercial Au plating solutions of the galvanic displacement type, K-24S(High Purity Chemetals Laboratory) and Lectroless Prep(Electroplating Engineers Japan, EEJA). However, a catalytic type solution, Lectroless Au (EEJA), was found to be ineffective. Therefore, it was concluded that the Au deposition proceeded due to the galvanic displacement of Si with Au. Due to the low nucleation density of the Au on the Si-H, the Au lines seen in the image are not continuous. However, the density was increased by wet etching a sample prior to plating. An aqueous solution of 25wt.% tetramethylammonium hydroxide was used for the etching. With this solution, etching preceeded area-selectively on Si-H while SiO_X remained unetched, and we succeeded in fabricating a continuous Au line as narrow as 30 nm[51].

A hydrogen termination layer on Si is very useful for template fabrication as demonstrated above. Furthermore, since it is thin and uniform in atomic scale, it can serve as resist of high spatial resolution approaching atomic scale. Lyding et al. have demonstrated the fabrication of patterns 1nm in width on Si-H sample surfaces using an STM in ultrahigh vacuum[41]. Unfortunately, a hydrogen termination layer has a serious disadvantage in its instability, since Si-H oxidizes in air within several hours. Once it oxidizes, chemical selectivity between the scanned and the unscanned regions is lost. Therefore, an alte-

rnative surface termintion layer is necessary for template preparation. The layer must be thin and uniform, stable in air and compatible with scanning probe nanoproc-essing. Organo silane SAMs are promising , since they are thin , uniform in molecular order and are stable. Furthermore, such monolayers are patternable by varios lithographic tools including SPM , as demonstrated in the previous section.

Patterned organosilane SAMs have been used as templates for the fabrication of micro-structures madeup of a variety of materials through various chemical modifications, including mineralization[26], immobilization of protein, fluorescent materials or biological cells[42-47], electroless plating[27, 43, 48], monolayer deposition[43, 49], and chemical vapor deposition[50, 51].

Figure 6 shows a schematic chart of two processes for the chemical synthesis of nanostructures, both of whic use a SPM-patterned TMS monolayer as a temloate. In the first case, a patterned sample was chemically etched similar to the process previously shown in Fig. 3. Due to this etching, anodic and surface oxides were dissolved in the SPM-scanned region and, consequently, substrate Si became exposed here (Fig. 6b). The etched sample was then immersed in a Au plating solution. Since the etched region is rfactive to electroless plating, similar to a Si-H surface , Au deposition proceeded selectively in the etched grooves (Fig. 6c). Therefore, a positive pattern of Au correspondung to that of the SPM-tip scan, as opposed to the negative pattern shown in Fig. 5, was fabricated on the Si-TMS sample. A SEM image of such Au nanostructures is shown in Fig. 7a.

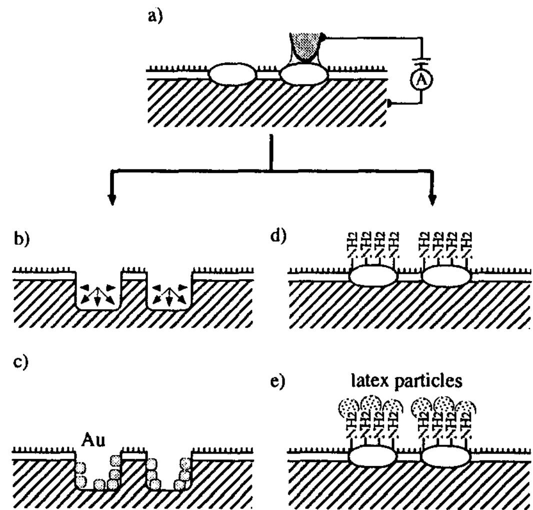


Fig. 6 Schematic diagram of the process for the chemical synthesis of nanostruct-ures.
(a) Template preparation.
(b) Chemical etching.
(c) Electroless plating.
(d) Aminosilane coating.
(e) Particle immobilization.

In the second process shown in Fig. 6, we employed the chemical reaction between the organosilane molecules and -OH groups on the oxide surface to chemically synthesize nanostructures. The hydrohilic regions where the TMS monolayer has been degraded due to the tip scanning in Fig. 6a become reactive again to organosilane molecules. The unscanned regions remain unreactive due to termination by the TMS monolayer. Therefore, a different type of organosilane molecule having functional groups other than alkyl groups can be attached ontothese scanned regions. To test this hypothesis, we deposited 3-aminopropyltrimethoxysilane (APS) molecules onto the fabricated template. An amino group is attractive due to its chemical reactivities. APS molecules reacted with the region where the TMS monolayer had been de-

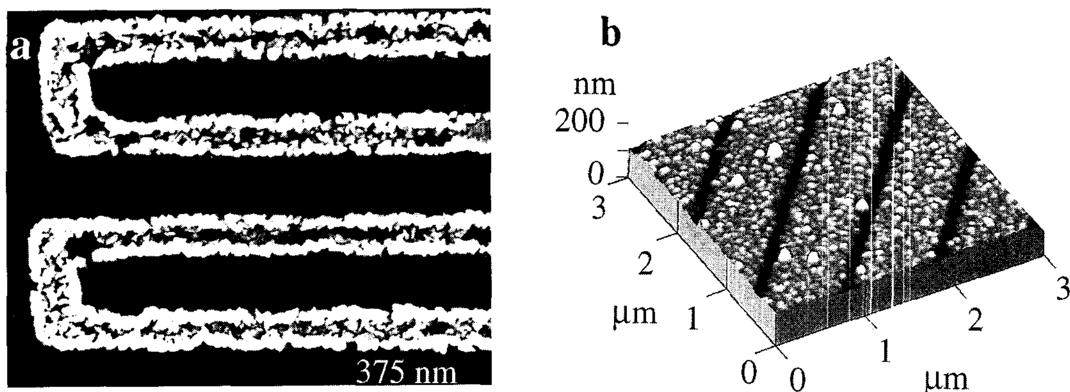


Fig. 7. (a) SEM images of Au nanostructures fabricated on an etched Si-TMS sample. The lithographic pattern was generated by STM-based scanning probe anodization in N_2(RH=20%) with V_S=+5.0V, i=0.2nA, and ν=0.3μm/s. Plating was performed for 5min at 50℃ after 5-min of etching in $NH_4F/H_2O_2/H_2O$ at room temperature. The Au nucleation did not occur uniformly in the entire groove area, but preferentially proceeded at the groove edges. The Au nucleation concentrated on the groove walls, probably due to a high defect density on the wall surfaces. However, it was found that the entire groove could be filled with Au deposits when the groove width was less than 50nm[48]. (b) AFM image of latex particles selectively deposited onto the tip-scanned area. An STM-tip had been scanned at V_S=+5.0V, i=0.2nA and ν=0.2μm/s in N_2 with 80% RH. The samples were washed in distilled water and ethanol in that order and dried by N_2 blow. Next, they were immersed in a fresh solution of 1 vol.% APS, 4 vol.% CH_3COOH and 4vol.% H_2O in methanol for 5min. After this, the samples were rinsed in methanol twice and then in distilled water. Finally, some of the APS-treated samples were immersed for 30min in 50mℓ of morpholinoethane sulfonic acid buffer(MES;50mM, adjusted to pH6.5 by adding aq-NH_4OH solution)and 0.2mℓ of an aqueous suspension of aldehyde-modified latex particles(Molecular Probes, L-5401, 2% solids in H_2O, diameter=29nm±20.1%). These samples were again rinsed in distilled water and then blown dry.

graded resulting in the formation of an APS monolayer confined to the pattern(Fig. 6d).

To confirm the area-selective growth of the APS monolayer, hte sample was labeled with latex nanoparticles whose surfaces were modified with aldehyde groups. It is known that an aldehyde group reacts with an amino group to form a chemical bonding as shown by eq. (4)[52]:

$$-CHO+H_2N- \rightarrow -CHN- +H_2O \qquad (4)$$

The particles were immobilized by this reaction between the amino groups in the APS molecules and the aldehyde groups on each particle (Fig. 6e). There were no particles found on the surrounding unscanned area. The AFM image in Fig. 7b shows the aldehyde-modifide latex particles deposited on the tip-scanned region of a sample treated in the APS solution. In addition, we confirmed that, after the APS treatment, the tip-scanned region remained unetched in a $NH_4F/H_2O_2/H_2O$ solution. An APS monolayer having a similar ability to block the etching had formed on the tip-scanned area. Therefore, it was concluded that APS molecules chemisorbed area-selectively onto the tip-scanned region.

CONCLUDING REMARKS

We have deseribed in this paper the successful fabrication of artificial nanostructures using SPM. Scanning probe anodization technology was applied to the nanoscale patterning of metals, semiconductors and organic thin films. A nanolithography process based on an arga-nosilane SAM resist wasdeveloped. The application of SPM-defined templates to chemical nanofabrication was also demonstrated.

The very slow patterning speed of SPM compared with that of electron beams has been believed to be a serious disadvantage for practical lithographic applications. However, ther have been several recent reports concerned with attaining pattering speeds in the order of mm/s. Snow et al. predicted AFM -patterning over 1 mm/s from their exterimental results on AFM-oxidation of Si-H[16]. Park et al. achieved 1 mm/s patterning speed using spin-on-glass as a resist[53]. We have demonstrated 0.5 mm/s patterning speed based on an organosilane monolayer resist[30]. Since this result do not represent the limit of resist sensitivity, but rather limitations of the instrument used for the experiments, we expect that patterning of organosilane monolayer resists is capable at a patterning speed of mm/s order.

In scanning probe lithography, a probe-tip writes lines one by one to construct an entire pattern, while, in photolithography, a whole pattern can be transferred at a single time from a predefined mask to resist. This shows also a shortcoming of scanning probe lithogrphy, but it can probably be overcome through multi-probe AFM. Minne et al. ave reported the parallel operation of multi-probe AFM allowing simultaneous patterning using up to 5 probes[54].

At present, the productivity of scanning probe nanoprocessing is insufficient. However, this nanotechnology has been generally accepted as a valuable tool for research laboratories. Among the various scanning probe nanoprocessing strategies, proximal probe oxidation is the most successful since it is reliable and readily applied to the fabrication of nano-scale electronic devices[11, 55-58]. In addition, compated with other high-resolution lithographies such as electron beam methods, scanning probe nanoprocessing as demonstrated in this paper is advantageous since it can be performed under ambient conditions. Scanning probe lithography enables the flexible combination of lithography with other methods in order to exactly locate the probe and/or characterize fabricated patterns *in situ*. As an example, Snow et al. have reported the AFM fabrication of metal-oxide devices with in situ control of electrical properties[59].

Scanning probe nanoprocessing is not restricted to nanoelectronics. The spatial arrangement of functional molecules on solid surfaces with artificial control at minute scales has attracted attention for the construction of novel chemical systems or devices. Potential applications range from fundamental scientific research in microchemistry to practical applications, such as chemical sensors and electronic or optical devices based on organic molecules[60, 61]. Our approach demonstrated here and in other papers[33, 34] involving the immobilization of organic molecules onto intended sites using nanostructured templates defined by scanning probe nanoprocessing willplay a key role in nanochemistry.

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