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SHORT COMMUNICATION

Highly selective modification of silicon oxide structures fabricated by an AFM anodic oxidation

Inhee Choi and Jongheop Yi†

School of Chemical and Biological Engineering, Institute of Chemical Processes,
Seoul National University, Seoul 151-742, Korea

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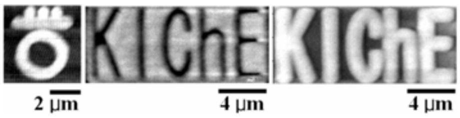
Abstract−Anodic oxidation via atomic force microscopy is a promising method for creating submicron-sized silicon dioxide patterns on a local surface. The area patterned by AFM anodic oxidation (AAO) has different chemical properties from the non-patterned area, and thus site-selective modification of patterned surfaces is quite possible. In this study, we combined the AAO with self-assembly method and/or wet chemical etching method for the fabrication of positive and/or negative structures. These locally modified surfaces could be used to the site-selective arrangement and integration of various materials based on a pre-described pattern.



Key words: AFM, Anodic Oxidation, Etching, Pattern, Self-assembly

INTRODUCTION

The fabrication of submicron-sized structures, especially those that are silicon-based, has attracted considerable attention due to the potential applications of such structures, including micro/nanoelectromechanical systems (MEMS and NEMS) [1] and miniaturized devices [2]. For this purpose, a wide variety of fabrication methods have been developed to generate patterns on the nano- and microscales. Conventional pattern-description techniques such as photolithography (e-beam lithography, x-ray lithography, and focused ion beam lithography) and soft lithography (μ-contact printing and capillary lithography), have been widely explored by many researchers. The application of such methods, however, is restricted due to their inherent limitations, which include high costs to reduce pattern size and requirement of complex systems that are derived by photo-mask design. Yet, in the case of nano-probe based patterning methods, such as dip pen lithography [3], nano-scratch [4] and anodic oxidation [5], submicron-sized patterns can be easily fabricated on a local area without an intended mask. Therefore, the ability to achieve patterns rapidly and reproducibly by using simple and flexible techniques can advance the integration of fabricated structures into micro/nano-systems.

In this study, we demonstrated a highly controllable surface modification method by employing AAO and further chemical treatment. The following three factors were major concepts in performing this method: (1) silicon oxide structures can be readily formed by AFM tip-induced local oxidation on a silicon surface, (2) silicon oxide structures have a high affinity to the silane moieties [6], and (3) silicon and silicon oxide have different etching rates in a specific etchants [7]. Based on these facts, constructive and destructive modification of pre-fabricated silicon oxide structures were successfully achieved by the treatments of organosilanes and etchants.

EXPERIMENTAL

1. Materials

The following materials and chemicals were used: p-type and <100>-oriented silicon wafers with LPCVD (low pressure chemical vapor deposition) silicon nitride as a resist, and KOH, IPA (isopropyl alcohol), HF and 3-aminopropyltriethoxysilane (APTES) as chemicals for the site-selective modification. Prior to use in the experiments, the wafers were cut into 1×1 cm^2 pieces and cleaned in acetone, alcohol, and deionized (DI) water under sonication to remove small particles and organic contaminants, followed by drying in a stream of N_2.

2. Formation of Local Silicon Oxide Structures: AFM Anodic Oxidation

Pattern inscription was carried out by pre-controlled, automated AFM oxidation [8], as shown in Scheme 1. A silicon cantilever coated with Ti-Pt (NSC36 series, MikroMasch) was used to pattern the substrates. Here, the contact mode was used to oxidize locally the silicon surface, which was performed under ambient conditions (23-25 °C and 60-70% relative humidity). During scanning at a rate of 10-20 μm/s, a positive bias of 10-20 V relative to the tip (cathode) was applied to the silicon nitride substrate (anode).

3. Constructive Modification of Silicon Oxide Structures

To perform an upward modification of silicon oxide structures, a 10 mM APTES solution in ethanol was added dropwise onto the pre-patterned region for 1 hr and the substrates were then rinsed with ethanol. The fabricated structure was directly characterized by using an AFM apparatus. Topographic and lateral images were simultaneously obtained in a single scan.

4. Destructive Modification of Silicon Oxide Structures

Destructive modification of the locally oxidized patterns was per-

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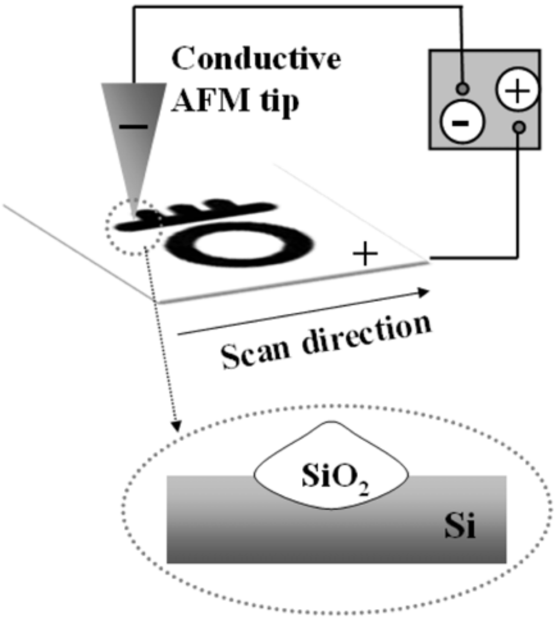
†To whom correspondence should be addressed.
E-mail: jyi@snu.ac.kr

formed by wet chemical etching. With a thin layer of silicon nitride as an etching resist, the protrusive silicon oxide patterns were selectively etched in an 1% HF solution, followed by rinsing with DI water to completely remove the etched silicon oxide remnants. For the further deep etching, anisotropic etching of the exposed Si surface was performed in a mixture of 20% KOH and IPA (5 : 1 v/v) aqueous solution, at 50 °C for 1 min. The etched substrates were thoroughly sonicated in DI water to obtain a smooth etching surface.

RESULTS AND DISCUSSION

For the fabrication of pre-designed local structure on a silicon surface, we used AFM anodic oxidation techniques. When a bias voltage is applied, a water bridge is formed between the tip and substrate, and local field-induced oxidation subsequently takes place. Therefore, protrusive patterns with high spatial resolution were formed on a local area via the volume expansion that resulted from the transition of crystalline silicon to amorphous silicon oxide, as shown in Scheme 1 [9]. Using this method, various patterned structures were established on a silicon surface according to the predesigned schemes. Fig. 1 shows various structures obtained from simple dot-array (Fig. 1(a)) and complex symbol (Fig. 1(b)) via pre-controlled automation system, in that a bias is applied only to the dark area of a designed pattern. Fig. 1c shows “KIChE” symbols with different sizes, and they were successfully constructed on areas with width of 1, 3 and 6 μm. The height of patterned structures can be controlled by experimental parameters, such as, applied voltage, relative humidity, scanning rate, and radius of the AFM tip [8]. Resulting structures of Fig. 1 are silicon oxide patterns with a thickness of ca. 2.5 nm that were produced at a bias voltage of 10 V. The structures fabricated by AAO have limitation with the z-axis directed growth and their maximum height reached at a several nanometer scale (ca., 5 nm). However, patterned structures have highly selective chemical properties that allow one to do further modification of patterned structures [10]. In order to fabricate more differentiated structures, we performed two types of strategies, as shown in Scheme 2. The first method is a self-assembly technique on a patterned structure via the application of affinity of organosilane moieties to the silicon oxide. Fig. 2 shows AFM images and cross-sectional depth profiles of the resulting surfaces corresponding to the constructive modifi-



Scheme 1. Schematic diagram of AFM anodic oxidation.

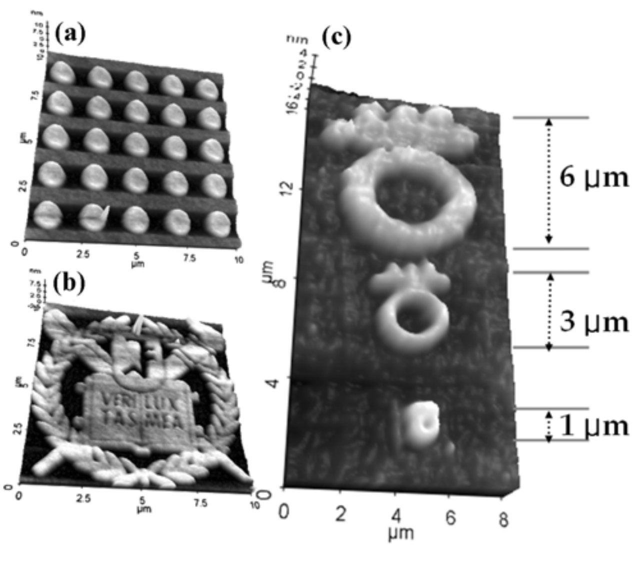
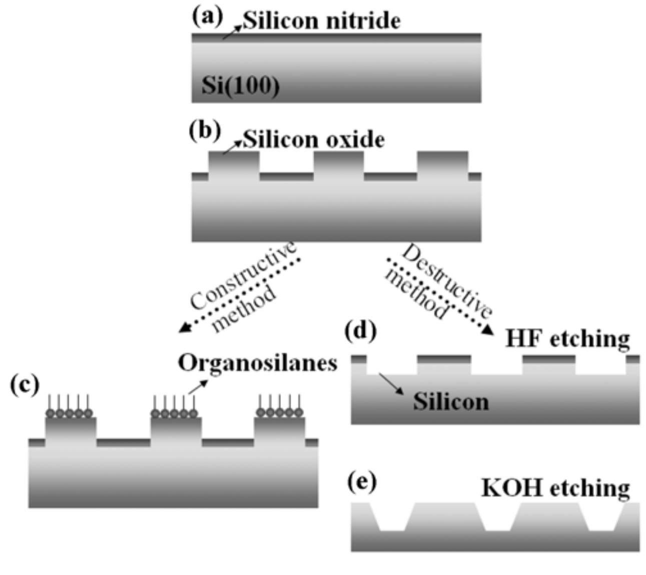


Fig. 1. Various structures fabricated by AFM anodic oxidation. (a) Simple dot-array, (b) Complex symbol, and (c) Main symbols of KIChE with different sizes



Scheme 2. Schematic diagrams of the experimental procedures. (a) A silicon nitride thin layer was formed on the Si substrate, (b) The protrusive square shaped silicon oxide patterns were obtained by AFM anodic oxidation, (c) Constructive modification: organosilanes were site-selectively assembled on a silicon oxide pattern, (c) and (d) Destructive modification: the selective removal of silicon oxide was achieved by HF etching and exposed silicon surfaces were further etched by a KOH/IPA etchant.

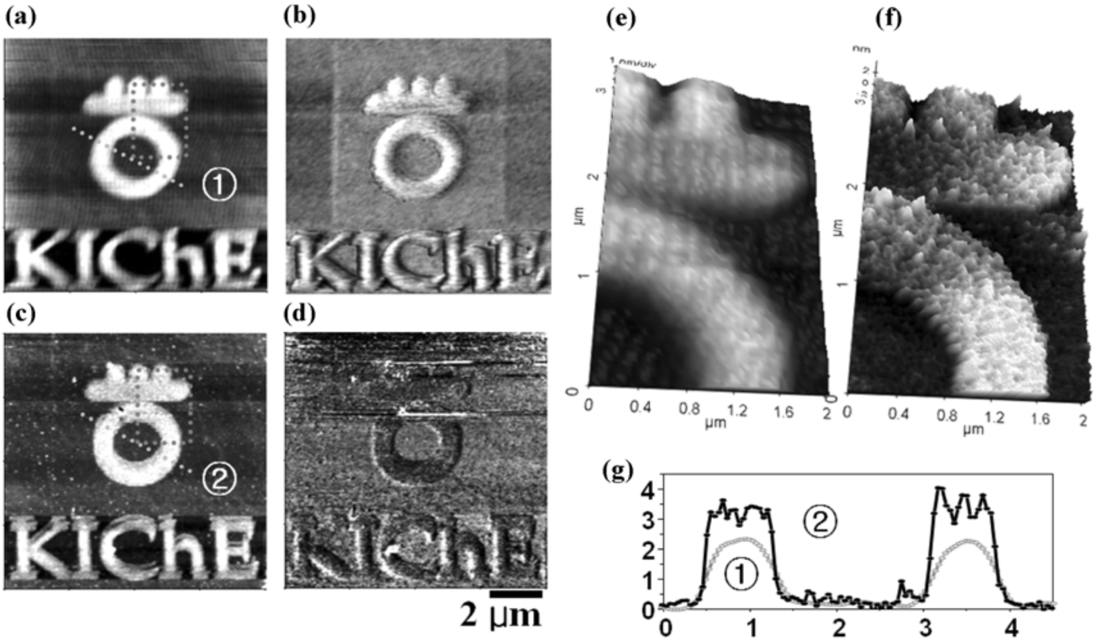


Fig. 2. AFM topographies ((a), (c), (e) and (f)), lateral images ((b), (d)) and depth profiles (g) during the constructive modification of pattern. (a), (b) and (e) Silicon oxide structure fabricated by AFM anodic oxidation, and (c), (d) and (f) Amine-functionalized silicon structure (scan size: 10 μm×10 μm).

cation procedure. The main symbol of "KIChE" with a thickness of 2.5 nm (gray line of Fig. 2(g) was produced on a surface. The patterned symbol was functionalized with APTES and its surface property was changed by amine moieties. In Fig. 2(a), (c) and (g), changes appeared in the roughness (from topographies) and thickness (from depth profiles) of the patterned surface. The change in the roughness was more clearly observed in magnified images (Fig. 2(e) and (f)) corresponding to the squared areas of Fig. 2(a) and (c). The thicknesses were ca., 2.5 nm and 3.5 nm, respectively, as shown in Fig. 2(g), which is consistent with the thickness variation in the functional modification material (APTES). Fig. 2(b) and (d) are lateral images according to the different surface properties, and were collected simultaneously with the topographic images. These findings demonstrate the different contrasts in the surface properties, which are due to interactions between the AFM tip and the surface functionality [11]. The amine-modified pattern is darker than an unmodified pattern, which is the result of weak interactions between the tip and NH$_2$-terminatied surfaces compared to the silicon oxide surface. It should be noted that this observation has an important role in distinguishing the functionalized regions.

In case of a destructive modification, AAO was sequentially combined with two wet chemical etching procedures, as shown in Scheme 2. In this procedure, the alphabetical letters of "KIChE" were described on a local surface. Fig. 3(b) shows negatively described letters via local oxidation of the background, while Fig. 3(g) shows positively written letters via selective oxidation. Although they were fabricated based on a design of equal size, the line widths of each letter were different. This finding reflects that volume expansion occurs because of the transition of crystalline silicon to amorphous silicon oxide. For the selective chemical etching of the patterned structures, we used silicon substrates passivated by thin silicon nitride film that has high chemical resistivity. When the patterned substrate

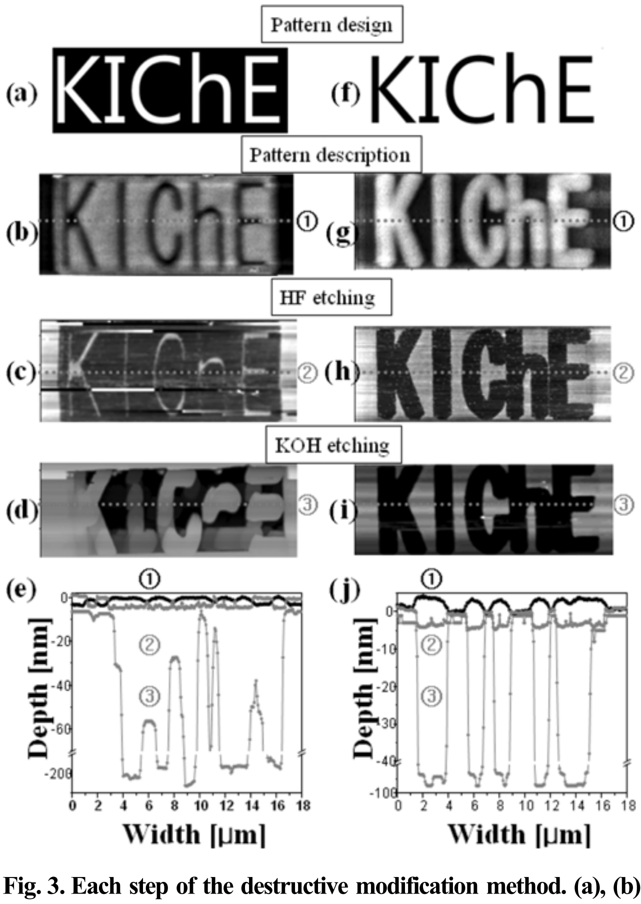


Fig. 3. Each step of the destructive modification method. (a), (b), (c), (d) and (e) Sequential etching procedure and depth profiles of negatively described letters of "KIChE", (f), (g), (h), (i) and (j) Sequential etching procedure of positively described letters (scan size: 18 μm×7 μm).

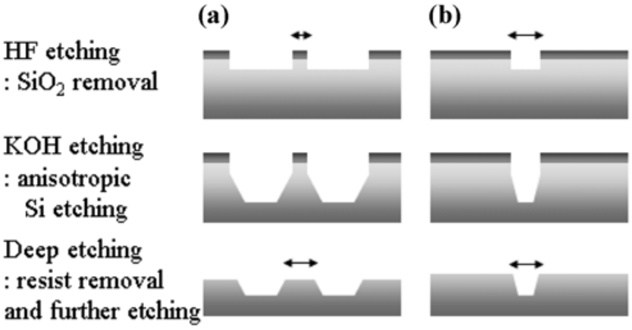


Fig. 4. Illustration of sequential etching steps: (a) Etching of background area, (b) Etching of designed area.

was dipped in a dilute HF solution, the oxidized patterns were easily removed and homogeneous silicon surfaces were newly exposed, as shown in Fig. 3(c) and (h). These exposed silicon surface was selectively etched by the KOH/IPA solution, which allowed us to produce deep etched structures (Fig. 3(d) and (i)) with depths of several hundreds nanometers (Fig. 3(e) and (j)). KOH anisotropic etching is an orientation-dependent etching (ODE), and its etching ratio according to the crystalline orientation of Si is known to be 600 : 400 : 1 for {110} : {100} : {111} [12]. Therefore, we obtained deep etched structures with tilted side-walls using a <100>-oriented Si surface. When a deep etching was performed for the complete removal of silicon nitride thin resist, the line width of the deep etched structure was increased, as shown in Fig. 3(d). Fig. 4(a) illustrates this result in view of the anisotropic etching mechanism. The etching rate of silicon nitride film is very slow; however, it can be also removed by severe etching conditions, such as high temperature and long etching time. In the case of a further deep etching procedure, the line width of the etched structures was different from the line width of the designed structures according to the region (background area or designed area) to be etched, because the structures with tilted sidewalls were fabricated by a KOH anisotropic etching, as shown in Fig. 4. These results demonstrate that destructive structures were successfully controlled by the etching time and original pattern size. Based on the results, a variety of structures can be produced by designing different fabrication routes and further utilized in the site-specific array system.

CONCLUSIONS

In summary, we have presented local modification methods via AFM tip-induced oxidation and site-selective chemical treatments. A variety of silicon-based structures were produced by employing pre-designed fabrication schemes in constructive and destructive ways. The ability to achieve patterns rapidly and reproducibly by using simple and flexible techniques will advance the integration of fabricated structures into micro/nano-systems. Furthermore, it can be used for the fabrication of noble structures in further investigations on the characteristics of various nano/biomaterials.

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