Communication

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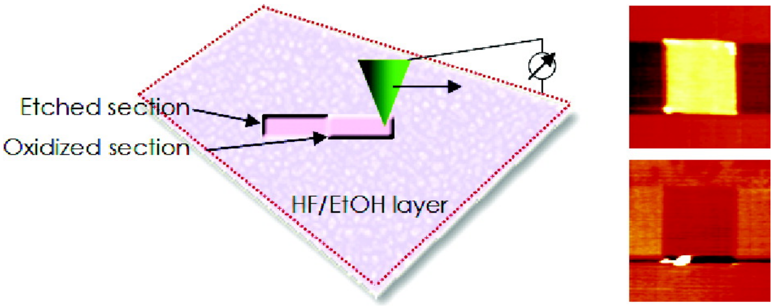

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In situ Negative Patterning of *p*-Silicon via Scanning Probe Lithography in HF/EtOH Liquid Bridges

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Scanning probe lithography (SPL) has received much attention due to its applicability in many areas of nanotechnology, such as molecular electronic devices and nanosized biological sensors.[1] Among the SPL techniques, the conductive atomic force microscope (AFM) technique that includes field-induced oxidation,[2] mechanical scribing,[3] and electrochemical dip-pen lithography[4] is the most versatile and desirable technique for creating submicron- or nanosized structures.

In AFM tip-induced oxidation of silicon, a highly resistive electrolyte forms between the tip and surface by a thin water film in wet gas atmosphere. This water meniscus acts as a source of oxyanion species for oxidation of silicon.[5] Recently, to enhance the vertical growth rate of local oxides, ethyl alcohol has been used as an electrolyte. Its polar characteristics are known to facilitate the field-induced formation of alcohol bridges between the tip and substrate, and the oxyanions are abundant to local oxidation.[6] In addition, the nanosized features have been fabricated on the hydrogen-passivated silicon using AFM oxidation in hexadecane,[5] *n*-octane, and toluene.[7] Thus, it is clear that inert (non)polar organics, even at low relative humidity, do not suppress oxidation of silicon.

A replica of the oxidized pattern can be used to isolate biomaterials, align nanoparticles, and fabricate deep-well structures.[8] Positive pattern oxidized by AFM can be easily transferred to negative pattern by using specific etchants, which has etching selectivity for resist and crystalline lattices. For example, the etch rates of SiO_2:Si in 40% HF and 30% KOH (60 °C) are about 1000:1 and 1:>180, respectively.[9] Therefore, AFM selective-oxidized organic resist is an excellent etch mask with both positive and negative pattern transfers depending on the etchant combination. In the case of an alkanethiol monolayer on a gold plate, a negative pattern was obtained without any etchants.[10] By applying appropriate positive or negative bias, the sulfur−gold bond was broken due to the oxidative desorption of the alkanethiol from a gold electrode. However, the resulting negative pattern was merely a chemically modified structure.

Here, we proposed an in situ negative patterning via SPL in the HF/ethanol phase. This new approach is comprised of two key processes, as shown in Figure 1. In this study, first, silicon oxide was formed by AFM local oxidation. Oxyanions in HF/ethanol were sufficient for local oxidation ($Si + h^+ + 2OH^- \rightarrow SiO_2 + 2H^+$). A few HF molecules were exposed to remove the grown oxide ($SiO_2 + 4HF \rightarrow SiF_4(g) + 2H_2O$), and then, the positive oxide was transferred to negative pattern. A physically modified negative pattern was also formed by an ex situ etching method. After the oxidation step that was conducted under the water meniscus formed in air, the grown oxide was easily removed by bulk HF solution. The presence of water molecules and excess holes facilitated the generation of positively charged defects of H_3O^+ ($\equiv Si{-}H + h^+ + H_2O \rightarrow \equiv Si{-} + H_3O^+$),[11] which in turn reduced the oxidation growth rate by capturing oxyanions and by creating an electrical field, which opposes the external field that drives that oxidation process.[6] Thus, the oxide structure that is formed and the well structure replicated by in situ method are more likely to be higher and deeper than those by the ex situ method.

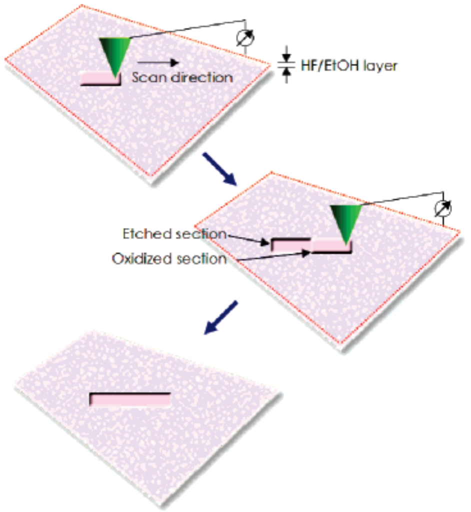

Figure 1. Schematic diagram of the procedure to fabricate a negative pattern by AFM oxidation and in situ etching.

Diluted HF in 99.9% ethanol (5 μL, HF:EtOH = 1:99) was dropped into a cleaned Si wafer (10 × 10 mm^2), followed by anodic oxidation using AFM. HF is highly toxic even at a low concentration, and thus the experiment should be carried out under a controlled box with ventilation. In this study, we used a liquid layer to ensure that only the selected solvent acts as the gap-bridging electrolyte. Patterning with XE-150 (PSIA, Korea) was conducted in tapping mode (5 kHz, 200 nm) to reduce tip wear and to enhance resolution through minimal surface contact.[12] When the HF/EtOH solution was dropped into a cleaned wafer, the substrate spread well over due to the hydrophilicity of surface (contact angle = ca. 20°). The initial thickness of the liquid layer was ca. 50 μm, but became thinner with time due to vaporization. Oxide fabrication by AFM oxidation was carried out at the pill-off time of the liquid layer, which is dependent on the water content of HF/EtOH (e.g., 120 s for 1% HF/EtOH). Thus, the locally condensed HF/EtOH vapors, instead of water, between the tip and substrate acted as a gap-bridging electrolyte.

A conductive tip is generally used in the investigation of AFM oxidation, and because HF was used as etchant in this study, the chemical resistance of the cantilever was a vital property. The experiments were performed with a Pt−Ti- or Au−Cr-coated NSC14 cantilever (MikroMasch, Estonia, $k_c = 5$ N/m and $f_o = 160$ kHz). The Pt−Ti-coated cantilever consisted of a 10 nm Pt layer on a 20 nm Ti sublayer, and the Ti layer showed readily soluble reaction with HF (100 nm/s).[13] The Au−Cr-coated cantilever, however, had a high resistance against HF, and thus, could be used

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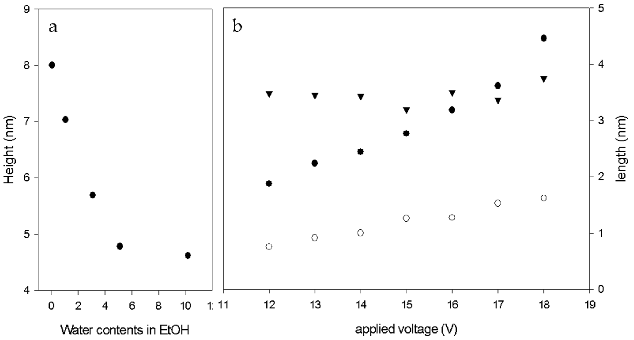

Figure 2. Oxide growth with (a) water contents in a EtOH liquid bridge, and (b) applied voltage (●: h, height; ○: d, depth; ▼: (h+d)/d, volume expansion ratio).

for the direct contact with the HF/EtOH electrolyte. The above results led us to recommend the use of an AFM operating in tapping mode with Au−Cr-coated cantilever for in situ negative patterning.

A kinetic study, comparing noncontact and contact AFM in wet air condition, was reported,[14] and contact AFM oxidation represented a slower oxidation rate due to the high effective energy barrier, including mechanical work energy needed to deflect the cantilever. Tapping AFM was used in order to minimize the mechanical energy of the cantilever and interruption of the liquid layer by tip-contact in this study. Oxide growth rate[15] ($h = bt^{\gamma}$, $1.90t^{0.31}$) of tapping AFM in air was slightly faster than that ($1.58t^{0.30}$) of contact AFM in air, but slower than that ($4.22t^{0.31}$) of tapping AFM in EtOH. These results show that the parameter b depends on the nature of liquid meniscus providing the oxyanions, and parameter γ is constant due to same applied voltage.

The oxyanion source in HF/EtOH was substituted with that in wet air for AFM oxidation, and water contents in HF/EtOH were found to readily affect the oxide growth. Positive square patterns were obtained by applying 18 V for different water contents (0, 1, 3, 5, and 10%) in purified EtOH. As shown in Figure 2a, the resulting height reached the height (3−4 nm) of the pattern fabricated in wet air with the increase in water contents. It was noted that, above 5% H_2O/EtOH, the inhibitory effect for oxide growth by water was larger than the enhanced effect by ethanol. HF solution (initial assay 49%) was diluted in EtOH, and thus 1% HF/EtOH contained ca. 1% of water. Since HF/EtOH solution is too concentrated such that it can cause damage to the cantilever and mirror in the AFM scanner head, only 1% HF/EtOH was used in this study.

Figure 2b shows the oxide growth with applied voltage in air. The height of silicon oxide was increased with increasing applied voltage, but the volume expansion ratio was approximately 3.4, which is similar to that reported for a bare Si wafer.[16] It should be noted that the more positive oxide has a more negative well structure because the volume expansion ratio is an intrinsic property of substrate. When the 1% HF/EtOH was used as the liquid bridging electrolyte during AFM oxidation, the grown oxide was easily etched by HF molecules, and thus the intrinsic height of the oxide could not be measured. Therefore, the height for 1% HF/EtOH should be estimated based on the corresponding height for 1% H_2O/EtOH through ex situ etching, which was 7 nm.

Through in situ and ex situ negative patterning, the results of which are shown in Figure 3, the height of square patterns in 1% H_2O/EtOH was about 2-fold higher than that by water meniscus in air. The difference in oxide growth and its rate was due to the different oxyanion source and its mobility ($\mu_{H2O} = 4.5\mu_{EtOH}$).[6] The depth of negative pattern obtained by ex situ etching was generally 1.6 nm, but that by in situ negative patterning was about 2 times deeper (3 nm). In addition, the negative structures in Figure 3c,d had a smooth edge and inclined to the surface plane. This can be explained in two ways: first, by isotropic etching of HF, and second, by Gaussian distribution of absorbed energy density for electrical field-induced AFM oxidation.[17]

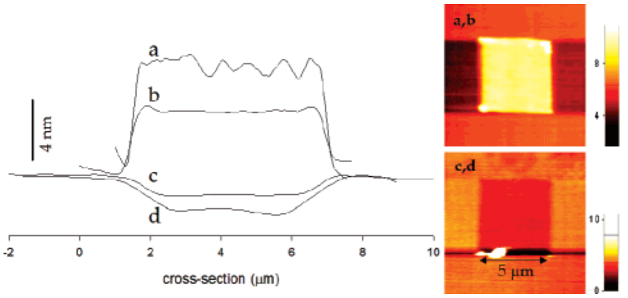

Figure 3. Positive patterns fabricated in (a) 1% H_2O/EtOH and (b) air condition, and negative patterns obtained by (c) ex situ 1% HF etching of (b) and (d) in situ 1% HF/EtOH etching.

In summary, we succeeded in extending local oxidation to in situ negative patterning in this study. HF/EtOH was used as both gap-bridging electrolyte and oxyanion source. EtOH and HF were found to be able to accelerate the growth of silicon oxide and simultaneously etch grown oxide, respectively. These findings are expected to open new possibilities in utilizing local oxidation nanolithography in order to directly fabricate deeper well structures while at the same time maintaining lateral sizes within the nanometer range.

Supporting Information Available: Details of the preparation of Si substrate, pill-off time of *x*% HF/EtOH on wafer (Figure S1), and kinetics for contact and tapping in air and EtOH (Figure S2) (PDF). This material is available free of charge via the Internet at http://pubs.acs.ogr.

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