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Nano-oxidation of Si using ac modulation in atomic force microscope lithography

Cheol Hong Park [a], Sukjong Bae [b], Haiwon Lee [a,b,*]

[a] Department of Nanostructure Semiconductor Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, South Korea
[b] Department of Chemistry, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, South Korea

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Abstract

In atomic force microscope (AFM) anodization lithography, voltage modulation is an important factor leading to enhanced oxide growth rate, increased aspect ratio of oxide patterns and greater control of oxide features. Through the reduction of space charge buildup in the oxide, ac modulation overcomes the self-limiting character of the oxide. When ac modulation was applied to substrates, the aspect ratio of protruded oxide patterns increased five-fold compared to dc pulse. Controlling electron exposure time between the positive and negative voltages is an important factor for controlling the aspect ratio of oxide patterns. This showed the dependence of applied voltage types and various electron exposure times in ac modulation. By adjusting electron exposure time and reducing space charge in the oxide, this study revealed that ac modulation is superior for obtaining high aspect ratios compared to dc pulse.

Keywords: AFM anodization lithography; Oxidation; Space charge effect; ac Modulation; dc Pulse

1. Introduction

To overcome limitations of photolithography, many lithography processes such as e-beam lithography [1], focused ion beam lithography [2], imprint lithography [3] and scanning probe microscope (SPM) lithography [4] have been developed. For many patterning processes, SPM lithography was introduced and studied by several research groups [4–7]. SPM lithography has been studied with a scanning tunneling microscope (STM) and an atomic force microscope (AFM). STM lithography is only suitable for conducting materials while AFM lithography can process semiconductor and metal substrates. AFM anodization lithography is a promising process for making nanostructures on metals and semiconductors. Recently, it has been used to fabricate nano-electronic devices [8] and sensor in local area.

AFM anodization lithography was performed by inducing electrochemical reactions between the tip and the substrate. The driving force is the faradaic current in the water column formed by capillary force. When the faradaic current flows into the water column, H_2O molecules are decomposed into oxyanions (OH^-, O^-) and protons (H^+). These ions penetrate into the oxide layer because of the electric field (order 10^7 V/M) [9]. The penetrated hydroxyl ions (OH^-) grow SiO_2 on a Si surface [10]. Moreover, hydroxyl ions can form an alcohol bridge between the tip and the substrate [11]. The hydroxyl ions penetrate the substrate, enhancing the aspect ratio of protruded oxide patterns compared to the water environment. Therefore, the penetrated and reduced hydroxyl ions are important factors for fabricating SiO_2 on a Si surface in AFM anodization lithography.

Several factors influence the fabrication of oxide patterns in AFM anodization lithography. Both the electron exposure time [7] and the speed of lithography [6] are important kinetic factors in electrochemical oxidation reactions. Humidity is related to the width of oxide patterns [12]. The speed of lithography and line-width of the pattern can be controlled with functional organic resist materials [13–16] on Si. In AFM anodization lithography, applied voltage type is the most important factor for determining the size of the oxide patterns [17,18]. Most studies are performed under dc pulse in AFM anodizaton lithography.

Applied voltage types have been investigated to determine how to overcome the limitations of pattern aspect ratios. Lateral

* Corresponding author at. The National Program for Tera-Level Nanodevices, Seoul 133-791, South Korea. Tel.: +82 2 2220 0945; fax: +82 2 2296 0287.
E-mail address: haiwon@hanyang.ac.kr (H. Lee).

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diffusion of oxyanions is restricted by the short duration time of the pulsed bias [7]. Pulsed bias voltage is synchronized with the resonance frequency of the cantilever in lithography processes using non-contact modes [17,19]. Dagata and co-workers showed that ac modulation (oxidation voltage, V_{ox}, and oxidation time, T_{ox}, reset voltage, V_{res}, reset time, T_{res}) is better than dc pulse (oxidation voltage, V_{ox}, and oxidation time, T_{ox}) in contact mode lithography [18]. This study investigated the effect of reduced space charge on the growth of protruded oxide patterns on Si surfaces using both dc pulse and ac modulation with controlled electron exposure times.

2. Experiments

The p-type Si (1 0 0) wafers (LG Siltron Inc., Korea: resistivity 10–15 Ω-cm) were cleaned by the piranha process (1:3 = 35% H_2O_2:98% H_2SO_4) for 15 min, rinsed with water (Milli-Q reagent grade 18 M Ω-cm, Millipore, USA) for 10 min and dried with N_2 gas blown at room temperature. The thickness of the natural oxide layer was confirmed as 1.5 ± 0.1 nm by an ellipsometer (Auto-E1, Rudolph Technology Inc., USA). The semi-contact mode was used to minimize damage between the tip and the substrate during scanning and patterning. The average frequency resonance of the cantilever (NSG11s/Pt, NT-MDT, Russia) was measured as 250 kHz by AFM (Solver P47, NT-MDT, Russia). The cantilever was coated with Au and Pt to improve conductance in AFM lithography. Relative humidity and temperature were maintained at 56% and 26.6 °C, respectively. The set point was fixed at 7.4 nA. When voltage was applied to the substrate, the tip was grounded in sample bias lithography. A scan speed of 10 μm/s was fixed during imaging and patterning. The imaging process was performed by a Solver P47 (NT-MDT, Russia). A home-made voltage amplifier was used to increase applied voltage up to 24 V.

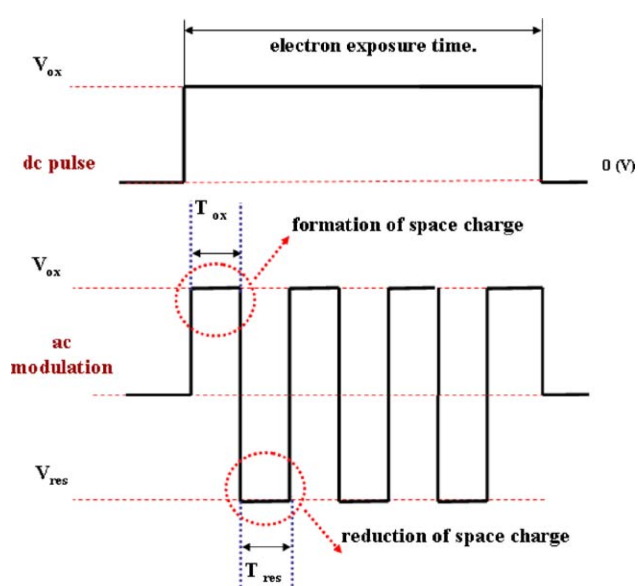

Fig. 1. Schematic diagrams of ac modulation and dc pulse. Applied positive voltage forms the space charge field and applied negative voltage reduces the accumulated space charge.

3. Results and discussion

When voltage was applied between the tip and the substrate, electrochemical reactions occurred in the water column. The chemical reactions occurred differently at the AFM tip-surface

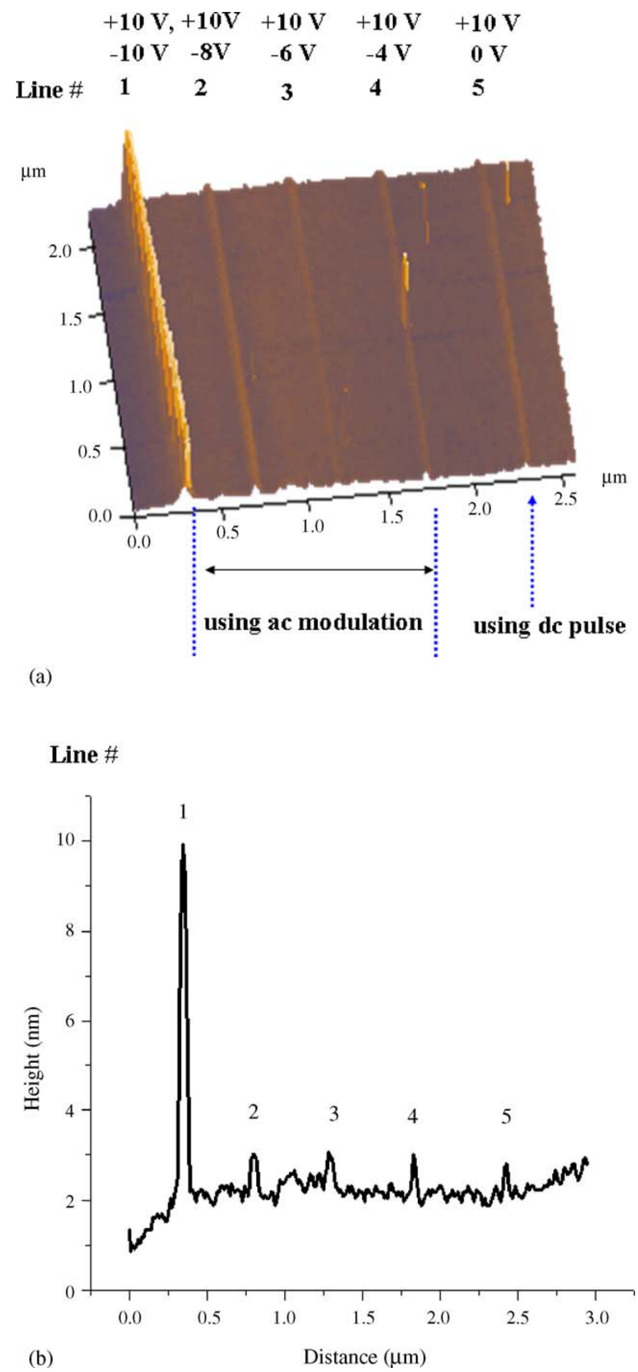

Fig. 2. Lithography patterns fabricated under: (a) ac modulation (V_{ox} = 10 V, values of V_{res} range from −10 to −4 V) and dc pulse (V_{ox} = 10 V) and its (b) height profile. Under ac modulation, the height and width of line # 1 are 7.6 and 48.7 nm, respectively. Under dc pulse, the height and width of line # 5 are 0.84 and 34.6 nm, respectively.

interface, in the water column and on the oxide layer. When the electron is introduced into the water column from the tip, H_2O molecules decomposed into hydroxyl ions (OH^-) and radicals ($H^\bullet$) as follows: $H_2O + e^- \rightarrow OH^- + H^\bullet$ [10]. The hydroxyl ions penetrated the natural oxide layer via the strong electric field and made a protruding SiO_2 pattern according to the following equation: $Si + 2OH^- - 4e^- \rightarrow SiO_2 + 2H^+$ [10]. $H^\bullet$ radicals recombined spontaneously into H_2. The hydrogen gas was removed from the water column. Accumulation of trapped charges in the protruded oxide layer can form a space charge field. When dc pulse was applied to the Si surface, the aspect ratio of protruded oxide patterns was governed by the space charge effect. [6,18,20]. Fig. 1 shows the reducing space charge effect. When ac modulation was applied to the substrate, the anode and cathode between the tip and the substrate changed. The rapid decline of high initial growth rate was restricted by ac modulation. To reduce the space charge effect, the first step was anodic oxidation followed by accumulation of space charge. Diminishment of accumulated space charge was the second step. The focus of this study was on voltage modulation between ac modulation and dc pulse for fabricating protruding oxide patterns. When comparing voltage modulation, it is not important to apply the same potential for ac modulation and dc pulse in order to enhance the aspect ratio of oxide patterns. Fig. 2 shows protruded patterns under both ac modulation and dc pulse. Protruded patterns were fabricated with both ac modulation ($V_{ox} = 10$ V, values of V_{res} range from −10 to −4 V) and dc pulse. The electron exposure time was fixed at 100 ms ($T_{ox} = 50$ ms, $T_{res} = 50$ ms, waveform frequency = 10 Hz) at each scan point (256 × 256). Reducing the space charge produced different aspect ratios for the patterns. The pattern with the highest aspect ratio on the Si surface was fabricated with ac modulation ($V_{ox} = 10$ V, $V_{res} = -10$ V). The aspect ratio increased greater than five-fold compared to the aspect ratio of the oxide pattern made by dc pulse. When accumulated charges were removed from protruding oxide patterns, the growth of the oxide pattern increased dramatically. Specifically, reduction of the space charge was related to increased vertical growth of the oxide patterns. The lateral growth of the oxide patterns was restricted by a strong electric field. By using the same potential between the positive and negative voltage, reduction of the space charge can be optimized. When ac modulation ($V_{ox} = 10$ V, values of V_{res} range from −8 to −4 V) was applied to the substrate, the aspect ratio of lines was low. However, ac modulation ($V_{ox} = 10$ V, $V_{res} = -10$ V) reached the maximum value. The lower negative voltage could not remove the space charge effectively. Space charge restricted the growth of oxide patterns.

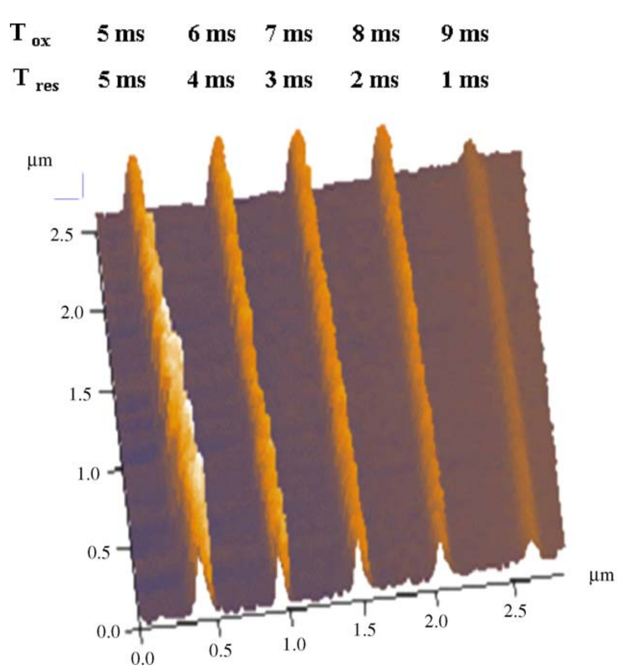

Fig. 3. Lithography patterns fabricated under various duty-ratios of ac modulation ($V_{ox} = 24$ V, $V_{res} = -24$ V, electron exposure time, 5:5, 6:4, 7:3, 8:2, 9:1 ms, $T_{ox} + T_{res} = 10$ ms).

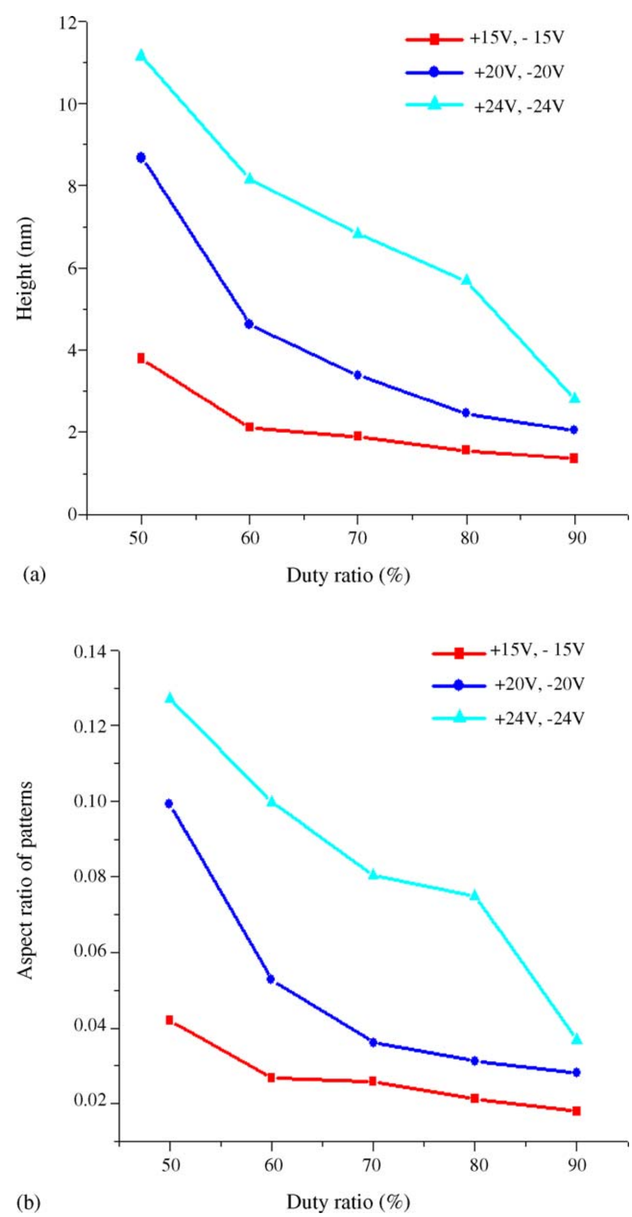

Fig. 4. Lithographic dependence of applied voltage under ac modulation ($V_{ox} = 24, 20, 15$, $V_{res} = -24, -20, -15$ V) with (a) line-height and (b) the aspect ratio of patterns at various duty ratios.

When ac modulation was applied to the substrate, controlled electron exposure times between the positive and negative voltages affected the protruding oxide pattern. Fig. 3 shows the tendency of duty ratio between the positive and negative voltages. The duty ratio is proportional to the ratios of both the effective and non-effective parts in the whole cycle. Applied voltage was fixed at 24 and −24 V and the electron exposure time was 10 ms at each scan point (256 × 256). T_{ox} was increased from 5 to 9 ms and T_{res} was decreased from 5 to 1 ms from left to right in Fig. 3. A 1:1 duty ratio was the best condition for reducing accumulated charge effectively and growing oxide patterns. When ac modulation was applied to the substrate, two steps fabricated the protruding oxide patterns. The first step was the anodic oxidation and accumulation of space charge. The second one was the vertical growth of the oxide pattern by reducing the space charge. In the case of protruding oxide patterns, it was not necessary to increase T_{res} to longer than T_{ox} to enhance the aspect ratio. When exposure times of the negative voltage decreased, the aspect ratio of the patterns decreased. Trapped charges could not be removed effectively under the short negative electron exposure times compared to the positive electron exposure times. The remaining space charge restricted the growth of oxide patterns. Fig. 4 shows the dependence of line height and aspect ratio on applied voltage. At each duty ratio, each pattern was affected by space charge reductions. When the applied voltage was increased, the line height and aspect ratio of patterns was enhanced. This showed that applied voltage types are important factors for enhancing oxide patterns.

4. Conclusion

AC modulation with a controlled electron exposure time was applied in AFM anodization lithography. The aspect ratio of protruded oxide patterns increased five-fold by applying ac modulation. When the positive and negative voltages were the same, space charge was reduced effectively. The highest aspect ratio of the patterns occurred when the duty ratio between the positive and negative voltage was 1:1, resulting in effective space charge reduction. With ac modulation, the rapid decline of high initial growth rate was restricted effectively by the electron exposure time when both the positive and negative voltages were the same.

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