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Nano-oxidation of silicon nitride films with an atomic force microscope: Chemical mapping, kinetics, and applications

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We demonstrate that local oxidation of silicon nitride films deposited on conductive substrates with a conductive-probe atomic force microscope (AFM) is a very promising approach for nanofabrication. Scanning Auger microscopy and spectroscopy are employed to verify the chemical changes after AFM-induced oxidation. Furthermore, the growth kinetics are found to have a logarithmic relationship of oxide height versus pulse duration \[ h \propto \ln(t/t_0) \]. In contrast to rather slow thermal oxidation process, AFM-induced oxidation on silicon nitride has an anomalously high initial oxidation rate \((\sim 30,000 \text{ nm/s at 10 V})\) and a small onset time \( t_0 \sim \text{(10 \mu s)} \). As for the applications in ultrahigh-density recording, an oxide dot array \((\sim 100 \text{ Gbit/in.}^2)\) produced by this process is demonstrated. The nitride film patterned by AFM can be utilized as an etching mask to fabricate ‘subtractive’ silicon nanostructures, due to the large etching selectivity of Si\(_3\)N\(_4\) : SiO\(_2\) : Si in various etchants. With this method, which is entirely compatible with the existing microelectronic processes, synthesis of ultrahigh packing density and ordered nanostructures could become readily achievable. © 2001 American Institute of Physics. [DOI: 10.1063/1.1339212]

I. INTRODUCTION

Silicon nitride (Si\(_3\)N\(_4\)) is a dielectric material widely used for both silicon and gallium arsenide processing due to its many superior material properties. In contrast to SiO\(_2\), Si\(_3\)N\(_4\) has unique chemical, electrical, and mechanical properties. For example, it has larger dielectric constant \((7.5 \text{ vs } 3.9)\), refractive index \((2.05 \text{ vs } 1.46)\), and density \((3.1 \text{ vs } 2.2 \text{ g/cm}^3)\), as compared with SiO\(_2\). In one of the most important applications, silicon nitride is used as an oxidation mask (oxidation rate is about 100 times less than silicon) during the local oxidation of silicon process. In order to achieve high levels of integration and speed, the scaling of ultralarge-scale-integrated (ULSI) circuits will develop into the nanometer regime \((<100 \text{ nm})\) and ultrathin SiO\(_2\) gate dielectrics of \(<2 \text{ nm} \text{ thick which will become necessary in the near future. To reduce the problem of direct tunneling in the case of ultrathin SiO}_2\), insulators with higher dielectric constants are more favorable as the gate dielectrics. Therefore, Si\(_3\)N\(_4\) and silicon oxynitride (Si\(_3\)O\(_y\)N\(_{1-y}\)) thin films are particularly interesting for this application. In addition, they have been used for passivation layers, barrier layers against impurity diffusion, ion implant masks, gate dielectrics in dynamic random access memory, and charge-trapping media in nonvolatile memory. The chemical selective etchings of oxide and silicon over nitride in many wet etchants or dry processes are also very important for the mask applications. As the decreasing of critical dimensions of ULSI circuits continues, an effective and reliable patterning process for silicon nitride film on the nanometer scale becomes increasingly significant.

Many researches have demonstrated that scanning probe microscope (SPM) induced oxidation can be used to achieve nanometer-scale patterning on semiconductors, metals, and to fabricate various devices, e.g., metal–oxide–semiconductor field effect transistor (MOSFET), side-gated FET, room-temperature single electron transistor, and high-aspect-ratio and high-packing-density silicon nanostructures. Recently, García et al. reported the fabrication of high-areal-density oxide dot arrays on a hydrogen-passivated silicon substrate using noncontact atomic force microscopy (AFM) and Cooper et al. reported the case of oxide array with an areal density of 1.6 Tbit/in.\(^2\) on a titanium film using a single-wall carbon nanotube grown on an AFM cantilever, revealing a new approach for ultrahigh-density data recording using AFM-induced oxidation. In principle, AFM-induced oxidation is a feasible process for nanometer-scale patterning on thin dielectric films deposited on conductive substrates. However, there are few reports in the literature to address this subject. In 1996, Day and Allee reported the possibility of local oxidation on silicon nitride using the tungsten tip of a scanning tunneling microscope.
microscope (STM). Very recently, we have successfully proved the conversion of Si$_3$N$_4$ to SiO$_x$ with a conductive-probe AFM.\textsuperscript{20}

In this article, we present the chemical analysis of the AFM-induced oxide using scanning Auger microscopy/spectroscopy (SAM/S) to show that AFM-induced oxidation is an effective method for conversion of silicon nitrides to oxides. We also present the oxide growth behavior and kinetics, although the exact AFM oxidation mechanism of silicon nitride is still unclear at this moment. Due to the small oxide onset time, the initial growth rate of oxide on silicon nitride is two orders of magnitude higher than that on silicon. Besides, we present examples of ultrahigh-density oxide dot array and nanostructures fabricated using a Si$_3$N$_4$ mask to demonstrate the prospective applications of AFM-induced oxidation on silicon nitride films.

II. EXPERIMENTAL CONDITIONS

The silicon nitride films were grown on $p$-type, 10 Ω cm, (100)-oriented Si wafers in a low pressure chemical vapor deposition (LPCVD) reactor at 780 °C using a mixture of SiCl$_2$H$_2$ (30 sccm) and NH$_3$ (130 sccm). Two films with thickness of 2.5 nm (sample A) and 5 nm (sample B) as measured by ellipsometry were used for this study. The sample B was further densified by rapid thermal anneal at 1000 °C in a nitrogen gas for 10 s. The film thickness was reduced to 4.2 nm after annealing. Local field-induced oxidation was performed with a commercial AFM/STM microscope operated in both contact and tapping modes in ambient air. The AFM cantilevers used for oxidation were highly doped (0.01–0.025 Ω cm) $n^+$-Si cantilevers. The typical tip radius, force constant, and resonance frequency of the contact mode cantilevers were 10 nm, 0.2 N/m, and 13 kHz, respectively. After coated with a 23 nm thick double layer of Cr and Pt/Ir, the typical tip radius became ~30 nm. The typical tip radius, force constant, and resonance frequency of the tapping mode cantilevers used were 10 nm, 32 N/m, and 273 kHz, respectively.

III. RESULTS AND DISCUSSIONS

A. SAM/S analysis

To investigate the conversion of silicon nitride to oxide, SAM/S was utilized to analyze the chemical composition. Three ~4×4 μm$^2$ squares on sample A were modified by the coated contact-mode cantilever at 0.4 μ m/s scan speed with a 10 V bias applied to the sample. Figure 1(a) is the scanning electron microscope (SEM) image, which shows the layout of the squares. The SAM mappings of the nitrogen and oxygen compositions at the same AFM-oxidized region are shown in Figs. 1(b) and 1(c), respectively, in which the gray level is proportional to the amount of the specific element. Obviously, in the modified area, the nitrogen content is suppressed but the oxygen content is enhanced. Auger spectra taken from the as-grown and modified areas are shown in Fig. 2. Both spectra have emission peaks of Si LVV at ~86 eV, Si KLL at ~1620 eV, and O KLL at ~512 eV. However, the peak of N KLL at ~385 eV in the as-grown area completely disappears after the film has been modified. Meanwhile, the magnitude of O KLL is much enhanced in the modified area as compared with that in the as-grown area. Therefore, it is clear that the nitrogen content is thoroughly replaced by the oxygen atoms. The results of SAM/S support the previous suggestion\textsuperscript{12} that the nitride films can be converted to oxides by a SPM oxidation process. The mobile oxyanions (OH$^-$) drift toward the anodic substrate in response to the intense local field beneath the AFM tip and react with silicon nitride at the oxide/nitride interface while the nitrogen-related species drift outward.

In addition to the LPCVD films, we also applied the AFM-induced oxidation process on a single-crystal nitride film. The film was grown on a Si(111) substrate by thermal nitridation using ammonia. The Si(111)- (7×7) surface was prepared in an ultrahigh vacuum (UHV) chamber at a base pressure of ~4×10$^{-7}$ Torr.

![Fig. 1. (a) SEM micrograph of the AFM-induced oxide squares on the LPCVD Si$_3$N$_4$ film. Two black spots observed on the oxide patterns result from the electron-beam damaging during Auger analysis. (b) and (c) SAM mappings of the nitrogen and oxygen elements on the same region. The gray scale is used to represent the element contents (brighter regions contain more of the specified element).](image)
The oxide height is proportional to the direct logarithm of pulse duration \( h = \ln(t) \) based on the data obtained by contact mode AFM oxidation on Si(100) substrates. An exponential dependence of oxidation rate on oxide height, \( dh/dt \propto e^{(-h/L_e)} \), can be deduced from this kinetics, where \( L_e \) is the characteristic decay length. They suggested that due to the fact that the molecular volume of \( \text{SiO}_2 \) is twice as large as that of Si, the development of stress leads to an additional activation energy barrier, causing rapid decrease of oxidation rate with increasing oxide height. Later, Calleja and García observed the same logarithmic behavior by noncontact mode AFM oxidation on Si(100).

In 1956, Uhlig obtained the direct-logarithmic form \( h = k_0 \cdot \ln(t+1) \) of oxide growth by assuming the oxidation rate is limited by the space charges increasingly trapped at and around the film–oxide interface. By using

![Graph](image)

**FIG. 3.** Auger electron spectra taken on the single-crystal Si\(_3\)N\(_4\) film before (upper spectrum) and after Ar ion sputtering (lower spectrum).
scanning Maxwell-stress microscopy, Dagata et al.\textsuperscript{20} directly observed the trapped charge within the grown oxide. Recognizing that space charge buildup is the main rate-limiting step, Dagata et al.\textsuperscript{30} further implemented the Uhlig model by explicitly incorporating the direct and indirect oxidation processes using the Alberty–Miller formalism\textsuperscript{31} for AFM-induced oxidation on silicon. They discovered that AFM oxidation on Si exhibits a two-stage kinetics. In the transient region (~0.5 s for Si), both power law and Uhlig direct-logarithmic law are adequate in describing the oxidation behavior. However, after entering the steady-state growth region, a full consideration using the Alberty–Miller formalism is required. Recently, using the concept of space charge limited growth, Dubois and Bubendorff\textsuperscript{32} have also successfully derived the power law form of AFM-induced oxidation on Si.\textsuperscript{30} In the inset, both types of logarithmic fittings [the dashed lines are fitted with \( h(t) = k_0 \cdot \ln(t + 1) \) and the solid lines are fitted with \( h(t) = L_c \cdot \ln(t_0) \)] are displayed for comparison as well as the previously reported result on Si(100) (Ref. 27). (b) Exponential decay relation of the oxidation rate vs the grown oxide thickness [\( dh/dt = R_0 \cdot \exp(-h/L_c) \)] derived from the kinetic data shown in (a), where \( R_0 \) is the initial oxidation rate and \( L_c \) is the characteristic decay length.

We studied the variation of oxide height with the applied voltage and exposure time on sample B using both contact and tapping modes of AFM. The AFM-induced oxide is topographically protruded since the molar volume of silicon oxide is larger than that of silicon nitride. Figure 5(a) and 5(b) are plots of the oxide height \( h \) versus applied voltage \( V \) for 200 ms pulse duration in contact mode and 100 ms in tapping mode, respectively. A linear dependence of oxide height on bias voltage with \( h \approx V - V_{th} \) is found, where \( V_{th} \) is the threshold voltage corresponding to \(-4.3\) and \(-8\) V for contact and tapping mode, respectively. The effective electrical field in the tapping mode is smaller for the dynamically oscillating cantilever and higher threshold voltage is required as compared with that of the contact mode.

For studying the oxidation kinetics, voltage pulses of various durations (1–1000 ms) were applied to the silicon nitride film and the patterned oxide dots were analyzed by contact mode AFM. Figure 6(a) displays the linear-log plots of oxide height versus pulse duration at biases of 9 and 10 V. The oxide height is found to increase as the logarithm of the pulse duration in both cases, that is similar to the empirical relationships obtained for silicon.\textsuperscript{26,27} Instead of the Uhlig direct-log form, \( h(t) = k_0 \cdot \ln(t + 1) \), where \( k_0 \) and \( \tau \) are constants and \( h(0) = 0 \), we find that it is better to fit the data with \( h(t) = L_c \cdot \ln(t_0) \), where \( L_c \) is a voltage-dependent constant. By extrapolating the fitted straight line as \( h(t) = L_c \cdot \ln(t_0) \) to the logarithmic time axis [as shown in Fig. 6(a)], we can find the oxide onset time \( t_0 \), which represents the period of time required for oxide to start growth upon applying voltage pulses. Also, an exponential decay relationship of the growth rate to oxide height [\( dh/dt = R_0 \cdot \exp(-h/L_c) \)] can be found from the kinetic data [Fig. 6(b)], where \( R_0 \) corresponds to the initial oxidation rate. Although the detailed chemical reactions are rather different, the AFM-induced oxidation process on both silicon nitride and silicon obeys the same logarithmic relationship of \( h \) and \( t \) and the expo-
TABLE I. Growth kinetic parameters of AFM-induced oxidation on silicon nitride and silicon.

<table>
<thead>
<tr>
<th></th>
<th>Bias (V)</th>
<th>$L_c$ (nm)</th>
<th>$t_0^a$ (s)</th>
<th>$R_0^b$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$</td>
<td>Contact mode</td>
<td>10</td>
<td>0.29</td>
<td>$8.7 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.24</td>
<td>$1.9 \times 10^{-2}$</td>
<td>$1.3 \times 10^{4}$</td>
</tr>
<tr>
<td>Si$^+$ (Ref. 26)</td>
<td>10</td>
<td>0.39</td>
<td>$4 \times 10^{-2}$</td>
<td>9.8</td>
</tr>
<tr>
<td>Si$^3$ (Ref. 27)</td>
<td>10</td>
<td>0.35</td>
<td>$1.3 \times 10^{-2}$</td>
<td>250</td>
</tr>
</tbody>
</table>

*a* Determined by the intercept at the logarithmic $t$ axis of the fitted line.

*b* Derived from $L_c/t_0$.

By contact mode AFM, $L_c$ is $0.9$ nm×log$_{10}(e)$. By noncontact mode AFM, $L_c$ is $0.1 + 0.03 \times 10^{-3} \times 10^{-2}$. $L_c^c$ is $0.5 \times 10^{-3}$. $L_c^c$ is $0.5 \times 10^{-3}$. $L_c^c$ is $0.5 \times 10^{-3}$.

Contrary to the thermal oxidation process where the oxidation rate of silicon nitride is two orders of magnitude less than that of silicon, the silicon nitride film has much higher stress in silicon nitride films grown on silicon substrates. Because of weaker electric field and compressive stress in the AFM-induced oxide grown on silicon substrates. As a result, the AFM-induced oxide grown on silicon nitride contains more stress than that in the AFM-induced oxide grown on silicon substrates. Because of weaker electric field and larger compressive stress in the AFM-induced oxide, both thickness-limited and stress-limited kinetic models cannot account for the anomalously high oxidation rate observed on Si$_3$N$_4$. In addition, compared with the rate coefficient $A \approx 1$ nm/min$^{235}$ ($h = Ar^{235}$) for the wet thermal oxidation at $1100^\circ$C and under 0.95 atm of water vapor, the rate of 0.82 nm/min for traditional anodic oxidation with a field intensity of $1.9 \times 10^9$ V/m at 7.5 mA/cm$^2$, AFM-induced oxidation rate of Si$_3$N$_4$ is many orders of magnitude faster than the conventional methods.

C. Image reversal

During our experiments, we sometimes observed the contrast reversal of contact-mode images of AFM-induced oxide taken interleave with opposite-direction scans either bottom to top followed by top to bottom or left to right followed by right to left after the silicon cantilevers (metal coated or uncoated) had been used extensively. In Figs. 7(a) and 7(b), a 4.5 μm diameter oxide circle was produced by 10 V pulses and imaged with interleaved scans. A protruded topography of 1.5 nm height was recorded from the bottom-to-top scan, while a depressed one of 1.0 nm depth was obtained from the top-to-bottom scan. Occasionally, the “apparent” height or depth can be as large as 100 nm. Definitely, the real AFM-induced oxide height cannot be so.
Large. Such a topographic reversal phenomenon was also observed for the AFM-induced oxide on silicon substrates. We believe that the space charges trapped in the grown oxide cause the image reversal. Space charges exert additional forces on the worn cantilevers and cause the response of the optical-lever feedback system to maintain a constant bending of the cantilever. Throughout our oxidation experiments discussed above for kinetics study, we always took AFM images in both scan directions to make sure that nearly identical oxide topographic heights were obtained, excluding fictitious effects from the trapped space charges.

IV. APPLICATIONS FOR DATA RECORDING AND NANOSTRUCTURE FABRICATION

Two of the most prospective applications of AFM-induced oxidation are ultrahigh-density data recording and AFM nanolithography process. In this section, we will present examples of AFM-induced oxidation on silicon nitride films for high-density surface modification and nanostructure fabrication. Shown in Fig. 8, we generated an oxide dot array with an areal density of $\sim$100 Gbit/in.$^2$ on sample B by applying pulses of +9 V and 5 ms duration on the predetermined locations with a tip moving speed of 0.5 $\mu$m/s. The total writing time is $\sim$30 s for this array. The oxide formation is very reproducible and uniform with $\sim$45 nm dot diameter and $\sim$1.2 nm oxide height. The AFM-induced oxidation on nitride film can be used as a write-once and read-many data recording technique with a higher areal density than the predicted superparamagnetic limit for the magnetic recording. Compared with hydrogen-passivated silicon substrates and titanium films oxidized in ambient, silicon nitride film is more superior as a data recording medium due to its resistance to oxidation under ambient conditions. Additionally, the high initial oxidation rate of silicon nitride requires a shorter writing time, so higher recording speed can be achieved. It should be noted that the slow probe speed (0.5 $\mu$m/s) used here is only due to the instrumentation limit. With the current advances in high-speed, large-area, and parallel-probe methods, the fundamental limit to the writing speed using this approach is the initial oxidation rate.

The patterned nitride films can be used as etch masks due to the large etch selectivity of silicon nitride to oxide and silicon. The etching rates in 1% HF solution determined by ellipsometry are 0.01 nm/s for the sample B and 0.27 nm/s for AFM-induced oxide, corresponding to an etch selectivity of 27. Therefore, HF dipping can remove the AFM-induced oxide without substantial etching to the nitride film. The patterned windows, exposing the Si substrate, can be used for subsequent fabrication process development of nanostructures.

The etching rate of silicon nitride film in a KOH solution is very slow. Under some conditions, the selectivity of Si/Si$_3$N$_4$ in a KOH solution is extremely high (1000:1). For the usage of the AFM oxidation technique, a thin mask film is preferred to produce high-areal-density patterned Si-exposing windows. Hence, before patterning, the nitride film (sample B) was thinned to 3 nm thick (measured by ellipsometry) by dipping in a 1% HF solution for 120 s. Figure 9 shows the process to produce a V-groove Si structure. First, oxide lines parallel to the $\langle 110 \rangle$ direction were written with 10 V bias and 0.08 $\mu$m/s writing speed [Fig. 9(a)]. The oxide is 2 nm high and with a full width at half maximum (FWHM) of 210 nm. After the sample was dipped in a 1% HF solution for 20 s at 26 °C, the oxide lines were selectively removed and the topography converted to 3 nm deep trenches with a FWHM of 230 nm [Fig. 9(b)]. The conversion ratio of total oxide volume to the consumed silicon volume defined by total oxide height divided by the buried oxide depth is about 1.67. After subsequent etching in a 20
wt % KOH solution for 20 s at 50 °C to transfer the pattern into silicon substrate, the V-groove terminal geometry is formed by two intersecting {111} crystal planes because of the anisotropic etching of silicon in KOH [Fig. 9(c)]. The V-groove opening on the surface is about 350 nm and depth is 150 nm.

Figures 10(a) shows an example of inverted pyramid pit array in Si. First, an oxide dot array pattern was made by applying +9 V pulses of 5 ms duration. The produced oxide dots have an average diameter of ~60 nm and a protruded oxide height of ~2 nm. After pattern transfer using aqueous KOH, each oxide dot converts to a ~60×60 nm² pit [Fig. 10(b)]. The inverted pyramidal etching pits, independent of the mask opening shape, are formed with four intersecting {111}-crystal-planes. And the etched depth is self-limited by the terminal etch geometry. This “subtractive” process could be used for fabricating nanostructures from thin films or multilayered structures, or as high-density read-only memory. Additionally, the “subtractive” structures can be utilized as templates for selective growth since the deposited materials tend to grow over the unmasked silicon surfaces. Recently, single-crystal silicon dots and lines have been successfully grown by selective CVD with AFM-patterned Si₃N₄/SiO₂ bilayer growth masks.

V. CONCLUSIONS

SAM and SAS have been used to prove the conversion of LPCVD-grown Si₃N₄ to SiO₂ by a conductive-probe AFM. The electrical field under the AFM tip promotes the bi-directional diffusions of O- and N-related species, although the exact reaction paths are still unknown. We also show that the AFM-induced oxidation performed on the single-crystal silicon nitride film is an atomic smooth process. In the study of oxidation kinetics, the oxide height is found to be linearly proportional to the bias applied to the sample in both contact and tapping modes of AFM. In addition, the oxide growth kinetics obeys the logarithmic relationship of oxide height and pulse duration as \( h(t) = L_c \cdot \ln(t/t_0) \), which is similar to the previous results on Si(100) conducted by contact and noncontact modes. We find that the initial oxidation rate \( R_0 \) can be related to \( L_c/t_0 \). Due to its anomalously small oxide onset time \( t_0 \) (~10 μs), the initial growth rate (~30 000 nm/s at 10 V) of oxide on nitride films is two orders of magnitude higher than that of silicon substrates under similar conditions. It is surprising that AFM-induced oxidation on elementary materials (e.g., Si) and on compounds (e.g., Si₃N₄) has the same growth kinetics and Si₃N₄, traditionally used as an oxidation mask, has an extremely high initial oxidation rate. The role of nitrogen seems to be critical for this process. Further studies are necessary to reveal the exact cause of these phenomena.

For practical applications, we have demonstrated two examples to show the feasible applications of AFM oxidation of nitride films on the nanometer scale. First, the AFM oxidation of nitride films can be employed for ultrahigh-density (~100 Gbit/in²) data recording with the advantages of high writing speed and resistance to oxidation under ambient conditions. Second, with the large etching selectivity of silicon oxide to nitride, the patterned nitride film can be employed as an etching mask to fabricate subtractive nanostructures (e.g., V-grooves and inverted pyramid pit array), which can be used as templates for selective-area growth (an “additive” process) or nanomechanical devices.

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4 Etch rate selectivity of Si₃N₄:SiO₂:Si in diluted HF (40%) at room temperature is about 1:1000:1 and in aqueous KOH (30 wt %) at 60 °C is two orders of magnitude higher than that on silicon substrates under similar conditions. It is surprising that AFM-induced oxidation on elementary materials (e.g., Si) and on compounds (e.g., Si₃N₄) has the same growth kinetics and Si₃N₄, traditionally used as an oxidation mask, has an extremely high initial oxidation rate. The role of nitrogen seems to be critical for this process. Further studies are necessary to reveal the exact cause of these phenomena.

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