Nanometer-scale conversion of Si$_3$N$_4$ to SiO$_x$


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It has been found that atomic force microscope (AFM) induced local oxidation is an effective way for converting thin (<$5$ nm) Si$_3$N$_4$ films to SiO$_x$. The threshold voltage for the 4.2 nm film is as low as 5 V and the initial growth rate is on the order of $10^3$ nm/s at 10 V. Micro-Auger analysis of the selectively oxidized region revealed the formation of SiO$_x$. Due to the large chemical selectivity in various etchants and great thermal oxidation rate difference between Si$_3$N$_4$, SiO$_2$, and Si, AFM patterning of Si$_3$N$_4$ films can be a promising method for fabricating nanoscale structures.

Previous reported results of AFM-induced oxidation have been limited to semiconductors and metals. However, it is not necessary that the modified surface is conductive. Even if there is a thin insulating film grown on the conductive substrate, the intense electrical field between the probe and the substrate still can drive the oxidant anions (most likely OH$^-$) to diffuse into the thin dielectric film (Si$_3$N$_4$ in this work). The reaction of oxidants and silicon nitride results in the replacement of nitrogen by oxygen. Hence, the local intensive field induced by an AFM probe can turn silicon nitride into silicon oxides or silicon oxynitrides.

The silicon nitride films were grown on $p$-type, 10 $\Omega$ cm, (001)-oriented Si wafers in a low-pressure chemical vapor deposition (LPCVD) reactor at 780 $^\circ$C using a mixture of SiCl$_2$H$_2$ and NH$_3$. Two as-grown film thicknesses of 5 (sample A) and 2.5 nm (sample B) measured by ellipsometry were used for this study. Sample A was further densified by a rapid thermal anneal of 10 s at 1000 $^\circ$C in a nitrogen gas atmosphere. The film thickness was reduced to 4.2 nm after annealing. Local electric-field-induced oxidation was performed in ambient using highly doped (0.01–0.025 $\Omega$ cm) n$^+$-Si AFM probes (contact-type Pointprobe, Nanostructures) and a commercial AFM (CP type, Park Scientific Instruments) operating in the contact mode. Both uncoated and PtIr-coated tips have been used. The typical force constant and the resonance frequency of the cantilevers used are 0.2 N/m and 13 kHz, respectively.

Figure 1(a) shows oxidized lines written on the densified sample A with 0.4 nA contact force and 0.1 $\mu$m/s scan speed at various sample biases ranging from +4 to +10 V with

$<1:0.3$.$^4$ Using an anisotropic aqueous KOH (30 wt %) etchant, typically used for wet bulk micromachining, selectivity of Si$_3$N$_4$:SiO$_2$:Si(100) at 60 $^\circ$C is about $1:14:2600$.$^5$ As a result, AFM selective-oxidized Si$_3$N$_4$ films can be excellent nanoscale etch masks both for positive- and negative-type pattern transfers depending on the etchant combination.

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protruded and buried parts as the volume of oxide after conversion. The conversion ratios of oxide volumes to consumed nitride volumes $[(h+d)/d]$ at higher sample biases (>7 V) are around a constant value of 2.23, indicating a nearly complete conversion of nitride film. However, this ratio is much higher than the reported conversion ratio of thermal oxidation of silicon nitride that is around 1.64. The protruded and buried parts as the volume of oxide after conversion.

To investigate the oxide growth rate, voltage pulses of varied height and duration (1–500 ms) were applied to the densified film $A$ and the produced oxide dot arrays were analyzed. We have found that the initial growth rate of AFM-induced oxide depends on the tip characteristics, but typically with a magnitude ranging from 500 to 1500 nm/s. An exponential decay relation of the growth rate with the grown oxide thickness $[d(1/(2d)) \exp(-h/L_c)]$ can be found from the kinetic data. In our experiments, the characteristic decay length $L_c$ is typically within the range of 0.3–0.6 nm. Compared with the rate coefficient $A \approx 1$ nm/min$^{2/3}$ ($h = A t^{2/3}$) for the wet thermal oxidation at 1100 °C and under 0.95 atm of water vapor, AFM-induced oxidation of Si$_3$N$_4$ is much faster than other methods and even faster than the AFM-induced oxidation rate of Si(001) (initial rate of 10 nm/s and $L_c = 0.9$ nm at 10 V). The observed low critical field strengths and high oxidation rates of AFM-induced oxidation on Si$_3$N$_4$ imply that the AFM oxidation of Si$_3$N$_4$ has an significantly different kinetics from that of common thermal oxidation mechanisms.

Auger electron spectroscopy was also utilized to investigate the chemical composition of the AFM-induced oxide. The Auger spectra taken from the as-grown and AFM-

![FIG. 1. (a) AFM image of silicon nitride film which shows oxidized lines written on the densified sample $A$ (4.2 nm thickness) with 0.4 mN contact force and 0.1 µm/s scan speed at various sample biases ranging from +4 to +10 V. (b) AFM image of the same area after HF dipping. (c) Cross-sectional profiles of images (a) and (b) showing the heights and depths of the protruded and buried oxides.](image)

![FIG. 2. Micro-Auger spectra of sample B (2.5 nm thickness) silicon nitride film at the as-grown area and the AFM-oxidized area. The peak of N-KLL at ~385 eV on the as-grown area completely disappears on the AFM-oxidized area. And, the magnitude of O-KLL at ~512 eV is much enhanced on the oxidized area as compared to that of the as-grown area.](image)
induced oxidized area of sample B 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 on the as-grown area completely disappears on the AFM-oxidized area. Meanwhile, the magnitude of O-KLL is much enhanced on the oxidized area as compared to that of the as-grown area. It is evident that the nitrogen content was thoroughly replaced by the oxygen atoms in the ultrathin film case. The results of Auger electron spectroscopy support the previous suggestion that the nitride films can be turned into oxides by AFM-induced oxidation.  

The high growth rate of AFM-induced oxide on Si$_3$N$_4$ is very useful for the mask applications. Figure 3(a) shows a 10x10 oxide dot array on the densified sample A, which was made by applying voltage pulses of +9 V and 5 ms duration to the sample with respect to the tip. The oxide dot formation is very reproducible and is uniform with an average diameter of ~70 nm and a height of ~2 nm. Subsequently, the sample was etched with a HF solution at room temperature and with a 20 wt% KOH solution at ~50 °C for 15 s [Fig. 3(b)]. After pattern transfer, each oxide dot converts to a square pit (~50×50×70×70 nm$^3$). For the anisotropic etching of (001)-oriented silicon using KOH solution, inverted pyramidal pit (independent of the dot mask shape) is formed with four intersecting [111] crystal planes. The AFM-measured etch depth as shown in Fig. 3(c) is around 20–35 nm. This value is in good agreement with the ideal value determined by the terminal etch geometry (35–50 nm), considering a finite probe size. At present, we have also succeeded in fabricating structures with depths on the order of a few hundred nm using AFM-modified nitride masks of 2–3 nm thick.

In summary, we have demonstrated that AFM-induced local oxidation is a very effective way for converting Si$_3$N$_4$ to SiO$_x$ with low threshold voltages and extremely fast oxidation rates. Pattern transfer using AFM-induced Si$_3$N$_4$/SiO$_x$ etch mask is now feasible. This is a potentially useful nanolithographic approach because the part of mask functions as etch stop is well structured Si$_3$N$_4$ instead of AFM-induced SiO$_x$. Also, it is compatible with the conventional microelectronic processing. The etched structures can be useful for fabricating microstructures, as templates for selective growth of nanostructures, or as high-density read-only memory.

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