

Selective plasma nitridation and contrast reversed etching of silicon

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A new method of selectively patterning a silicon substrate with silicon dioxide and silicon nitride is demonstrated. An oxide patterned silicon substrate is directly nitrided using a microwave generated nitrogen plasma. Upon subsequent selective wet chemical etching using KOH, the oxide is removed and etching proceeds into the silicon, revealing a contrast reversed pattern of the oxide. The etch resistance of the nitrided surface is maximized by increasing the microwave power, pressure, and nitridation duration. The etch rate of silicon dioxide is negligibly affected and its etch rate is nearly the same as before nitridation. Compositional analysis of the nitride and the nitrided oxide using x-ray photoelectron spectroscopy confirms that microwave plasma nitridation produces Si–N covalent bonds. © 2001 American Vacuum Society. [DOI: 10.1116/1.1395616]

I. INTRODUCTION

Patterning without the use of spun-on organic photoresists has several advantages for device fabrication.¹ Examples of such techniques include resistless photopatterning of native oxides on GaAs,¹ and oxidation of Si by surface profiling microscope (SPM) based proximal probe lithography² and by electron-beam direct writing in the presence of small amounts of water vapor.³ These patterns can then be used as natural resists for subsequent etching operations. High resolution, sub-30 nm structures have been produced by dry plasma etching.⁴ In our first studies of structures written using an atomic force microscope (AFM), we were unable to bring out the vertical $\langle 111 \rangle$ plane on (110) Si by anisotropic wet chemical etching, perhaps due to the Gaussian-shaped AFM written oxide.⁵ We expect that some selective treatments that either thicken and reinforce the SiO₂ or which selectively coat the exposed Si with an alternate resist could provide improved etch resistance and potentially steeper sidewalls. The approach evaluated in this article is the latter, in which a microwave-generated plasma of N₂ is used to selectively nitride the exposed silicon. We report on the wet etching of this material system both for photolithographically and for proximally probe patterned SiO₂ on Si.

The ability of the method to form reverse contrast patterns is shown in Figs. 1(a) and 1(b). A thermally grown oxide on (100) silicon (*p*-type) is photolithographically patterned and aligned to the (110) wafer flat to produce the SiO₂ line in Fig. 1(a). The sample is exposed to a nitrogen plasma in an ASTeX 5010 reactor chamber with an ASTeX 2115 1500 W microwave source. With a 30 Torr nitrogen pressure and a 900 W microwave power, the sample is treated for 6 h. The sample is then etched in a 30% (by weight) solution of KOH at 70 °C for 4 min with moderate stirring. The resulting pattern in Fig. 1(b) is a contrast-reversed trench of the line in

Fig. 1(a). The slanted sidewall is identified with the slow etching (111) plane of silicon. Figure 1(c) shows SiO₂ on (100) silicon that was direct written using an electrically biased AFM tip together with condensation from the air to anodically oxidize² the sample. This sample is nitrided in 30 Torr nitrogen at 550 W microwave power for 3 h. Wet chemical etching of this sample in 30% (by weight) KOH produces the 30 nm deep groove shown in Fig. 1(d). The bottom of the trench is 270 nm or about the width of the original oxide line in Fig. 1(c). The width across the top of the trench is 780 nm and this very shallow sidewall angle appears to be due to erosion or undercutting of the nitride close to the trench opening. The lower quality line definition of the AFM line possibly is due to the very thin oxide produced by AFM writing, the extended tails of the AFM written oxide line, and the penetration of nitrogen through such thin oxides. If the processing is such that either much less nitride or much more nitride is formed, then the trench may not appear at all during the etch. Some insight into this result can be gained from the materials analyses that follow in the succeeding sections.

The new patterning method can be compared with other nitridation methods. The most widely used form of nitridation in device fabrication is blanketing of a substrate with chemical vapor deposition grown Si₃N₄. This is the first step in the localized oxidation of silicon process.⁶ The nitride is then patterned, etched, and locally oxidized. The new method reverses the order of nitridation and oxidation using pure nitrogen plasma as the nitridation agent. Note that a pure N₂ plasma has been used to convert thin layers of deposited Si to nitride for the purpose of forming a passivation layer on GaAs devices.⁷ Another approach to developing the desired material system is the AFM proximal probe based conversion of nanometer thickness SiN films to SiO_x.⁸

II. EXPERIMENT

To gain greater insight into the formation of the patterns we plasma processed bare silicon and SiO₂ coated silicon

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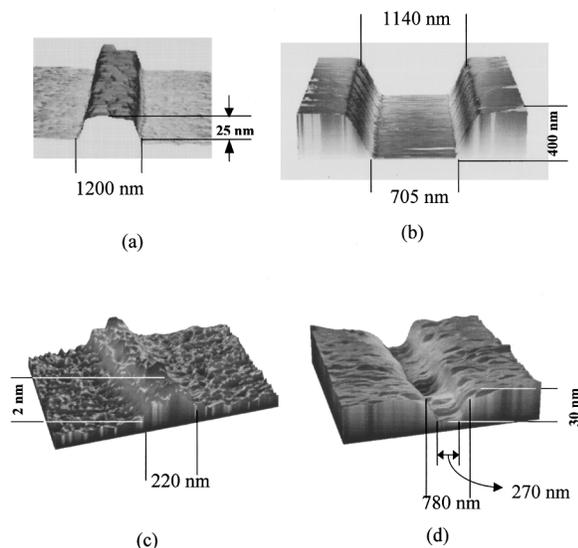


FIG. 1. Etch patterns after selective nitridation and etch in KOH. (a) Image of a photolithographically patterned oxide line on silicon, and (b) pattern reversal of the oxide line in (a) after nitridation and etching. (c) An AFM written oxide line on silicon and (d) a 30 nm deep trench after nitridation and etching of (c). All topography images were profiled by AFM.

substrates under various nitridation conditions. The nitridation is performed in the same ASTeX reactor that was used as part of the patterning demonstration above. Before nitridation, the *p*-doped (100) Si blank surfaces are cleaned using a 48% HF solution followed by ultrasonic cleaning in 2% HF in order to remove contaminants and any native oxide. Nitridation is performed at pressures of 30, 50, and 100 Torr, with microwave powers of 550, 650, 900, and 1100 W for 1 and 3 h. Nitrogen flow rate into the reactor is 100 sccm. Small amounts of hydrogen (1.2% of N₂ flow rate) are introduced for nitridation at microwave power values of 900 and 1100 W to stabilize the plasma and increase the nitridation temperature. Some substrates are thermally oxidized to film thicknesses of between 25 and 200 nm of SiO₂ and these are also treated with the nitrogen plasma at settings identical to those for the silicon.

The etch rates of the blank silicon, silicon dioxide, nitrided silicon, and nitrided silicon oxide are compared. Etching is performed by partially dipping a substrate in a 30% (by weight) KOH solution at ~70 °C for specific durations. An optical interferometric profiler (WYKO NT 2000), which has a minimum depth resolution of 3 Å is used to measure the resulting step heights.

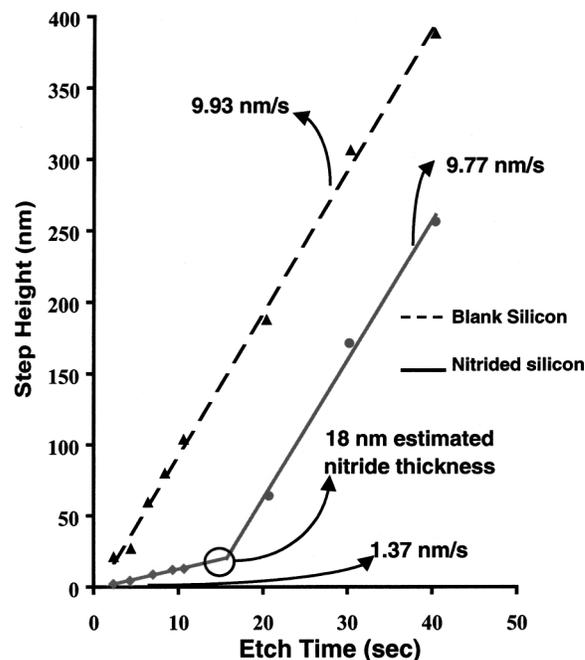


FIG. 2. Variation of etched step height with etch duration for bare silicon and nitrided silicon at 550 W microwave power, 30 Torr pressure for 1 h.

X-ray photoelectron spectroscopy (XPS) is used to determine the composition of the nitrides. The XPS analysis done in this work is angle-resolved in the sense that the angle of emission of the analyzed electrons is well defined; i.e., it is normal to the surface $\pm 6^\circ$. The x-ray source has an Al anode and it does not have a monochromator. The depth profiles are obtained by Ar⁺ ion etching the surface and analyzing after each etch.

III. VARIATIONS IN PROCESSING CONDITIONS

The etch rates for silicon and nitrided silicon (for the least harsh conditions: 30 Torr, 550 W, 1 h) are compared in Fig. 2. For time scales on the order of less than 10 s, there is no definitive etch interface observed. For this time scale the difference between the surface roughness of the etched and unetched regions is taken as the step height. The etch rate is determined by fitting a straight line to the etch step height vs etch duration data. It is found that the silicon etches at a rate about ten times faster than the nitrided silicon. As etching continues the nitride layer is depleted. After a certain breakthrough time, the rate approaches that of blank silicon. For four nitridation process conditions, the nitride layer is thin

TABLE I. Nitride breakthrough depths for various nitridation conditions.

Microwave power (W)	Pressure (Torr)	Nitridation time (h)	Etch rate (nm/s)	Breakthrough depth (nm)
550	30	1	1.37	19
550	50	1	1.35	32
900	30	1	1.006	22.5
900	50	1	0.975	34.5

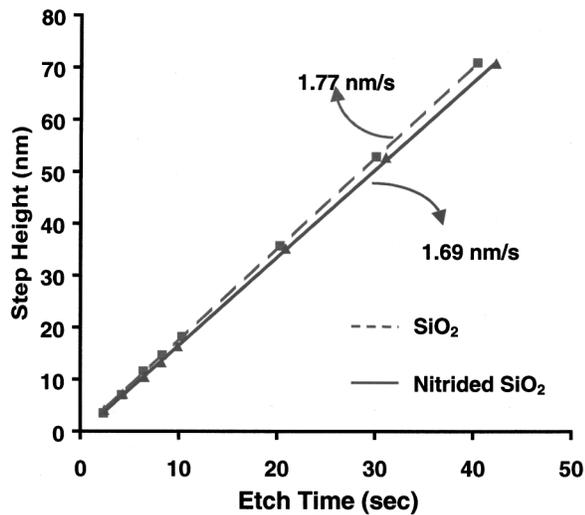


FIG. 3. Variation of etched step height with etch duration for silicon dioxide and nitrided silicon dioxide at 550 W microwave power, 30 Torr pressure for 1 h.

enough and the etching times long enough to estimate a breakthrough depth as in Fig. 2. These depths are reported in Table I. Figure 3 shows that the etch rate of the SiO_2 processed under the same conditions as the nitrided silicon in Fig. 2 etches at nearly the same rate both before and after nitridation. The oxide etches only about $1.3\times$ faster than the nitrided silicon. However, as shown in Fig. 4, by increasing power, pressure, and processing time, the etch rate decreases which increases selectivity between equally thick nitrided silicon and oxide to $\sim 3.5\times$. The breakthrough depth is increased by a factor of at least $\sim 2\times$ (as indicated by Table I) and probably more, which further increases selectivity.

A composition analysis of the surface of the nitrided (100) silicon using XPS indicates a peak at ~ 398.5 eV as would be expected for the 1s level of Si-N covalent binding (as shown in the inset of Fig. 5.⁹) The largest peak is that obtained from the as-prepared surface (prior to sputtering) and is at a higher intensity than that of the nitride peaks from beneath the original surface. XPS measurements of composition with depth for (100) Si that is nitrided at 30 Torr, 550 W for 3 h

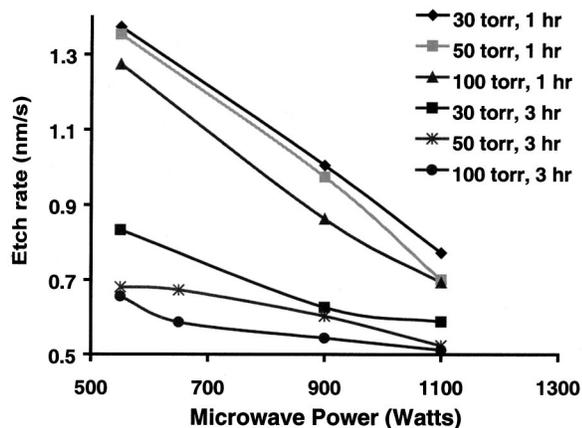


FIG. 4. Etch rates of nitrided silicon for various nitridation conditions.

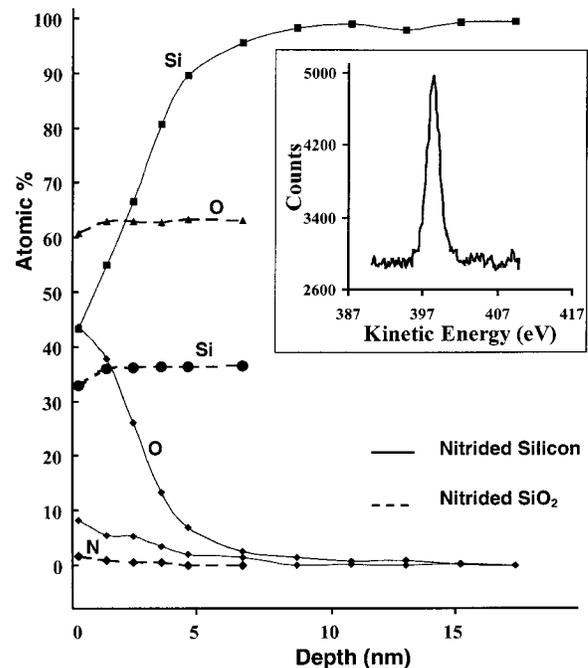


FIG. 5. Nitrogen incorporation into (100) silicon and SiO_2 after nitridation in a 30 Torr nitrogen plasma at 550 W microwave power for 3 h as measured by XPS depth profiles. Percentages total to 100% with the addition of residual carbon, which is not plotted. Inset: XPS spectrum at the surface prior to profiling. The peak binding energy of 398.5 eV indicates that the nitrogen is covalently bonded to silicon.

are shown in Fig. 5. Nitrogen concentration at the surface is 8 at.%, which drops to 0 at. % at 15 nm. Also SiO_2 processed in an identical nitrogen plasma as the silicon absorbs much less nitrogen, and the nitrogen penetration is much less than for the silicon, as shown by the XPS depth profiles in Fig. 5. The small amount of nitrogen incorporated by the SiO_2 corresponds with the small degree of change in the oxide etch rate after nitridation (see Fig. 3).

We also nitrided (110) silicon under the same nitridation conditions. In this case the XPS analysis shows that the surface nitrogen concentration for nitrided (110) silicon is approximately 20 at.% as compared to 8 at.% for nitrided (100) silicon and nitrogen incorporation into (110) silicon is found to a depth of ~ 5 nm compared to ~ 15 nm in the (100) silicon surface.

IV. VERTICAL ETCHING OF NITRIDED SILICON

A final demonstration of the pattern reversal process is shown in Fig. 6 where an oxide pattern of lines [Fig. 6(a)] is transferred into a pattern of grooves [Fig. 6(b)] after plasma nitridation and etching. The initial oxide lines are photolithographically patterned. Their width as measured with an AFM was found to be 28 nm high and 500 nm wide at the base (closest to the silicon surface). The linewidths, as determined by etching the oxide pattern in 30% KOH for 3 min at 50 °C, is ~ 450 nm across the top of the line, as measured from the SEM image in Fig. 6(a). An identically patterned oxide pattern is nitrided in the plasma reactor for 3 h at 800 W, 50 Torr nitrogen, a 100 sccm nitrogen flow rate, and with 0.75%

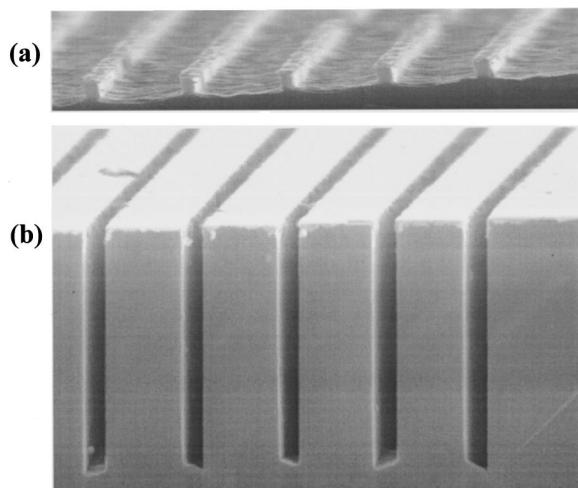


FIG. 6. Pattern reversal of oxide lines into grooves in (110) nitrided silicon. (a) Initial oxide pattern brought out after 3 min of etching in KOH. The lines are $\sim 1 \mu\text{m}$ tall, 450 nm wide on average, and with a $2.1 \mu\text{m}$ pitch. (b) Pattern resulting from nitridation of an identical oxide line pattern followed by 11 min of KOH etch. An additional 3 min of TMAH etch was used to smooth prominent striations found on the sidewalls. The grooves are ~ 500 nm, $5 \mu\text{m}$ deep, and with a pitch of $2.1 \mu\text{m}$. The SEM picture in (a) has been digitally compressed in the vertical direction to bring its perspective into coincidence with (b).

hydrogen. The nitrided sample is then etched for 11 min in 30% KOH at 50°C . The oxide breaks through in the first 5 min. A subsequent etch is performed in a solution of 83 parts TMAH (45% by weight) to 17 parts isopropyl alcohol (by weight) which serves to smooth out roughness and striations resulting from the aggressive KOH etch. The resulting contrast reversed pattern contains grooves that are 500 nm wide and $5 \mu\text{m}$ deep [Fig. 6(b)].

The maximum etch depth is limited by the time it takes the KOH to break through the nitrided surface. A sample prepared identically to the one in Fig. 6(b) was etched until this breakthrough was apparent. Using the Wyko profiler we measured trench depth, ridge width, and surface roughness of 10–20 μm features as a function of etch time. After 45 min of etch the surface roughness increases rapidly from 20 to 30 nm (R_A , average absolute deviation from average height) to as much as 180 nm (at 65 min). The roughness was observed to decrease to as low as 60 nm after 90 min (when the etching was stopped.) Apparently the maximum roughness is caused by the presence of nitride islands that continue to resist the etch. Also after 45 min the narrowing of the ridges becomes apparent and the width reduces at 150–200 nm/min. At 45 min the trench depths reached 12 to 13 μm . The maximum depth produced was between 14 and 16 μm found at 70–75 min of etch. Additionally we also found for several samples prepared at 550–575 W, 30–50 Torr for 4–6 h that nitride breakthrough (judged on notice-

ably increased surface roughness) occurs at between 40 and 70 min of KOH etch. It appears that the etch depth could be increased further by increasing the power, pressure, and duration of the plasma nitridation process. Alternatively other chemistries, particularly reactive ion etch, might have increased selectivity, while permitting etching in arbitrary directions, independent of the orientation of the crystalline planes of silicon.

V. SUMMARY

A method of using a nitrogen plasma to selectively increase the etch resistance of (100) and (110) silicon over both SiO_2 and untreated silicon and has been presented. After etching, the SiO_2 pattern is converted into a negative relief pattern of the original pattern in silicon. This appears to work reliably for photolithographically patterned SiO_2 of thicknesses between 7 and 30 nm. However, it is difficult to use on AFM written lines because the oxide is both thin and low in aspect ratio, making it an imperfect barrier to nitrogen penetration (see Fig. 5) and making it difficult to predict the trench width that would result for a given oxide line. One possible approach to evaluating this is to use Wei and Eres' electron-beam lithography method to directly oxidize the silicon.³ These oxides can be much thicker and of higher aspect ratio than that of AFM written lines. For the photolithographically patterned silicon we also noted that the selective nitridation method works over a wider range of processing conditions for (100) silicon than it does for (110) silicon. This may be related to the reduced penetration depth of nitrogen into (110) silicon and the increased surface concentration of the nitrogen.

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