Improvement of nitrogen retained dose using ammonia as a precursor in nitrogen plasma immersion ion implantation of silicon

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(Received 8 December 2004; accepted 31 May 2005; published 22 July 2005)

The low nitrogen retained dose due to competition from oxygen coimplantation diminishes the efficacy of nitrogen plasma immersion ion implantation in silicon. In this work, we aim at improving the nitrogen retained dose by using ammonia as a precursor. Ammonia is introduced into the nitrogen plasma during plasma immersion ion implantation of silicon to improve the nitrogen reactivity and reduce the competition from oxygen in the residual vacuum. Our x-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy results indicate that the ammonia precursor can indeed improve the N retained dose effectively, and the hydrophilic properties of the surface change with different ammonia to nitrogen ratios. © 2005 American Vacuum Society. [DOI: 10.1116/1.1991870]

I. INTRODUCTION

Silicon nitride is of scientific and technological interest because of its attractive physicochemical as well as mechanical properties. The material has found many applications in microelectronics, optoelectronics, solar cells, protective coatings against wear and corrosion, and so on.1–4 Silicon nitride has also shown potential in biomedical microelectromechanical systems (BioMEMS) for drug delivery as well as biosensors by serving as the thin “window” film, thin dielectric membrane, and/or insulating barrier layer.5–7 Plasma immersion ion implantation (PIII) is an effective method to synthesize silicon nitride films with high adhesion strength due to inherent ion mixing. As a non-line-of-sight technique, this process is also applicable to samples possessing a complex geometry such as mechanical sensing devices.8 We have recently investigated the use of nitrogen PIII to modify the surface wetting properties of silicon but observed low efficiency of nitrogen implantation due to competition from oxygen coimplantation. Oxygen contamination exists in the residual vacuum in most plasma implanters as these machines are typically not ultrahigh vacuum (UHV) compatible. Owing to the strong affinity of oxygen to silicon, even a trace amount of oxygen in the nitrogen plasma can drastically mitigate the efficacy of the N–PIII process. Consequently, significant oxygen incorporation results in reducing the nitrogen retained dose. In order to obtain better surface properties such as hydrophilicity, the nitrogen retained dose must be improved. We propose to introduce ammonia into the nitrogen plasma as a precursor. Ammonia, which contains hydrogen, ionizes more readily than nitrogen and the formation of hydrogen-containing nitrogen species promotes the reactivity thereby reducing the effects of oxygen. In this work, we study the influence of different ammonia to nitrogen flow ratios on the nitrogen retained dose as well as the surface wetting properties of silicon. Our water contact angle results indicate that the surface hydrophilic properties that determine many physiochemical properties vary with the different flow ratios.

II. EXPERIMENT

P-type (100) silicon wafers were processed in our PIII instrument.9,10 The base pressure in the vacuum chamber was $8 \times 10^{-6}$ Torr. After the samples were sputter cleaned for 10 minutes using a 500 W radio-frequency (rf) argon plasma, a mixture of ammonia and nitrogen (varied by different NH$_3$/N$_2$ flow ratios) was bled into the plasma chamber to a working pressure of about $5.5 \times 10^{-4}$ Torr and the plasma was ignited by 1000 W rf. Plasma implantation was conducted by applying a pulsed voltage of ~20 kV to the
samples. About $2.2 \times 10^6$ ion pulses of 30 $\mu$s pulse duration were implanted. For comparison, one sample was plasma-implanted with nitrogen without ammonia. The instrumental parameters are summarized in Table I.

Fourier-transform infrared spectroscopy (FTIR) was conducted using a Perkin-Elmer 1600 to determine the bonding states. The absorbance was measured between 500 and 1500 cm$^{-1}$.

X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5600 equipped with a monochromatic Al K$_\alpha$ x-ray source to determine the composition and chemical states in the near-surface region. The XPS spectra were acquired after removal of 10 nm of the surface using argon sputtering. Raman scattering was conducted on a Renishaw RM3000 micro-Raman system, equipped with a laser wavelength of 514 nm. The wavelengths were scanned from 1500 to 4000 cm$^{-1}$ to detect hydrogen incorporation and bonding states.

The hydrophilicity was determined by a contact angle test using the sessile drop method on a JY-82 contact angle goniometer. Doubly distilled water was used and, in each test, six measurements were conducted to obtain good statistics.

### III. RESULTS AND DISCUSSION

Figure 1 shows the FTIR absorbance spectra acquired from the plasma-implanted samples. A broad absorption band from 780 to 1000 cm$^{-1}$ can be observed in all the samples. The asymmetric band can be deconvoluted into a peak centered at approximately 820 cm$^{-1}$ corresponding to the asymmetric in-plane Si–N stretching vibration mode$^{11,12}$ and another one at around 900–1000 cm$^{-1}$ attributable to the Si–N–O bending mode$^{13,14}$ Complete deconvolution of the broadband is not easy and remains controversial due to the complexity of oxygen coordination with nitrogen and silicon. Nonetheless, increasing peak intensities can be seen in samples A1 to A3 compared to No. 0, which has undergone nitrogen only PIII. The results indicate higher N retained doses arising from ammonia incorporation. Sample No. 0 shows a clear, albeit weak, peak at around 1050 cm$^{-1}$ that can be assigned to the Si–O stretching mode.$^{13,14}$ This is proof of oxygen coimplantation into the silicon. In comparison, this peak is quite weak in samples A1, A2, and A3, indicating much less oxygen influence in the NH$_3$/N$_2$–PIII samples.

Figure 2 depicts the XPS spectra of the Si 2$p$, N 1$s$, and O 1$s$ photoelectron peaks acquired from the four samples. Table II lists the elemental compositions determined from the spectra. The nitrogen retained dose increases with the use of the ammonia precursor and that of oxygen changes in an opposite fashion. The oxygen content near the surface is reduced from about 26 at. % (sample No. 0) to about 8 at. % (sample A1) under the same total pressure conditions. At the same time, the nitrogen retained dose increases from about 29 to about 44 at. %. It should be noted that the difference in the retained doses among the three NH$_3$/N$_2$–PIII samples is not large. That is, A1, A2, and A3 do not exhibit significant differences in both the nitrogen and oxygen contents. This is believed to be due to strong etching of the Si surface by the nitrogen plasma under high voltage and this anomaly has, in fact, been observed in pure nitrogen implantation.$^{15}$

The binding energy spectra in Fig. 2 were calibrated using the Ar 2$p$ peak at 241.9 eV according to the handbook published by Physical Electronics (PHI).$^{16}$ For the Si 2$p$ photoelectron, an obvious energy shift can be seen in the implanted samples with and without ammonia as a precursor, confirming that the chemical configuration has changed. Sample No. 0 shows a broad peak that consists of at least two main components including one at 103 eV indicative of Si–O and another one at a lower energy attributable to Si–N–O or some Si–N species.$^{17}$ In comparison, the lower energy peaks at around 101.3 eV observed from samples A1, A2, and A3 indicate dominant Si–N bonding after introducing ammonia as the precursor. Again, only slight differences can be observed in the energy shifts as well as intensities.

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### Table I. PIII instrumental parameters.

<table>
<thead>
<tr>
<th>Sample Nos.</th>
<th>Voltage (kV)</th>
<th>Frequency (Hz)</th>
<th>Pulse width (µs)</th>
<th>rf power (W)</th>
<th>NH$_3$/N$_2$ (sccm)</th>
<th>Working pressure ($10^{-4}$ Torr)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>300</td>
<td>30</td>
<td>1000</td>
<td>0/30</td>
<td>5.6</td>
<td>120</td>
</tr>
<tr>
<td>A1</td>
<td>20</td>
<td>300</td>
<td>30</td>
<td>1000</td>
<td>5/25</td>
<td>5.6</td>
<td>120</td>
</tr>
<tr>
<td>A2</td>
<td>20</td>
<td>300</td>
<td>30</td>
<td>1000</td>
<td>10/20</td>
<td>5.6</td>
<td>120</td>
</tr>
<tr>
<td>A3</td>
<td>20</td>
<td>300</td>
<td>30</td>
<td>1000</td>
<td>16/16</td>
<td>5.6</td>
<td>120</td>
</tr>
</tbody>
</table>

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![FTIR absorbance spectra](image)  
**Fig. 1.** FTIR absorbance spectra of the samples.
among the three NH$_3$/N$_2$–PIII samples. The N 1$s$ photoelectron peak confirms that nitrogen in the silicon has different bonding states. Compared to samples A1–A3, sample No. 0 possesses a higher binding energy of approximately 397.6 eV, indicating that the retained N is predominantly in the Si–N–O configuration with less Si–N$^{17,18}$ The peaks around 397.2 eV observed from samples A1 to A3 can be attributed to Si–N. A similar trend can be observed for the O 1$s$ photoelectron peak, thereby corroborating the existence of significantly higher Si–O and Si–N–O after nitrogen only plasma implantation compared to NH$_3$/N$_2$–PIII.

The water contact angle, which is an indication of the surface hydrophilic property, depends largely on the chemical bonding states on the surface. It is of thermodynamic and kinetic importance from the perspective of adsorption and adhesion processes at the solid/liquid (or vapor) interface.$^{19}$ Figure 3 shows the water contact angles measured by the sessile drop from our samples. Sample No. 0 exhibits a water contact angle of 40.8°, and sample A1 is most hydrophilic at 31.8°, while samples A2 (43.7°) and A3 (47.5°) exhibit more hydrophobicity. We have shown experimentally that increased Si–N and Si–N–O may improve the hydrophilicity of nitrogen-implanted silicon due to the more polar contribution of the bonding states,$^{20}$ and that more Si–O bonds, particularly in oxygen implanted silicon, give rise to more hydrophobic properties. Therefore, the observation that A1 is more hydrophilic due to increased Si–N bonds, as compared to No. 0, which consists of a significant amount of Si–O, can be explained based on our previous studies. Our observation, that samples A2 and A3, which have been implanted with a higher ratio of ammonia, are more hydrophobic, may be accounted for by excessive hydrogen incorporation into silicon to form Si–H bonding, or N bonding with excessive hydrogen to form N–H on the surface. As shown in the Raman spectra (Fig. 4), samples A1, A2, and A3 all show Si–H bonding in the band 2000–2300 cm$^{-1}$, and N–H bonds at around 3230 and 3450 cm$^{-1}$. For samples A2 and A3, more H competes with oxygen or nitrogen, and so more Si–H bonds form reducing the chance of forming hydrophilic

![FIG. 2. Si 2$p$, N 1$s$, and O 1$s$ photoelectron spectra acquired from the four samples.](image)

**TABLE II. Compositions of the ammonia+nitrogen plasma-implanted silicon wafers as determined by XPS.**

<table>
<thead>
<tr>
<th>Sample Nos.</th>
<th>O (O 1$s$)</th>
<th>N (N 1$s$)</th>
<th>Si (Si 2$p$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>26.8</td>
<td>28.9</td>
<td>44.3</td>
</tr>
<tr>
<td>A1</td>
<td>8.6</td>
<td>43.3</td>
<td>48.1</td>
</tr>
<tr>
<td>A2</td>
<td>7.2</td>
<td>44.5</td>
<td>48.3</td>
</tr>
<tr>
<td>A3</td>
<td>7.7</td>
<td>43.7</td>
<td>48.6</td>
</tr>
</tbody>
</table>

![FIG. 3. Water contact angles of the samples measured by contact angle testing.](image)
Si–N–O or Si–N bonds. We do observe increased intensities of Si–H peaks in samples A2 and A3 as shown in Fig. 4. Some N–H bonds have also been observed to enhance hydrophobic hydration of organic materials.\textsuperscript{22} In the present work, our objective is to investigate the relationship between silicon-based materials.

The presence of hydrogen on the surface wetting properties of silicon and it may play an important role in the enhancement of surface biological properties of silicon.

Our results demonstrate that the surface wetting properties of silicon may be affected significantly by varying the ammonia to nitrogen ratios during nitrogen PIII. The findings are important for surface biological and biomedical properties of silicon-based materials.

Significant surface oxygen is always observed in N–PIII due partly to unavoidable surface oxidation and also to the non-UHV conditions in most PIII equipment. We have proposed a means to alleviate this problem by introducing a hydrogen-containing precursor, ammonia. Ammonia is more easily ionized than nitrogen and hydrogen-containing nitrogen species are more chemically active. The enhanced activity reduces the relative competition from oxygen thereby giving rise to more abundant Si–N bonds as observed in this study. Our investigation also reveals a means to change the surface wetting properties such as hydrophlicity using different NH\textsubscript{3} to N\textsubscript{2} ratios. The phenomenon appears to be due to the relative amounts of Si–N–O, Si–N, Si–H, and N–H bonds on the silicon surface.

**ACKNOWLEDGMENTS**

This work was financially supported by Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grant (CERG) Nos. CityU 1137/03E and CityU 1120/04E, City University of Hong Kong Strategic Research Grant (SRG) No. 7001642, as well as NSFC No. 30370407 of China.


\( ^{7} \) Y. Kuo, Vacuum 51, 741 (1998).


\( ^{11} \) D. R. Ciarnio, Biomol. Microdevices 4, 63 (2002).


**IV. CONCLUSION**

To increase the nitrogen retained dose in silicon during nitrogen plasma immersion ion implantation, ammonia is used as a precursor in the plasma. Our results show that the nitrogen retained dose can be effectively increased as compared to nitrogen only PIII under the same working pressure and implantation conditions. The process also offers a means to change the surface wetting properties such as hydrophilicity using different NH\textsubscript{3} to N\textsubscript{2} ratios. The phenomenon appears to be due to the relative amounts of Si–N–O, Si–N, Si–H, and N–H bonds on the silicon surface.