Etching of Si₃N₄ by SF₆/H₂ and SF₆/D₂ plasmas

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Abstract. Selective plasma etching of silicon nitride (Si₃N₄) over silicon oxide (SiO₂) is one of critical steps in the nanofabrication processes, where a direct plasma etching of Si₃N₄ is required for some applications. It was reported recently that Si₃N₄ etching by remote plasma source can be initiated by the vibrationally excited HF(v) molecules at the low concentration of atomic fluorine. Generally, the main source of HF(v) in plasma is reaction of atomic fluorine with H₂ molecule. Due to this fact, the kinetic isotope effect should be observed during Si₃N₄ etching if replace the H₂ source gas on deuterium gas (D₂). The data presented here are the Si₃N₄ and SiO₂ etching by the SF₆/H₂ and SF₆/D₂ plasmas. A different amount of H₂ and D₂ have been added to the SF₆ discharge during the Si₃N₄ and SiO₂ etching. It was shown that at low H₂/D₂ flow rate the Si₃N₄ etch rate is lower in the SF₆/D₂ discharge. This one confirms the hypothesis about Si₃N₄ etching by HF(v) and indicates on the fact that HF(v) gives contribution to Si₃N₄ etching by the direct plasma (not only by the remote plasma) at relatively high concentration of atomic fluorine.

1. Introduction

Plasma etching is widely used in semiconductor industry where the selective Si₃N₄/SiO₂ etching is one of the critical steps. The precision isotropic Si₃N₄ etching is required during the production of 3D-NAND memory devices [1], where the remote plasma source is used for such kind of processes [2,3,4,5]. On the other hand, the anisotropic etching of Si₃N₄ spacer is used during the production of FRAM memory where the selectivity relative to SiO₂ is also required [6]. It was reported that in the afterglow the Si₃N₄ etching can be initiated by vibrationally excited HF(v) molecules at low concentration of atomic fluorine, while not etching of SiO₂ [4,5]. Therefore, it is important to understand the contribution of HF(v) to the Si₃N₄ etching in a plasma zone. The etching by the vibrationally excited molecules should be suppressed or decreased if replace HF(v) on deuterium fluoride DF(v). Indeed, the vibrational quantum of HF is 0.31 eV which is lower than vibrational quantum of HF (0.49 eV). This difference should be essential for chemical reactions which proceed according to Arrhenius law. HF molecule at the ground state needs to overcome a significant barrier to etch both Si₃N₄ and SiO₂. For example, the SiO₂ can be etched by the dry HF gas only at T > 1000 K [7]. The vibrational energy of HF(v) molecule can be utilized for overcoming the barrier in the reactions with Si₃N₄ surface resulting in etching [4,5]. Thus, this catalytic effect coming from internal energy of HF(v) molecule should be lower in the case of DF(v) molecule.
2. Experiment details

Here we use SF<sub>6</sub>/H<sub>2</sub> and SF<sub>6</sub>/D<sub>2</sub> plasmas for the Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> etching in the plasma zone, where the HF(v) and DF(v) molecules are produced according to the following reactions:

\[ \text{SF}_6 + e \rightarrow \text{SF}_{6-x} + x\text{F}, \quad (1) \]

\[ \text{F} + \text{H}_2 \text{ (or D}_2) \rightarrow \text{H} \text{ (or D)} + \text{HF(v) (or DF(v))}. \quad (2) \]

It has been shown that initially the Si<sub>3</sub>N<sub>4</sub> etching increases at small addition of H<sub>2</sub> to the SF<sub>6</sub> discharge, while the Si<sub>3</sub>N<sub>4</sub> etching monotonically decreases in the SF<sub>6</sub>/D<sub>2</sub> discharge at the similar conditions. The density of atomic fluorine measured by actinometry decreases at H<sub>2</sub>/D<sub>2</sub> flow rate rise, therefore it cannot explain the different Si<sub>3</sub>N<sub>4</sub> etch rate in SF<sub>6</sub>/H<sub>2</sub> and SF<sub>6</sub>/D<sub>2</sub> discharges. Also, in OES spectrum we observe the bands coming from S<sub>2</sub>dimer. It was reported that reaction probability of F- atoms with Si is unusually high in SF<sub>6</sub> discharge, and it was assumed that this effect occurs due to a surface activation by S, S<sub>2</sub>, SF<sub>x</sub> etc. \[8\]. Therefore, we consider here how S<sub>2</sub> production depends on the H<sub>2</sub>/D<sub>2</sub> flow rate assuming that S<sub>2</sub> can affect the Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub> etching also.

We used direct capacitively coupled plasma etcher operating at 40.68 MHz. Two parallel plate electrodes are positioned vertically inside the chamber. The etcher is equipped with spectrometer (AvaSpec-2048 from Avantes) for optical emission spectroscopy (OES) diagnostic in the wavelength range of 200-1100 nm. Spectrometer is collecting emission from plasma bulk at the center of the discharge near the sample film (figure 1). OES was calibrated using known H<sub>2</sub> spectrum. Ar (1 sccm) was added to the reaction mixture for actinometry measurements. H<sub>2</sub> and D<sub>2</sub> flow rates are varied between 0 and 10 sccm while other process conditions kept the same: 3 sccm SF<sub>6</sub>; power 300 W; pressure 60 mTorr.

![Figure 1. Scheme of experimental setup from two perspectives.](image)

3. Results and discussions

3.1. OES measurements

The typical spectrum of SF<sub>6</sub>/H<sub>2</sub>/Ar discharge observing in our experiments is shown in figure 2a. The emission corresponding to B<sup>1</sup> Σ<sub>u</sub>(v) → X<sup>3</sup> Σ<sub>u</sub>(v) transitions of S<sub>2</sub> dimer (figure 2b) was identified using the data from \[9\].

The size of etched samples (around 1 cm<sup>2</sup>) was significantly smaller than the size of electrodes, and by-products of the etching (O, OH, NH etc.) are not detected in the OES spectra, therefore we assume that volatile by-products has no influence on the OES spectra. Only emission from N<sub>2</sub> (see figure 2b) has been detected which is one of the by-products of Si<sub>3</sub>N<sub>4</sub> etching. But this emission is detected in the SF<sub>6</sub> discharge without etched samples, and the intensity of this emission was not changed when the
Si₃N₄ samples were etched in the chamber. Molecule nitrogen is the admixture of SF₆ gas, therefore the small amount of N₂ is injected into the etcher from the SF₆ balloon, the same was observed in the [10].

Actinometry was used to measure the density of F-atoms in the plasma zone (figure 3a). We used 685 nm (3p ⁴D⁰ → 3s ⁴P) line of F and 750 nm (4p'[1/2] → 4s'[1/2]o) line of Ar. Actinometry coefficient \( C_{Ar}^F = 4.6 \pm 0.9 \) corresponding to these lines has been measured in [11]. Fluorine density \( n_F \) was obtained using the following equation:

\[
    n_F = C_{Ar}^F \cdot \frac{I(F)}{I(Ar)} \cdot n_{Ar},
\]

where \( I(F) \) and \( I(Ar) \) are intensities of fluorine and argon lines and \( n_{Ar} \) is a density of argon species. In both H₂ and D₂ containing plasmas dilution causes the similar drop of fluorine concentration. It seems that D₂ doesn’t provide additional production or loss mechanism for F-atoms compared to H₂.

The S₂ density cannot be measured by actinometry because the excitation threshold energies for S₂ and Ar are quite different. Therefore, the intensity of the \( \text{B}^3 \Sigma_u^-(v0) \rightarrow \text{X}^3 \Sigma_u^-(v9) \) S₂ (283 nm) transition was normalized on the intensity of Ar (750 nm), assuming that this \( \frac{I_{S2}}{I_{Ar}} \) value correlates with the production rate of S₂. \( \frac{I_{S2}}{I_{Ar}} \) ratio similarly increases in both SF₆/H₂ and SF₆/D₂ discharges achieving a plateau at H₂/D₂ flow rate at 5 sccm (figure 3b).

![Figure 2](image-url)

**Figure 2.** Typical OES spectrum of SF₆/H₂/Ar discharge observed in our experiments (a). And S₂ spectrum (b) where \( \text{B}^3 \Sigma_u^-(v) \rightarrow \text{X}^3 \Sigma_u^-(v) \) transitions are shown (the first ‘v’ number corresponds to the excited state, the second is to ground state), the dotted lines mark the emission coming from N₂ admixture.
Figure 3. Dependence of fluorine density (a) and normalized $I_{52}/I_{Ar}$ intensity (b) on $H_2/D_2$ flow rate.

3.2. Etching data

The total thicknesses of the samples were 2000 Å and they are fully etched. The etch rate values are calculated as a thickness of film (2000 Å) divided by time of the etching. The time of etch stop was determined by optical interferometer.

The etch rate data are shown in figure 4, according to these data the etch rate of $Si_3N_4$ is higher than $SiO_2$ even in the $SF_6$ discharge without $H_2$ and $D_2$. The small addition of $H_2$ increases the $Si_3N_4$ etch rate which has a peak at 2 sccm $H_2$. On the other hand, there is no peak in $SF_6/D_2$ discharge, moreover $Si_3N_4$ etch rate monotonically decreases at $D_2$ flow rate rise. The difference in the $Si_3N_4$ etch rates by $SF_6/H_2$ and $SF_6/D_2$ plasmas cannot be explained by the production rates of F-atoms or $S_2$ dimers. Note, the F density monotonically drops at $H_2$ and $D_2$ flow rate rise therefore the $Si_3N_4$ etching cannot be increases by the F-atoms at 2 sccm $H_2$. The production of $S_2$ increases with the addition of 2 sccm $H_2$ or $D_2$ to the reaction mixture. If we assume that $S_2$ can enhance the $Si_3N_4$ etching then the etching must be enhanced in the both discharges with $H_2$ and $D_2$. Thus, the higher etch rate of $Si_3N_4$ in the $SF_6/H_2$ plasma can be explained by the fact that HF(v) gives the contribution to the etch rate. On the other hand, the $Si_3N_4$ etch rate monotonically drops in the $SF_6/D_2$ plasma as $D_2$ flow rate rise because F-atom density decreases and DF(v) molecules are not able to initiate the etching. The kinetic isotope effect is not as high as it can be expected, because F density is still quite high and they give the main contribution to the etch rate. Moreover, the etching occurs in the plasma zone, where the $Si_3N_4$ etching initiated by HF(v) molecules should be suppressed, because ions remove HF molecules from the surface. According to the proposed mechanism in [4,5] the HF(v) initiates $Si_3N_4$ etching in the afterglow zone paired with the adsorbed HF molecule.

The etch rate of $SiO_2$ weakly depends on $H_2$ and $D_2$ flow rate despite the fact that density of F atoms, which is well known etchant of $SiO_2$ [12], drops at $H_2/D_2$ flow rate rise (figure 3a). It can be explained by the passivation mechanism of $SiO_2$ surface, for example, by $S_2$ dimer. The production of $S_2$ increases and density of F atoms decreases at 10 $H_2/D_2$ (figure 3b) resulting in the lower etch rate.
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Figure 4. The dependence of Si$_3$N$_4$ and SiO$_2$ etch rate on H$_2$ and D$_2$ flow rate.

4. Conclusions
The direct plasma etching of Si$_3$N$_4$ and SiO$_2$ in the SF$_6$/H$_2$ and SF$_6$/D$_2$ discharges have been studied. It was shown that the Si$_3$N$_4$ etch rate is slightly lower in the SF$_6$/D$_2$ discharge than in the SF$_6$/H$_2$. Moreover, the Si$_3$N$_4$ etch rate monotonically decreases at the D$_2$ flow rate rise, at the same time the etch rate in the SF$_6$/H$_2$ discharge has a peak at 2 sccm H$_2$. It can be explained by the fact that in the discharge with H$_2$ the HF(v) gives the contribution to the Si$_3$N$_4$ etch rate as it was reported early. This contribution is not observed from the DF(v) molecule because vibrational quantum of DF(v) is lower than the one of HF(v). The experiments were performed in the plasma zone, where the Si$_3$N$_4$ etching initiated by HF(v) is suppressed due to ion bombardment. Therefore, the atomic fluorine gives the main contribution to the Si$_3$N$_4$ etch rate. These facts explain the relatively weak kinetic isotope effect on the Si$_3$N$_4$ etching. Anyway, this effect is visible and should be taken into account in the plasma direct etching of silicon nitride.

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