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Research Article

A Study of Parameters Related to the Etch Rate for a Dry Etch Process Using NF_3/O_2 and SF_6/O_2

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The characteristics of the dry etching of SiN_x:H thin films for display devices using SF_6/O_2 and NF_3/O_2 were investigated using a dual-frequency capacitively coupled plasma reactive ion etching (CCP-RIE) system. The investigation was carried out by varying the RF power ratio (13.56 MHz/2 MHz), pressure, and gas flow ratio. For the SiN_x:H film, the etch rates obtained using NF_3/O_2 were higher than those obtained using SF_6/O_2 under various process conditions. The relationships between the etch rates and the usual monitoring parameters—the optical emission spectroscopy (OES) intensity of atomic fluorine (685.1 nm and 702.89 nm) and the voltages V_H and V_L—were investigated. The OES intensity data indicated a correlation between the bulk plasma density and the atomic fluorine density. The etch rate was proportional to the product of the OES intensity of atomic fluorine ($I(\mathbf{F})$) and the square root of the voltages ($\sqrt{V_h + V_l}$) on the assumption that the velocity of the reactive fluorine was proportional to the square root of the voltages.

1. Introduction

In the fabrication of flat panel displays, SF_6 is used to etch various thin films. NF_3, on the other hand, is used for two reasons in particular. First, it is used to etch Si. Focus is put on films such as SiO_2 and Si_3N_4, which are used for semiconductor devices [1–7]. Second, NF_3 is used to clean the chamber in the plasma enhanced chemical vapor deposition (PECVD) process [8]. Previous studies have looked at the etching characteristics and mechanisms of films with NF_3. In these studies, a number of analysis tools, including a quadrupole mass spectrometer (QMS), ellipsometer, X-ray photoelectron spectrometer (XPS), and optical emission spectroscopy (OES), were used. With these studies in mind, this current paper postulates that NF_3 could be used as an alternative to SF_6 in the dry etching process for flat panel display manufacturing.

The replacement of SF_6 with NF_3 would offer certain advantages Manufacturers would be able to change the etching gas on demand and would still be able to use existing facilities. Moreover, because of increasing concerns regarding the greenhouse effect, many research groups have looked for gases that could be used to replace SF_6 to reduce the global warming potential (GWP). Low GWP gases such as F_2 [9, 10], C_4F_8 [11], CHF_3O_2 [12], C_3F_8 [7], and C_3F_6O [13] in the dry etch process have been studied. These investigations indicated that it would be possible to use low GWP gases to replace SF_6 in the etching processes. Of importance to this current study, it has also been shown that the use of NF_3 would decrease the GWP of the flat panel manufacturing process [14–17].

To evaluate the possibility of replacing SF_6 with NF_3, the SiN_x:H dry etching characteristics using SF_6 and NF_3 were compared. The similarities and dissimilarities between the processes using the two gases were studied. Because simple parameters such as the voltage of the input power and optical emission lines are commonly monitored in manufacturing equipment, the relationships between these parameters and the etch characteristics could be investigated in this work.

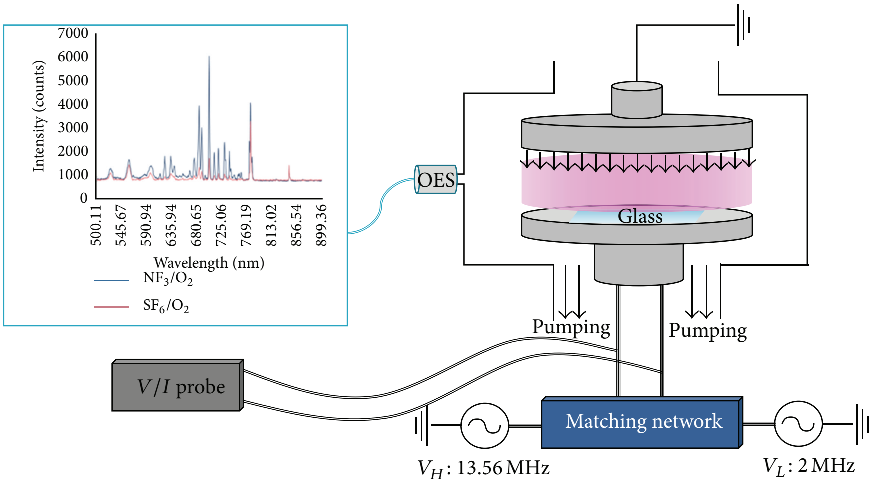
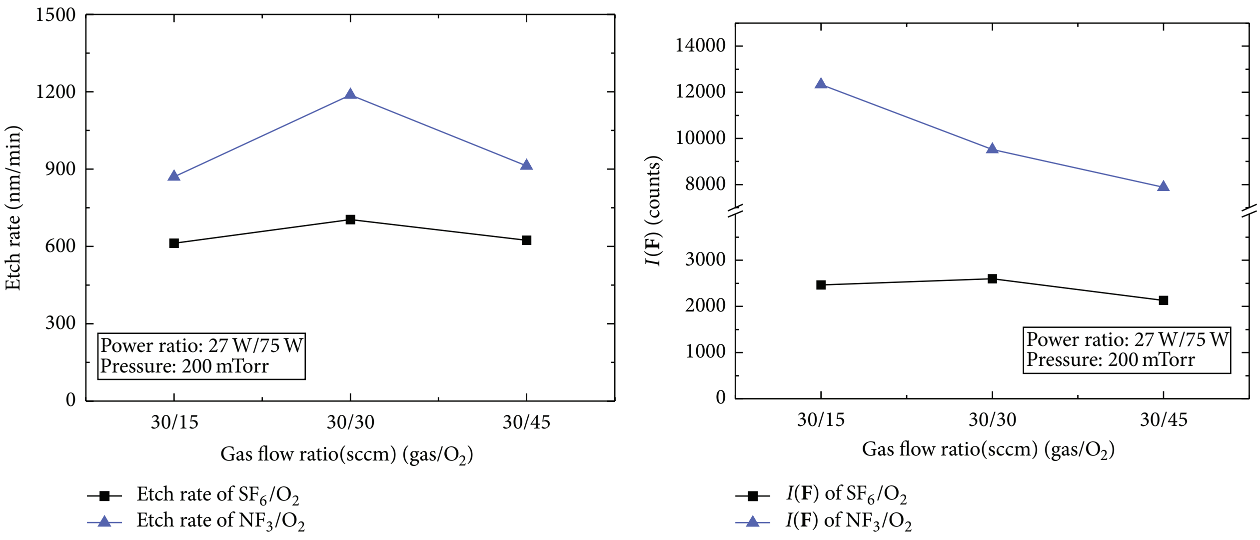


FIGURE 1: Diagram of the dual-frequency CCP-RIE with OES and *V-I* probe.



(a) (b)

FIGURE 2: (a) Etch rates of SF_6/O_2 and NF_3/O_2 and (b) optical emission intensity of fluorine for SF_6/O_2 and NF_3/O_2 as a function of gas flow ratio.

In this paper, Section 2 provides details regarding the experimental setup and process conditions. In Section 3, the results and a description of the experiment are presented. Section 4 covers the interpretation and analysis of the results.

2. Materials and Methods

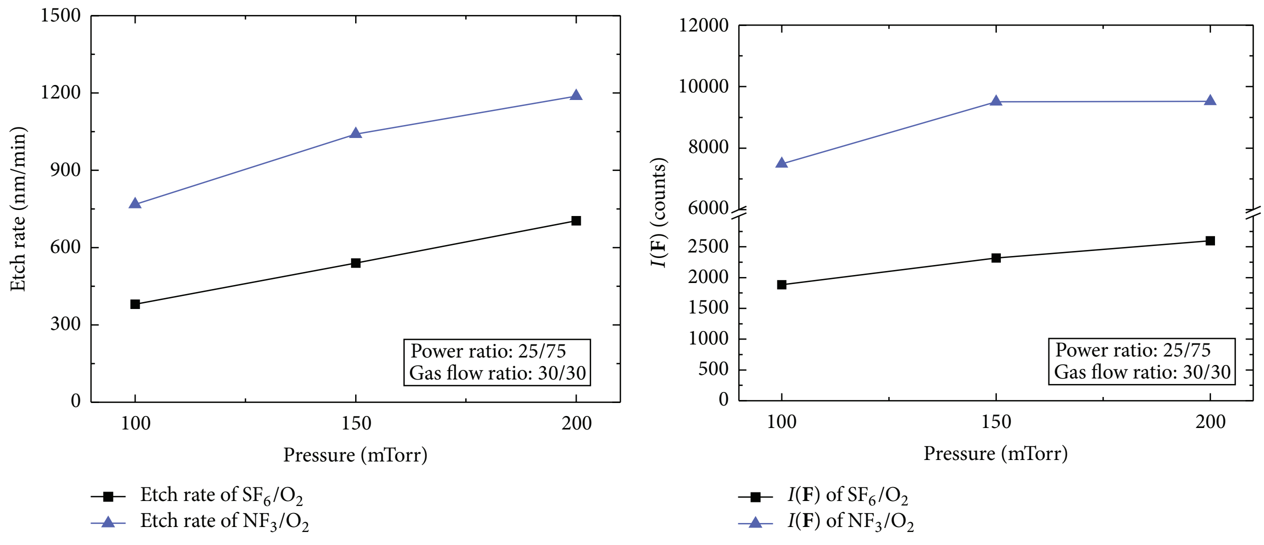
The SiN_x:H film samples were deposited on a glass substrate using PECVD and etched using a dual-frequency CCP-RIE system with SF_6/O_2 and NF_3/O_2 gas mixtures. The reference process conditions consisted of a gas flow ratio (gas/O_2) between the fluorine gas (SF_6 or NF_3) and O_2 of 30 sccm/30 sccm, a pressure of 200 mTorr, and a dual-frequency power ratio (13.56 MHz/2 MHz) of 25 W/75 W.

The gas flow ratio was varied by varying the O_2 flow rate from 15 sccm to 45 sccm. The pressure was varied from 100 mTorr to 200 mTorr at an interval of 50 mTorr, and the power ratio was changed between values of 25 W/75 W and 75 W/25 W, where the total power was fixed at 100 W.

The etch rate was measured with a general procedure as follows.

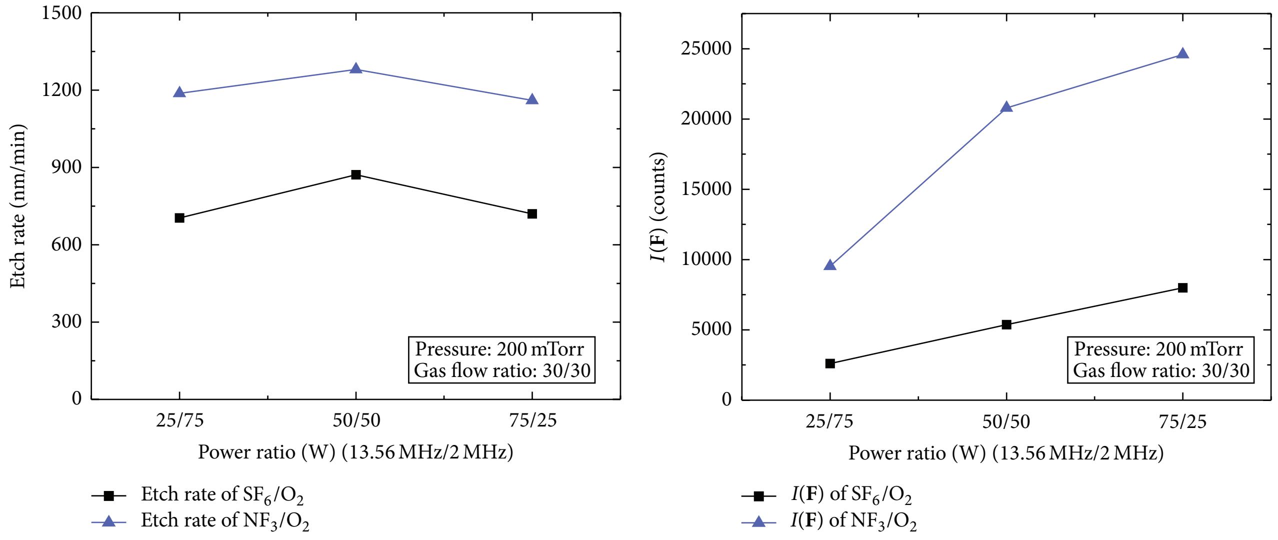
First, the photoresist was deposited on the SiN_x:H film using the photolithography process, after which the thickness of the deposited photoresist was measured using a surface profiler (α-step). Second, the thickness of the etched film and the oxidized photoresist was measured using the surface profiler after dry etching using a CCP-RIE. Third, the thickness of the etched film was measured using the surface profiler after stripping the oxidized photoresist.

A schematic diagram of the dual-frequency CCP-RIE system for the dry etching process is shown in Figure 1. The optical emissions from the plasma were collected through



(a) (b)

FIGURE 3: (a) Etch rates of SF_6/O_2 and NF_3/O_2 and (b) optical emission intensity of fluorine for SF_6/O_2 and NF_3/O_2 as a function of pressure.



(a) (b)

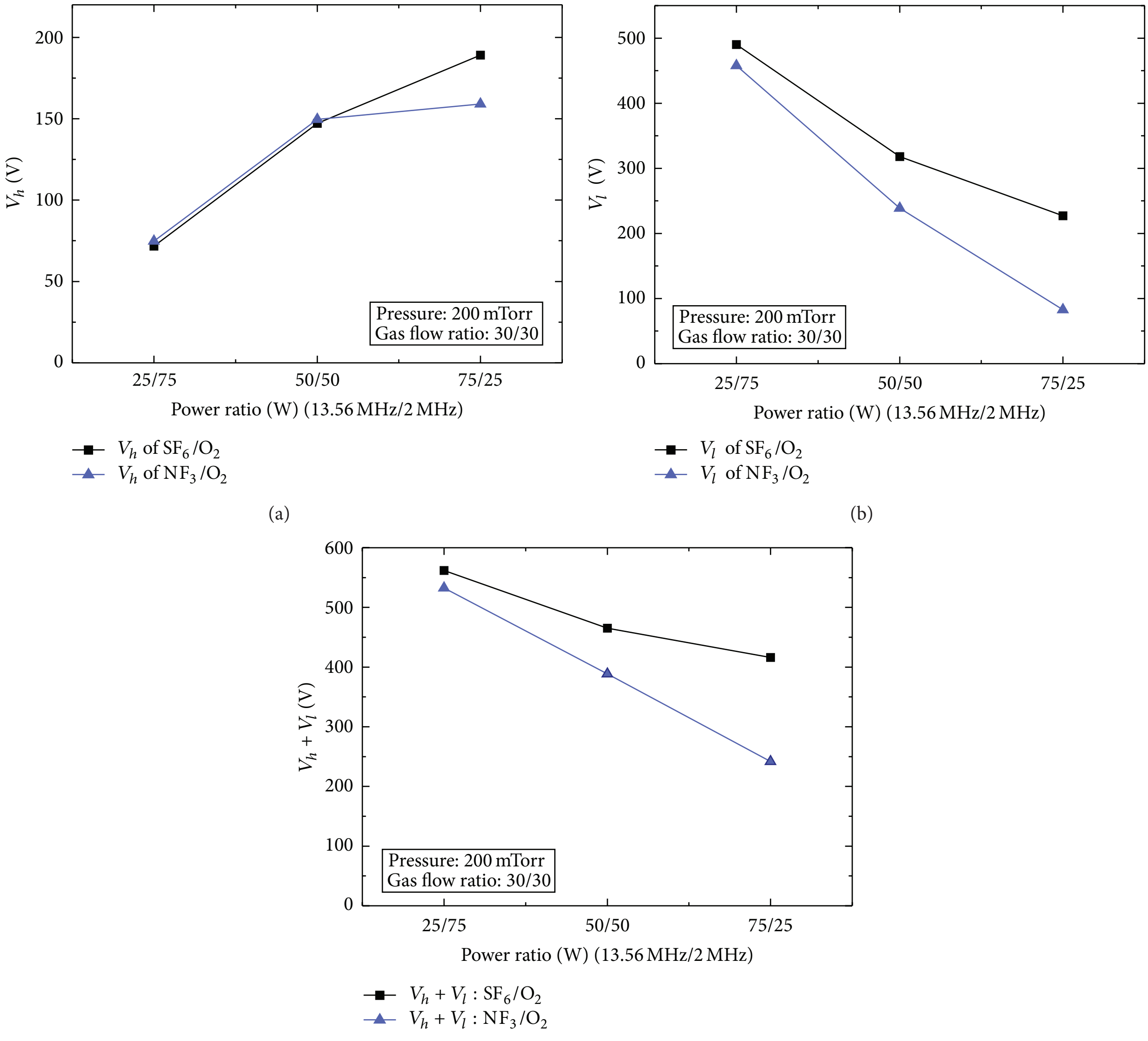
FIGURE 4: (a) Etch rates of SF_6/O_2 and NF_3/O_2 and (b) optical emission intensity of fluorine for SF_6/O_2 and NF_3/O_2 as a function of power ratio.

a view port on the chamber side wall. A *V-I* probe (*V-I* probe 4100 by MKS, ENI Products) measured the loads *V* and *I* for the RF plasma discharge. The optical emissions were analyzed with a spectrometer. The spectrometer (HR2000+ by Ocean Optics Inc.) with optical resolution of 0.035 nm and range of 200–1100 nm was used.

Typically, various radicals such as NF_2 and SF_5 participate in the dry etching processes. However, the optical emission intensity of atomic fluorine was measured to observe the common element between the SF_6 and NF_3 processes. The emission peaks of atomic fluorine at 658.6 nm and 703.7 nm were used [18–20] and the sum of them referred to the optical emission intensities of atomic fluorine ($I(\mathbf{F})$) in this experiment.

3. Results and Discussion

3.1. Results. The dry etching conditions and results are given in Table 1. Figure 2 shows the etching characteristics and optical emission intensities of atomic fluorine ($I(\mathbf{F})$) obtained using the two gases for different gas flow ratios (gas/O_2) at a fixed RF power ratio (13.56 MHz/2 MHz) of 25 W/75 W and 200 mTorr. A small increase in O_2 flow increased the etch rate, while further increases in the O_2 flow rate decreased the etch



(a)

(b)

(c)

FIGURE 5: (a) Voltage of high-frequency RF source V_h, (b) voltage of low-frequency RF source V_l, and (c) sum of V_h and V_l as a function of power ratio.

rate, as is usual [21]. In Figure 2(b), the behavior of $I(\mathbf{F})$ for SF_6/O_2 follows the etch rate behavior.

Figure 3 shows the etching characteristics and $I(\mathbf{F})$ for the two gases obtained using different pressures with a power ratio (13.56 MHz/2 MHz) of 25 W/75 W and a gas flow ratio of 30 sccm/30 sccm. The etch rate and $I(\mathbf{F})$ tended to increase as the pressure increased.

Figure 4 shows the results obtained when the power ratio of high and low RF frequencies was varied with a fixed total power of 100 W at 200 mTorr and a gas/O_2 flow ratio of 30 sccm/30 sccm. Although $I(\mathbf{F})$ increased as the power of the 13.56 MHz source increased, the etch rate did not directly depend on $I(\mathbf{F})$.

In Figure 5, the voltages obtained under the same conditions are shown. As was the case in Figure 4(a), the etch rate did not directly depend on the voltages.

3.2. Discussion. When SiN_x:H film is etched using fluorine-based gases such as SF_6 and NF_3, the film is eliminated in the form of SiF_x. In this mechanism, the gas-phase reactions that create the reactive species (F) are as follows [22, 23]:

"Reactions of SF_6"

$$\begin{gathered}
SF_6 + e \longrightarrow SF_5 + F + e \\
SF_6 + e \longrightarrow {SF_5}^+ + F + 2e \\
SF_6 + e \longrightarrow {SF_4}^+ + 2F + 2e \\
SF_6 + e \longrightarrow {SF_3}^+ + 3F + 2e
\end{gathered} \tag{1}$$

Table 1: (a) Experimental conditions and results for SF_6 (b) experimental conditions and results for NF_3.

(a)

Number	Power (W) 13.56 (MHz)	Power (W) 2 (MHz)	Pressure (mTorr)	Gas (sccm) SF_6	Gas (sccm) O_2	Etch rate (nm/min)	13.56 (MHz) Vpp (V)	2 (MHz) Vpp (V)
1	25	75	200	30	30	704	71.68	490.13
2	50	50	200	30	30	872	147.19	318.04
3	75	25	200	30	30	720	189.06	227.10
4	25	75	150	30	30	540	74.76	476.85
5	25	75	100	30	30	380	84.71	589.88
6	25	75	200	30	15	612	71.60	490.78
7	25	75	200	30	45	624	73.42	483.61

(b)

Number	Power (W) 13.56 (MHz)	Power (W) 2 (MHz)	Pressure (mTorr)	Gas (sccm) NF_3	Gas (sccm) O_2	Etch rate (nm/min)	13.56 (MHz) Vpp (V)	2 (MHz) Vpp (V)
1	25	75	200	30	30	1,188	74.85	105.86
2	50	50	200	30	30	1,280	149.65	211.64
3	75	25	200	30	30	1,160	159.00	224.86
4	25	75	150	30	30	1,040	77.96	110.26
5	25	75	100	30	30	768	77.24	109.24
6	25	75	200	30	15	870	75.63	106.96
7	25	75	200	30	45	912	75.99	107.48

"Reactions of NF_3"

$$\begin{gathered} NF_3 + e \longrightarrow NF_2 + F + e \\ NF_2 + e \longrightarrow NF + F + e \end{gathered} \tag{2}$$

Because the different reactions that create the reactive F cause differences in the etch rate and lead to different characteristics of the SF_6 and NF_3 processes, the optical emission intensity was observed as an alternative to a quantitative analysis of the reactive F.

In dual-frequency RF discharges, the following relationship between the density of the bulk plasma and the voltage of the RF sources exists [24]:

$$n_p \propto \frac{\omega^2 V_{\mathrm{rf}}}{\varepsilon_c}, \tag{3}$$

where n_p is the density of the bulk plasma and ε_c is the collisional energy loss per electron.

In the etching of Si containing films in fluorine-based plasma, the F-atom density is directly involved in the etching process [25]. Although the plasma density would not be directly proportional to the atomic fluorine density, there would be a strong relation between them. As shown in Figure 3, $I(\mathbf{F})$ increased as the pressure increased. It seems that the increase in pressure led to a higher bulk plasma density, and this higher density caused $I(\mathbf{F})$ to increase. To confirm this reasoning, the $I(\mathbf{F}) \propto \omega^2 V_{\mathrm{rf}}$ relationship was investigated in Figure 6. In this work, the value of $\omega_h^2 V_h$ was dominant, so that $\omega_h^2 V_h + \omega_l^2 V_l \approx \omega_h^2 V_h \gg \omega_l^2 V_l$. When the linear fitting model (least square fitting method) was applied to Figure 6, different slopes were obtained for SF_6/O_2 and NF_3/O_2. It is assumed that the different ε_c values and different reactions for the two gases led to the different slopes. In conclusion, $I(\mathbf{F})$ was proportional to $\omega_h^2 V_h + \omega_l^2 V_l$, and the density of atomic fluorine (n_{F}) could be described as directly dependent on $I(\mathbf{F})$. Figure 7(a) shows the proportional relation between the etch rate and $I(\mathbf{F})$. If we assume that the atomic fluorine density directly depends on $I(\mathbf{F})$, this shows that a relationship exists between the density

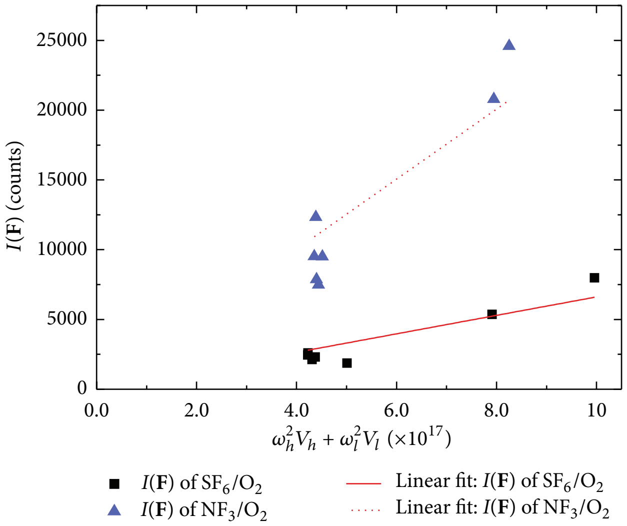
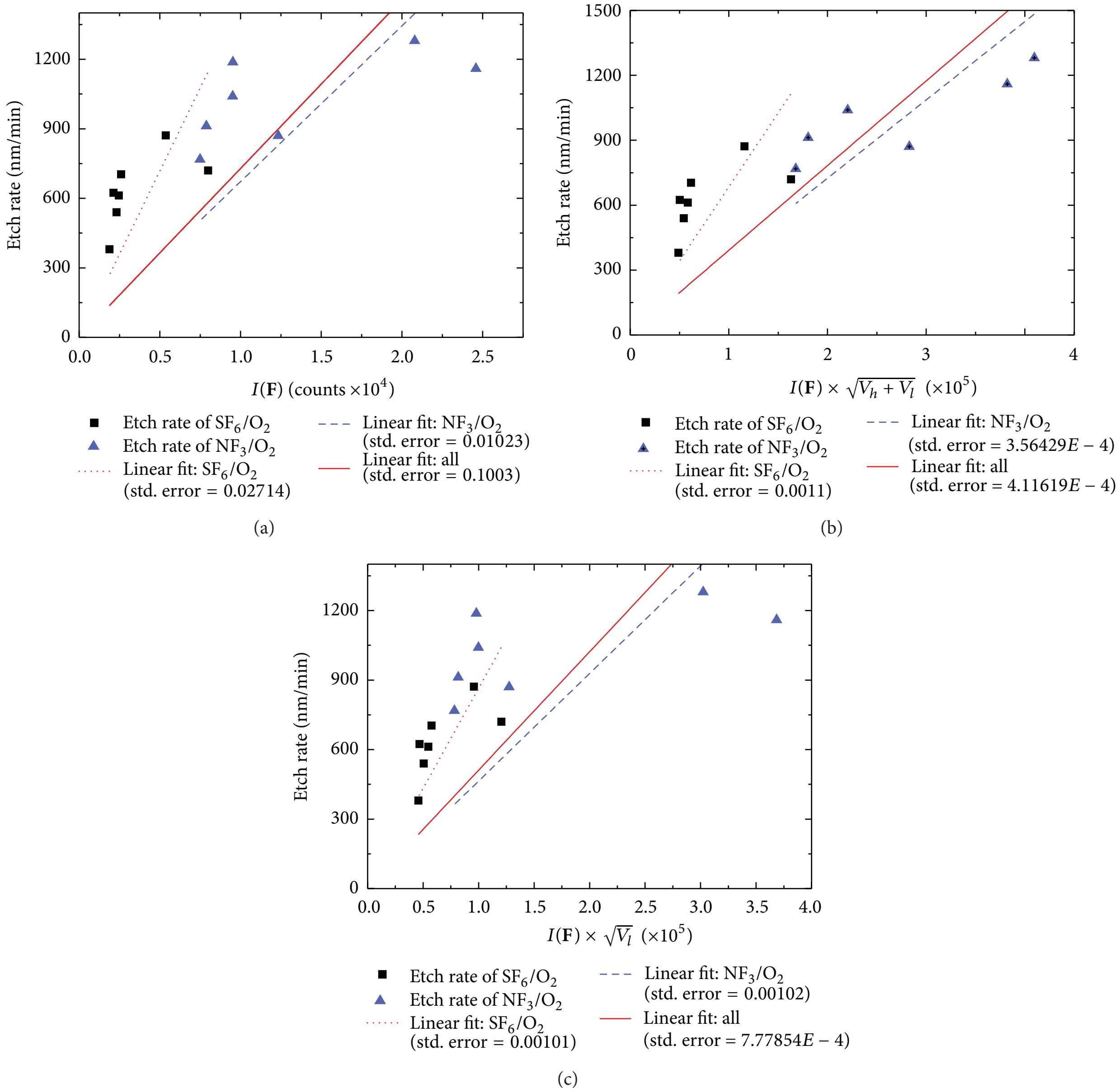


Figure 6: Distribution of optical emission intensity of fluorine versus $\omega_h^2 V_h + \omega_l^2 V_l$.



(a)

(b)

(c)

FIGURE 7: (a) Distribution of etch rate versus $I(\mathbf{F})$, (b) distribution of etch rate versus $I(\mathbf{F}) \times \sqrt{V_h + V_l}$, and (c) distribution of etch rate versus $I(\mathbf{F}) \times \sqrt{V_l}$.

of the atomic fluorine and the SiN_x:H etch rate. In fact, a number of recent studies have produced similar results to utilize a relation between the OES intensity and plasma density [26–28].

In Figures 4(a) and 5, the etch rate did not depend on the voltage (V_h, V_l or $V_h + V_l$) directly. In the bulk plasma, the velocity of the fluorine ion was proportional to $\sqrt{V_h + V_l}$. This increased the velocity of the reactant atom (v_F) via an ion-neutral momentum transfer collision or charge exchange. However, the etch rate was not dependent on v_F alone. Generally speaking, an etch rate is influenced by the flux of the reactant transported to the substrate. If n_F is related to $I(\mathbf{F})$ and v_F is proportional to $\sqrt{V_h + V_l}$, the etch rate will be proportional to $I(\mathbf{F}) \times \sqrt{V_h + V_l}$. Under the same linear fitting model, the relation of the etch rate to $I(\mathbf{F}) \times \sqrt{V_h + V_l}$ is shown in Figure 7(b). It was found that the standard fitting errors were reduced when the voltage was considered. This shows that the etch rate had a closer relationship with $I(\mathbf{F}) \times \sqrt{V_h + V_l}$ than it did solely for $I(\mathbf{F})$. In the dual-frequency CCP, it is believed that the bias (lower frequency) power contributed more to the ion energy than the source (higher frequency) power. Therefore, it is believed that the bias power had a greater effect on the etch rate. In Figure 7(c), only the bias power voltage is considered to see the bias power effect. The fitting results were similar to those of Figure 7(b). If the assumption that the velocity of the atomic fluorine was affected by voltage is invoked, this result shows that the major contribution on the flux of the atomic fluorine comes from bias power.

4. Conclusion

In this paper, the etch characteristics of SF_6/O_2 and NF_3/O_2 were compared for different process conditions using a CCP-RIE system, and the similarities and dissimilarities between the processes using the two gases were analyzed. The etch rate of SiN_x:H using NF_3/O_2 rather than SF_6/O_2 increased by 1.4–2.0 times in the same process conditions. These results indicate that the etch time can be reduced to obtain similar results by replacing gases. Because the GWP of SF_6 is 3.1 times higher than that of NF_3, the gas replacement can reduce the GWP by factor of 1/4.3–1/6.2, while obtaining the same process results.

An optical analysis using an OES showed that the density of the atomic fluorine was dependent on the intensity of the atomic fluorine. By inspecting the relationships between the etch rate of SiN_x:H and $I(\mathbf{F})$, the effects of atomic fluorine density on the etch rate and its proportionality could be monitored indirectly. A larger $I(\mathbf{F})$ (more abundant atomic fluorine) enabled a capacity to contribute to the etch rate. An electrical analysis using a *V-I* probe indicated that the velocity of the reactive F was proportional to $\sqrt{V_h + V_l}$. The flux of the atomic fluorine was interpreted as $I(\mathbf{F}) \times \sqrt{V_h + V_l}$, and it was proportional to the etch rate. The importance of the bias power on the etch rate was examined indirectly, and it was concluded that the greatest contribution to the etch rate was from the bias power. This suggests the possibility of utilizing the flux of the atomic fluorine for the simple monitoring parameters (OES and voltages).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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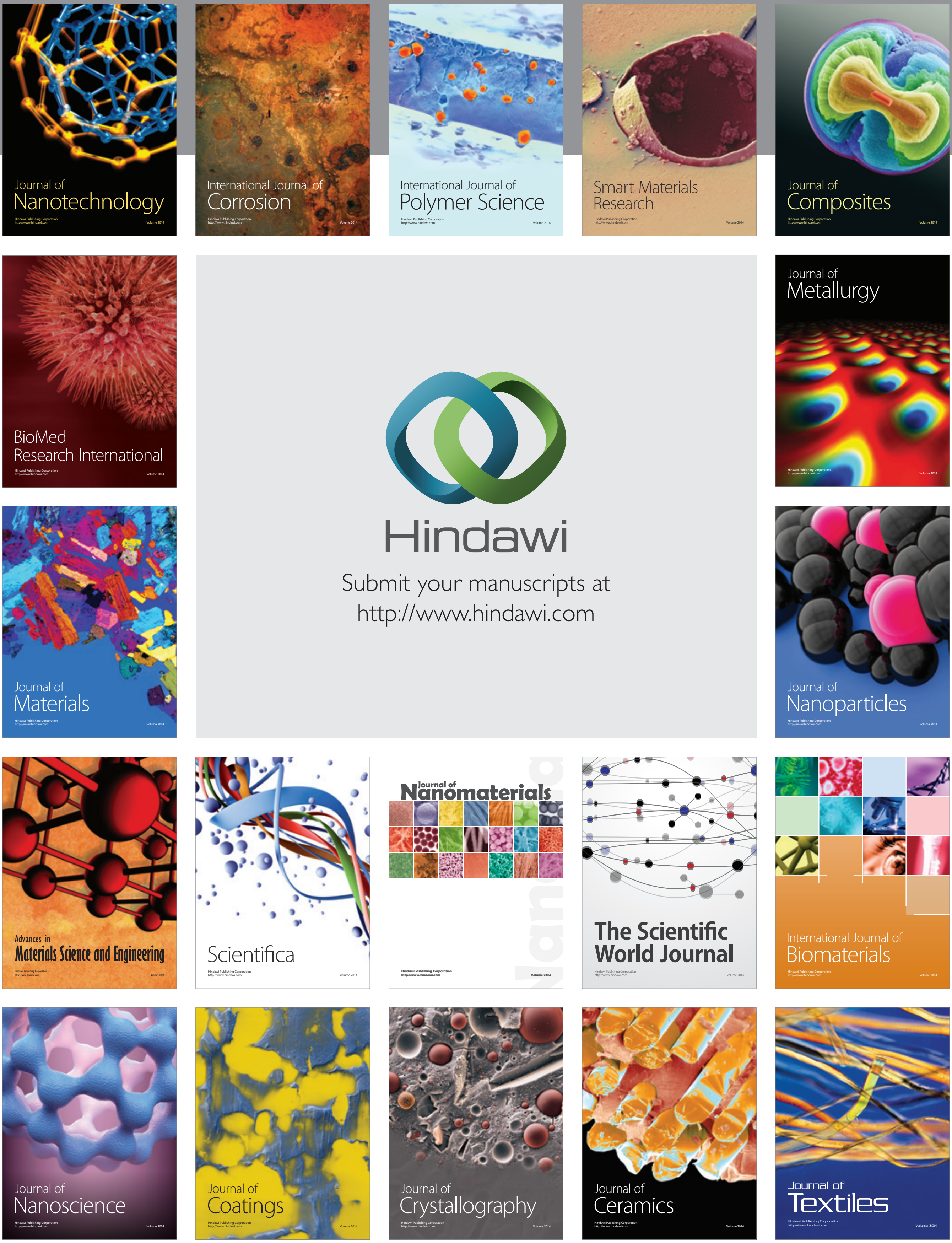
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