

## Comparison of Reactivity of Excited Nitrogen Species Generated in RF Plasma and Atmospheric Pressure Plasma

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The nitridation reactivity of excited species generated in radio frequency (RF) plasma was compared to that generated in atmospheric pressure (AP) plasma. Optical emission spectroscopy revealed that in the RF plasma, the excited molecular species originated from the N<sub>2</sub> first positive system were predominantly generated at the RF power below 137 W, and the dominant excited species drastically changed to the excited atomic species above 137 W. In the case of AP plasma, the excited molecular species originating from the N<sub>2</sub> second positive system were primarily generated regardless of the plasma conditions. Little nitridation at the surface of Si occurred in the RF plasma, in which the emissions from N<sub>2</sub> first positive system were mainly observed. Silicon nitride film was formed when the Si wafer was exposed in the plasma that the excited atomic species or when the excited molecular species generated through N<sub>2</sub> second positive system were dominant.

Key words: nitrogen plasma, silicon nitride

### 1. INTRODUCTION

Nitride semiconductors such as GaN, AlN, InN, and their solid solutions have been drawn considerable attention due to their intriguing properties.<sup>1-4</sup> Electron cyclotron resonance (ECR) and radio frequency (RF) plasma have been used extensively as nitrogen sources for molecular beam epitaxy. In the case of RF plasma, although the excited atomic species can be generated using pure nitrogen gas, the plasma source can be used at the limited gas pressure ranging from 10<sup>-5</sup> to 10<sup>-3</sup> Torr, which may yields the nitrogen defects in nitride films.

On the other hand, atmospheric pressure (AP) plasma may offer a solution to the nitrogen defect issue. For stable discharging at or near atmospheric pressure, the addition of He in the plasma gas is normally required because of its longer mean free time (6×10<sup>5</sup> sec) than that of N<sub>2</sub> (2 sec).<sup>6</sup> Recently, it has been reported that AP plasma is generated by applying an alternative pulsed voltage.<sup>7,8</sup> AP plasma enables the maintenance of stable discharging even when using the pure nitrogen gas.

In this paper, the nitridation reactivity of the excited species generated in RF plasma is compared to that generated in AP plasma. The excited nitrogen species in RF plasma and AP plasma were evaluated by optical emission spectroscopy (OES) and their reactivity was examined by nitriding the Si wafers.

### 2. EXPERIMENT

Nitrogen gas (99.9999%) was injected in an ultra high vacuum chamber with a base pressure of 5×10<sup>-10</sup> Torr through a gas purifier (SAES Getters, FACILI TORR) to remove H<sub>2</sub>O and O<sub>2</sub>. In the case of RF plasma, a PBN discharging tube surrounded a water cooling tube and an

electrode RF coil. An operating frequency, 13.56 MHz, was used with electric power below 500 W. The AP plasma was generated by applying an alternative pulse voltage with an amplitude ranging from 1 to 3 kV, a pulse width of 5 μsec, and a frequency of 30 kHz between two parallel electrodes with a gap of 1 mm. OES at the wavelength from 250 to 950 nm was carried out to evaluate the transition process of the excited species occurring in RF plasma and AP plasma. Inside of the discharging tube was directly observed from the back-side of the plasma source in the case of OES for RF plasma. The optical emissions generated in the AP plasma were measured using the optical fiber fixed at 5 mm above the electrode.

For the nitridation, p-type (111) Si wafers with a carrier concentration of 5×10<sup>15</sup> cm<sup>-3</sup> were used. The (111) Si wafers were soaked in a hot solution of HCl : H<sub>2</sub>O<sub>2</sub> = 2 : 1 followed by chemical cleaning in a hot solution of NH<sub>4</sub>OH : H<sub>2</sub>O<sub>2</sub> = 1 : 1. Hydrogen termination treatment was performed just before insertion into the vacuum chamber. Nitridation by the RF plasma and AP plasma was performed at the fixed pressure of 1.0×10<sup>-5</sup> Torr and 500 Torr, respectively. For each nitridation, the nitridation time and the substrate temperature were varied from 0.5 to 180 min and from 25 to 500 °C, respectively. The film composition and chemical bonding state were evaluated using x-ray photoelectron spectroscopy (XPS). Regarding the current - voltage characteristics, Au top electrodes with an area of 4.5×10<sup>-2</sup> mm<sup>2</sup> were deposited with the electron beam gun at a pressure of 5×10<sup>-5</sup> Torr and the leakage current density measurements were carried out using HP4104B.

### 3. RESULTS AND DISCUSSION

The emissions from the  $N_2$  first positive system, which is denoted as  $N_2$  1st p.s. ( $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ ), were predominantly observed when the RF plasma source was operated below 137 W. The typical emission spectra are shown in Fig. 1 (a). Emissions at the wavelengths of 541, 594, 661, 773, and 889 nm are clearly observed. Above 137 W, the dominant transition process changes from  $B^3\Pi_g \rightarrow A^3\Sigma_u^+$  to  $3s^4P \rightarrow 3p^4S$ ,  $3p^4P$  or  $3p^4D$ , where emissions are observed at the wavelengths of 747, 821, and 868 nm as shown in Fig. 1 (b).<sup>9</sup>

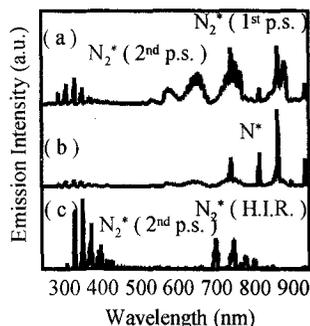


Fig. 1. Optical emission spectra observed in the nitrogen plasma generated at the RF power of 100 W, (a), 400 W, (b), and at 500 Torr in the AP plasma, (c).

At the gas pressure of  $1.0 \times 10^{-5}$  Torr, the dominant excited species change at a RF power of 137 W. At a RF power below 137 W, the excited molecular species generated through  $N_2$  1st p.s. are dominant. The emissions by the transition process resulted in generating atomic species start to appear at the RF power 137 W, and they drastically increase with an increase of applied RF power. The emissions from  $N_2$  1st p.s. disappear at a RF power above 137 W.

In the case of AP plasma, emissions from  $N_2$  second positive system, which is denoted as  $N_2$  2nd p.s. ( $C^3\Pi_u \rightarrow B^3\Sigma_g$ ), are observed at emission wavelengths of 296, 315, 337, 358, 380, 400, and 427 nm, and emissions from the  $N_2$  Herman infrared system ( $C^5\Pi_g \rightarrow A^5\Sigma_u^+$ )<sup>10</sup>, which is denoted as  $N_2$  H.I.R., are also observed at emission wavelengths of 700, 707, 745, 772, 782, and 808 nm as shown in Fig. 1 (c). These three kinds of excited species, including excited atomic species and excited molecular species ( $N_2$  1st p.s. and  $N_2$  2nd p.s.) are mainly generated in RF or AP plasma. Therefore, the nitridation was carried out using the above mentioned typical three excited species.

Figure 2 (a) and (b) show the XPS spectra of the silicon nitride films fabricated with the excited molecular species ( $N_2$  1st p.s.) and excited atomic species generated in the RF plasma. The RF power for generating the excited molecular species ( $N_2$  1st p.s.) and excited atomic species were 100 and 400 W, respectively. Other nitridation conditions include a nitridation temperature of 350°C and a time period of 60 min. As shown in Fig. 2 (a), distinct nitridation is not recognized when the excited molecular species ( $N_2$  1st

p.s.) are used for nitridation. The use of excited atomic species drastically enhances the nitridation as shown in Fig. 2 (b). The thickness and the composition of the nitride films evaluated by XPS<sup>11, 12</sup> are 1.6 nm and

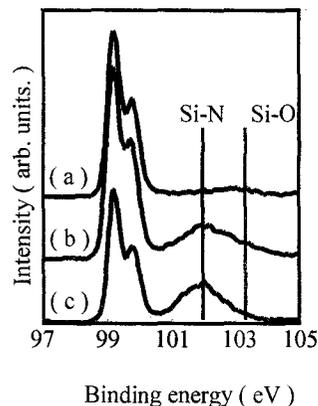


Fig. 2. Si 2p X-ray photoelectron spectrum of silicon nitrided at the RF power of 100 W, (a), at 400 W, (b), and at the pressure of 500 torr in AP plasma (c).

$Si_3N_3.5O_{0.7}$ , respectively. Fig. 2 (c) shows the XPS spectrum of the film fabricated with the excited molecular species ( $N_2$  2nd p.s.) generated in the AP plasma. The nitridation was carried out at 350°C for 10 min. The composition the nitride films is calculated as  $Si_3N_3.5O_{0.7}$ , which is completely identical to that of the film fabricated using with the excited atomic species generated in the RF plasma. Therefore, film fabricated by the excited molecular species ( $N_2$  2nd p.s.) generated in AP plasma has almost the same nitridation capability as that of the excited atomic nitrogen species. Although the impurities of  $O_2$  and  $H_2O$  were kept at less than 1ppb by inserting the absorbing gas purifier and each nitride was fabricated by different plasma sources with completely different nitrogen pressure, each film has the same oxygen content. Therefore, it can be considered that the oxidation occurred during the ex-situ XPS

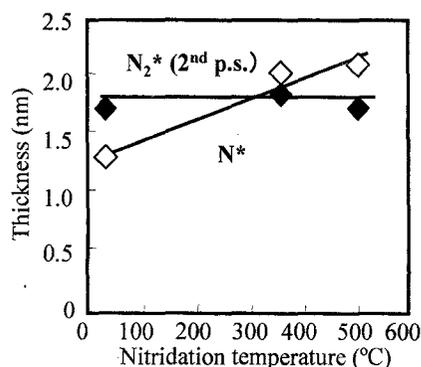


Fig. 3. Change in thickness by varying the nitridation temperature. Used active nitrogen species are atomic nitrogen species generated in the RF plasma,  $\diamond$ , and excited molecular species ( $2^{nd}$  p.s.) generated in the AP plasma,  $\blacklozenge$ .

measurement after deposition.

Figure 3 shows the change in the film thickness by varying the nitridation temperature. The thicknesses of the films fabricated by the excited atomic species generated in the RF plasma increases with increasing nitridation temperature. On the other hand, for the films fabricated by the excited molecular species ( $N_2$  2nd p.s.) generated in the AP plasma, the thickness is regardless of nitridation temperature. Furthermore, all the films nitrided by the excited atomic species generated in the RF plasma and those by the excited molecular species ( $N_2$  2nd p.s.) generated in the AP plasma have the same composition of  $Si_3N_{3.5}O_{0.7}$ .

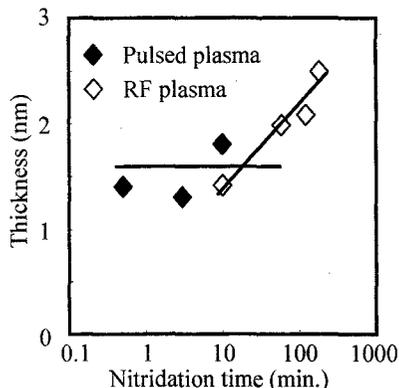


Fig. 4. Change in the thickness with increasing nitridation time.  $\blacklozenge$  and  $\diamond$  denote the thickness for the film fabricated by the AP plasma and RF plasma. Nitridation temperature was fixed as  $350^\circ\text{C}$ .

Figure 4 shows the change of the film thickness plotted against nitridation time. The thickness of the film nitrided with the excited molecular species ( $N_2$  2nd p.s.) generated in the AP plasma shows a fixed value of 1.6 nm even if the exposure time is shortened to 30 sec. On the other hand, the thickness of the film fabricated by the excited atomic species still increases with nitridation time up to 180 min.

As mentioned above, the excited molecular species ( $N_2$  2nd p.s.) generated in the AP plasma have very high

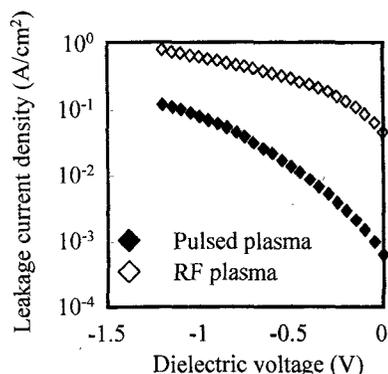


Fig. 5. I - V characteristics of the silicon nitride films.  $\blacklozenge$  and  $\diamond$  denote the film fabricated by the AP plasma and RF plasma.

nitridation capability. It is almost the same as that of the excited atomic species generated in the RF plasma. However, these nitridation kinetics are different.

To study the quality of the films fabricated with the AP plasma and RF plasma, the leakage current characteristics of the  $Au/Si_3N_{3.5}O_{0.7}/p\text{-Si}$  (111) capacitor were measured. The results are shown in Fig. 5. The film nitrided by the excited molecular species ( $N_2$  2nd p.s.) generated in the AP plasma shows less leakage current than the film fabricated with the excited atomic species generated in the RF plasma.

#### 4. CONCLUSION

The comparison of the nitridation reactivity of the excited nitrogen species generated by the RF plasma and AP plasma was carried out. In the case of RF plasma, at the applied power of 100 W, emissions from  $N_2$  1st p.s. were observed. Since the silicon oxynitride was formed at this power, it is considered that this condition was not suitable for fabricating silicon nitride film. At 400 W, emissions due to the formation of the excited atomic species were observed and the composition of the film was calculated as  $Si_3N_{3.5}O_{0.7}$ . In the case of AP plasma, on the other hand, the emissions from  $N_2$  2nd p.s. and  $N_2$  H.I.R. were observed at the pressure of 500 Torr, and the composition of the film was calculated to  $Si_3N_{3.5}O_{0.7}$ . The film thickness fabricated by the RF plasma depends on the nitridation temperature and the period. At the same time, in the case of AP plasma, almost the same thickness was recognized regardless of the nitridation conditions and the fact that the leakage current of these films was lower by one order of magnitude than those fabricated by the RF plasma.

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