

The Nitridation Process of Silicon with Atmospheric Pressure Plasma

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The reaction process model in the initial nitridation of Si (111) using atmospheric pressure plasma source was constructed. In atmospheric pressure plasma, predominantly molecular excited species that correspond to the existence of emissions from the N₂ second positive system were observed. By exposing the atmospheric pressure plasma at the substrate temperature range from 25 to 500°C, silicon nitride films with a thickness below 1.8 nm were formed. In order to study the growth mode of the films, the changes in the film thickness against the substrate temperature and nitridation time were studied at a pressure range from 50 to 700 torr. The film thickness strongly depends on the nitridation pressure but does not on the substrate temperature. From the time dependence of the film thickness at various nitridation pressures, it was revealed that these experimental results were well fitted to a Langmuir-type adsorption model. The nitridation characteristics when an atmospheric pressure plasma source was used were compared to those using a radio frequency plasma source.

Key words: nitrogen plasma, silicon nitride, atmospheric pressure and Langmuir-type adsorption

1. INTRODUCTION

The discharging technique of nitrogen plasma has been widely studied for application to integrated devices such as the gate insulator of metal-oxide semiconductor (MOS) devices: nitridation mechanisms of Si or SiO₂ also have been proposed.^{1-2,3} Usually, nitridation processes were performed under high-vacuumed conditions (10⁻⁷~10⁻³ torr)⁴ using such sources as radio frequency plasma^{1,2} and electron-cyclotron-resonance plasma.³ For plasma nitridation many methods have been used such as NH₃,⁵ atomic nitrogen⁶ and NO¹ as a gas source. In this paper, pure nitrogen gas was used to avoid contamination from H and O in the films.

On the other hand, to obtain the glow discharge at atmospheric pressure, it is necessary to avoid rapid amplification of the primary avalanches, which initiate the arc discharge. Therefore the addition of He or other noble gases in plasma source gas is normally required because of the longer mean free time (He: 6×10⁵ sec) than that of N₂ (2 sec). But a new type plasma source enables the maintenance of stable glow discharging even when using pure nitrogen gas generated by applying an alternative pulsed voltage.⁷ In the case of plasma denoted as atmospheric pressure plasma (AP plasma), it was reported that emissions from excited molecular species are observed at the remote position located 5 mm above the electrode position. Their transitions correspond to N₂ second positive system (N₂ 2nd p.s.) and N₂ Herman's Infrared system (N₂ H.I.R.).⁸ The molecular excited species were unique because in the RF plasma source, atomic excited species were mainly observed.

In this paper, the nitridation mechanism of Si (111) surface using an AP plasma source was investigated at a gas pressure range from 50 to 700 torr. A comparison of nitridation characteristics in the case of using RF plasma was also investigated.

2. EXPERIMENTAL

Nitrogen gas (99.9999%) was injected in an ultra-high vacuum chamber with a base pressure of 5×10⁻¹⁰ torr through a gas purifier (SAES Getters, FACILI TORR) to lower contamination from H₂O and O₂ below 1 ppb. The AP plasma was generated by applying an alternative pulse voltage with an amplitude ranging from 1 to 5 kV, a pulse width of 5 μsec and a frequency of 30 kHz between two parallel electrodes with a gap of 1 mm. Analysis of optical emission spectrum (OES) at the wavelength from 250 to 950 nm were carried out to evaluate the transition process of the excited species generated by AP plasma using an optical fiber fixed at 5 mm above the electrode (remote position). In the case of RF plasma, a PBN discharging tube surrounded a water cooling tube and an electrode RF coil. An operating frequency of 13.56 MHz was used with electric power below 500 W. OES measurement was performed inside of the discharging tube from the back-side of the RF plasma source.

For the nitridation, p-type (111) Si wafers with a carrier concentration of 5×10¹⁵ cm⁻³ were used. The Si (111) wafers were soaked in a hot solution of HCl : H₂O₂ = 2 : 1 followed by chemical cleaning in a hot solution of NH₄OH : H₂O₂ = 1 : 1 and finally native oxide was removed by soaking in a 1% of HF solution.

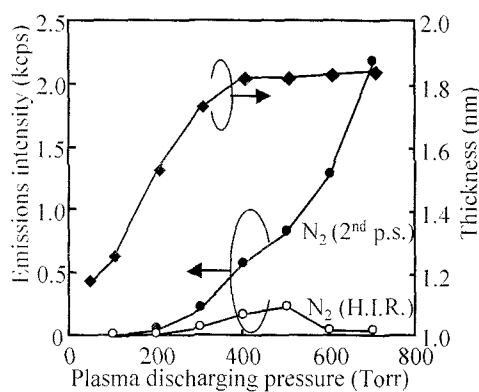


Fig. 1. Dependence of the thickness of the silicon nitride film and emission intensity from N_2 2nd p.s. and N_2 H.I.R. at various pressures.

Hydrogen termination treatment was performed just before inserting into the vacuum chamber. Nitridation of Si with the AP plasma source was performed at 5mm above the electrode (remote position) at a pressure ranging from 50 to 700 torr. In the case of nitridation with RF plasma (OXMI), the substrate was fixed at 12cm above the top of the discharging tube at a gas pressure of 1.0×10^{-5} torr. In addition, the nitridation time using AP plasma and RF plasma sources was varied from 0.5 to 15 min and from 10 to 180 min, respectively. The nitridation temperature was varied from room temperature to 500°C. The chemical bonding states of the films were evaluated using x-ray photoelectron spectroscopy (XPS: KRATOS AXIS-165). Film thickness was evaluated using the intensity ratio of the Si 2p bulk to chemically shifted Si2p after sensitivity correction.^{9,10}

3. RESULTS AND DISCUSSION

The effect of plasma discharging pressure on the OES and the thickness of the Si nitride was examined. Although our plasma system was not always operated at atmospheric pressure, in this paper, we refer to this system as AP plasma. Figure 1 shows changes in the emission intensities from N_2 2nd p.s. (using the intensity at 380 nm) and emissions from N_2 H.I.R. (using that of 707 nm) against discharging pressure. The change in the film thickness is also shown in the figure to examine the relationship between these intensities and the thickness of the nitride. The nitridation temperature was fixed at 350°C and nitridation time was 10 min. As the plasma discharging pressure increases, the emission intensities of N_2 2nd p.s. increase. Although those of N_2 H.I.R. also increase, they start to decrease at a discharging pressure above 500 torr. Regarding film thickness, on the other hand, it also increases with increasing gas pressure. However, it does not decrease above 500 torr, and nitride with the same thickness can be obtained even at 700 torr, at which emission from N_2 H.I.R. is no longer observed. Based on the above evidence, we can conclude that the excited species generated through N_2 2nd p.s. transition mainly contribute to the nitridation of the Si surface. Above 400 torr, the thickness saturates despite the fact that the emission intensity still increases. This suggests that the number of excited species

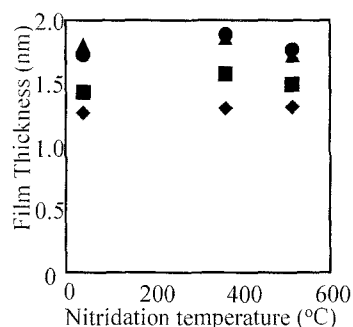


Fig. 2. Dependence of the thickness of the silicon nitride film fabricated at a range of 25 to 500°C. Fabricated at 50 Torr (◆), 200 Torr (■), 500 Torr (●), 700 Torr (▲).

generated through N_2 2nd p.s. transition controls the nitridation, and enough excited species to form the nitride would be supplied at 400 torr.

Figure 2 shows the temperature dependence of the film thickness at each discharging pressure. Other nitridation conditions are the same as those used in Fig.1. Even at 25°C, nitride film can be obtained. Furthermore, the saturated thickness does not depend on the nitridation temperature but on the discharging pressure. We also reported that dielectric properties also do not also depend on the nitridation temperature. This nitridation process, which is independent of the substrate temperature, suggests that the activation energy required to form nitrides in the 25-500°C range is extremely small.^{11,12}

Figure 3 shows a time dependence of film thickness at elevated gas pressure of 50, 200, 500 and 700 torr. A nitridation temperature of 350°C was used. The thickness of the film increases with increasing nitridation time below 100 torr, and it does not saturate. Above 500 torr, however, the thickness saturates at 1.8 nm at the nitridation time even for 10 min. From these results, the nitridation on Si using AP plasma is considered to be the initial surface reaction, and the reaction seems to be limited by supplied excited species.

Because a nitridation was performed at low temperature, Langmuir-type kinetic model, which neglects of desorption of the adsorption species can be applied to our experimental results.

Many reports have been published that describe the adsorption and reaction of N or O atoms using a Langmuir-type model.^{13,3} We also attempted to describe our experimental results using a Langmuir-type growth model:

$$d = a_1 + a_2 (1 - \exp - a_3 t) \quad (1)$$

$$a_3 = kn \quad (2)$$

where d , t and k are the film thickness, exposure time and nitridation rate constant, respectively, and n is the concentration of excited species, which is determined using the emission intensity of N_2 2nd p.s. shown in Fig. 1. In addition, a_1 , a_2 and a_3 are the constants at each discharging pressure. Constant a_1 corresponds to the initial film thickness and the value of $(a_1 + a_2)$ represents

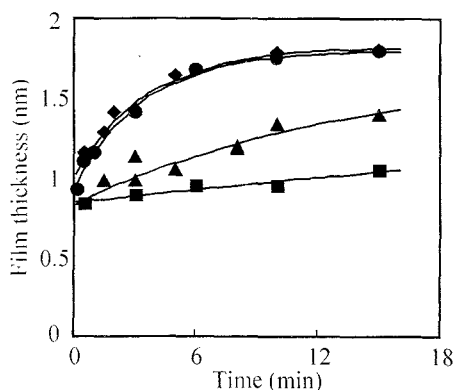


Fig. 3. The time dependence of film thickness fabricated at 50 Torr (■), 200 Torr (▲), 500 Torr (●) and 700 Torr (◆). The solid line shows the fitting values by equation (1).

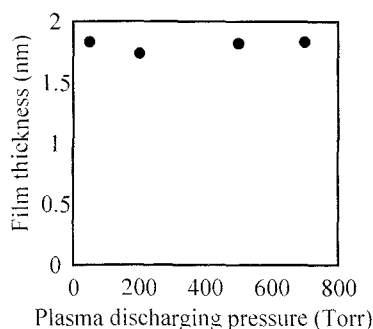


Fig. 4. Saturated film thickness against various plasma discharging pressures.

the saturate film thickness. Constant a_3 corresponds to the concentration of the reaction species. Fitted parameters using equation (1) are listed in Table 1. Because the correlation factors, χ^2 , are very small, the experimental data are considered to be explained by Langmuir-type physical adsorption and reaction. Constant a_1 , the initial nitride film thickness, increases with an increase in discharge pressure. The value of (a_1+a_2) , saturated film thickness is calculated as 1.8 nm regardless of the discharging pressure as shown in Fig. 4.

In addition, constant a_3 , which corresponds to the concentration of the reaction species, increases with an increase in the discharge pressure at the pressure range below 500 torr, then saturates. By using these fitting parameters, we can estimate final (saturated) nitride thickness formed at each discharging pressure as shown in Fig. 5. It is clearly understood that final thickness is around 1.8 nm regardless of the pressure.

Based on these results, the nitridation process using AP plasma can be well explained by a Langmuir-type physical adsorption model. Therefore, the final thickness of 1.8 nm might correspond to the depth from the surface where the active species can reach and react with Si keeping the active state. This model is unique for nitridation using AP plasma, in which molecular

Table 1 The constants estimated by fitting the experimental data

constant	50 (Torr)	200 (Torr)	500 (Torr)	700 (Torr)
a^1	0.84	0.82	0.92	1.05
a^2	0.98	0.84	0.88	0.8
a^1+a^2	1.82	1.72	1.80	1.82
a^3	0.02	0.08	0.29	0.30
χ^2	0.002	0.005	0.002	0.001

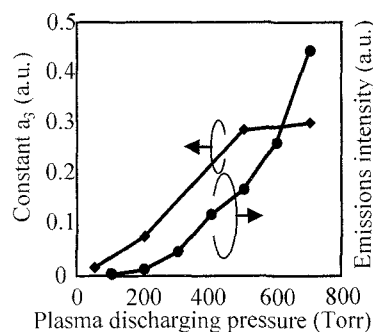


Fig. 5. Dependence of the value of constant a_3 and the emission intensity from N_2 2nd p.s. and N_2 H.I.R at various pressures.

nitrogen active species are important for nitridation. In the case of nitridation using RF plasma, on the other hand, atomic active nitrogen plays an important role in nitridation. Therefore, the nitridation process using RF plasma was compared to that using AP plasma.

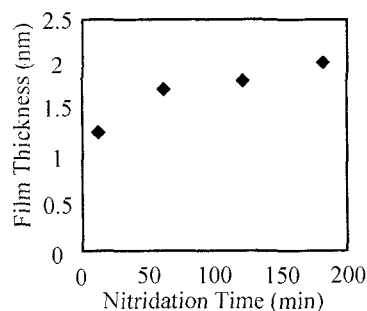


Fig.6. Nitridation time dependence of film thickness fabricated using RF plasma.

Figure 6 shows the change in film thickness plotted against nitridation time by using the RF plasma source. An operating frequency of 13.56 MHz was used, with the electric power below 500 W. At this applied power, only the atomic nitrogen active species were observed in OES. The thickness of the film still increases at the nitridation time up to 180 min.

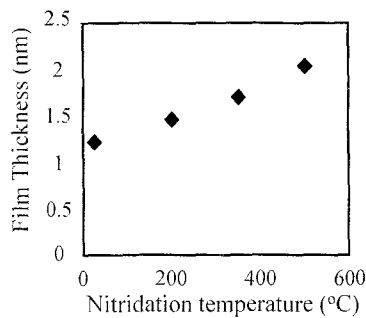


Fig.7. Temperature dependence of film thickness fabricated using RF plasma.

Figure 7 shows a comparison of the change in the thickness of the films fabricated using a RF plasma source and an AP plasma source by varying the nitridation temperature. Nitridation was performed for 60 min with the RF plasma source. The thicknesses increases with increasing nitridation temperature. This growth model is different from the model shown in Fig. 2. It may be concluded that the difference in the growth model between AP plasma and RF plasma was what contributed to the difference of the excited species in the plasmas.

4. CONCLUSION

We investigated the reaction process model in the initial nitridation of Si (111) using an atmospheric pressure plasma source at a low substrate temperature below 500°C. In the atmospheric pressure plasma, molecular excited species corresponding to the existence of emission from the N_2 2nd p.s. was dominantly observed. At the substrate temperature range from 25 to 500 °C, silicon nitride ultra-thin films with a thickness below 1.8 nm were formed. The growth mode of the films was determined by changes in the film thickness against the substrate temperature and nitridation time at the pressure range from 50 to 700 Torr. The film thickness did not change regardless of the substrate temperature. From the time dependence of the film thickness at various nitridation pressures, it was found that the experimental results fit well to a Langmuir-type adsorption model. It was also found that this nitridation process of adsorption model using an AP plasma source is different from that using a RF plasma source.

5. REFERENCES

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