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Low-Temperature Formation of Silicon Nitride Films using Nitrogen Plasma near Atmospheric Pressure

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Stable discharging of pure nitrogen can be maintained even at atmospheric pressure when alternative pulsed voltage is applied between two parallel plate electrodes. From optical emission spectroscopy, strong emissions from the N_2 2nd positive system, weak emissions from N_2 Herman's infrared system, and N_2 1st positive system are observed. The electron temperature evaluated from the double probe measurement increases with increasing nitrogen pressure. Using this atmospheric pressure plasma, 1.6 nm-thick silicon nitride film was obtained at a nitridation temperature as low as 25°C, and the thickness was regardless of the nitridation temperature. Furthermore, the thickness decreases with decreasing nitrogen pressure and the thickness change against the nitrogen pressure well corresponds to the change in emissions from the N_2 2nd positive system in optical emission spectroscopy. We can conclude that the excited species generated through N_2 2nd p.s. in the nitrogen plasma generated near atmospheric pressure contribute to nitridation of silicon and that it has extremely high reactivity. Furthermore, the thickness could be intentionally controlled by controlling the amount of the excited species generated through the N_2 2nd positive system.

Key words: atmospheric pressure, nitrogen plasma, silicon nitride, x-ray photoelectron spectroscopy, optical emission spectroscopy

1. INTRODUCTION

Nitrogen plasma has been used in fabricating silicon nitride films[1,2] and III-V nitride semiconductors such as GaN[3]. For these applications, nitrogen plasma sources are normally applied at pressure ranging from 10^{-3} to 10^{-6} Torr, which may cause nitrogen vacancy. Nitrogen plasma generated near atmospheric pressure should be one solution to solve this problem. However, it is very difficult to maintain a stable, arcless, and nonequilibrium nitrogen plasma because the transition time from glow discharging to arc discharging drastically decreases with increasing nitrogen gas pressure. Although corona discharging is one well known nonequilibrium nitrogen plasma using pure nitrogen at atmospheric pressure,[4,5] this is not suitable for surface reaction because the gas temperature is as high as 1,000 K. Over the past several years, a number of plasma sources such as helium plasma, which operates at atmospheric pressure, have been developed by inserting the dielectric layers between two parallel plate electrodes.[6,7] This dielectric barrier discharge (DBD) is widely used in the field of environmental application.[8]

Recently, we have developed a new plasma source that maintains the stable discharging in pure nitrogen by applying alternative pulsed voltage at atmospheric pressure.[9,10] In previous studies, we reported that the thickness of the silicon nitride film fabricated at 500 Torr was 1.6 nm at a nitridation temperature as low as 25°C, and the excited species in nitrogen plasma generated by this plasma system contributes to high reactivity for silicon compared to atomic nitrogen species.[11] However, the thickness could not be controlled intentionally, because it was independent of the nitridation temperature and saturated for a few minutes.

This paper describes the relationship between the thickness of nitride film and the intensity of optical emission spectroscopy against nitrogen pressure, if the thickness is controlled. We also discuss which excited species mainly contribute to the nitridation of Si.

2. EXPERIMENT

Two parallel plate electrodes separated by a uniform gap of 1 mm were mounted in a vacuum chamber at a base pressure below 8×10^{-10} Torr. Nitrogen plasma was generated by applying an alternative pulse voltage ranging from 1 to 15 kV, a pulse width of 5 μsec and a frequency of 30 kHz between the two parallel plate electrodes. High-purity nitrogen (99.9999%) was flown at a

rate ranging from 1.5 to 10 *l*/min. To reduce impurities such as H_2O and O_2, an absorbing purifier (SAES Getters, FACILI TORR) was used.

The optical emission spectroscopy (OES) and the double probe measurement (DPM) at the downstream of nitrogen gas were used to evaluate the excited species and the electron temperature in nitrogen plasma generated near atmospheric pressure. The schematic of the configuration of OES and DPM is shown as Fig. 1. The probe current was measured with a Hewlett Packard model 4140B.

For the nitridation, p-type (111) Si wafers with a carrier concentration of 5×10^{15} cm^{-3} were used. The (111) Si wafers were soaked in a hot solution of HCl : H_2O_2 (=2:1) followed by chemical cleaning in a hot solution of NH_4OH : H_2O_2 (=1:1). Hydrogen termination treatment was performed just before insertion into the vacuum chamber. The nitridation was carried out at a nitrogen pressure ranging from 50 to 700 Torr and the nitridastion temperature was varied from 25 to 500°C. The composition of the films and the chemical bonding state were determined by X-ray photoemission spectroscopy (XPS).

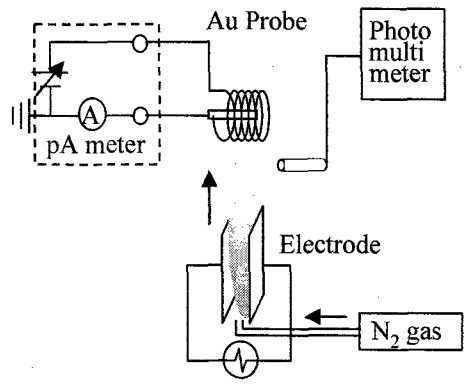

Fig. 1. A configuration scheme of the optical emission spectroscopy and the double probe measurement to evaluate nitrogen plasma.

3. RESULTS AND DISCUSSION

Figure 2(a) shows the OES of the nitrogen plasma generated at a pulsed voltage of 3 kV and a frequency of 30 kHz. The flow rate of the nitrogen gas was fixed at 10 *l*/min. At 500 Torr, emissions from the N_2 2nd positive system, which is denoted as 2nd p.s. ($C^3\Pi_u \rightarrow B^3\Pi_g$), were primarily observed at emission wavelengths of 296, 315, 337, 358, 380, 400, and 427 nm. Emissions from the N_2 Herman's infrared system, which is denoted as H.I.R. ($C^5\Pi_g \rightarrow A^5\Sigma_g^+$), were observed at wavelengths of 700, 707, 745, 772, 782, and 808 nm.[12] Emissions from N_2 2nd p.s. and N_2 H.I.R. were scarcely observed in nitrogen plasma generated by conventional RF plasma and ECR plasma sources operated at a pressures ranging from 10^{-3} to 10^{-6} Torr. It is a unique phenomena in plasma generated near atmospheric pressure.[13] At wavelengths of 541, 594, 661, 773, and 889 nm, emissions from the N_2 1st positive system, which is denoted as 1st p.s. ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$), were also observed. Although the intensity was much lower than that from N_2 2nd p.s., considering the transition probability, the density of excited species generated through N_2 1st p.s. became almost the same order of magnitude as that of the excited species generated through N_2 2nd p.s. because the transition probabilities of the N_2 1st positive system were generally several hundred times smaller than those of the N_2 2nd p.s.[14] Emissions from the N_2^+ 1st negative system and atomic nitrogen were not observed.

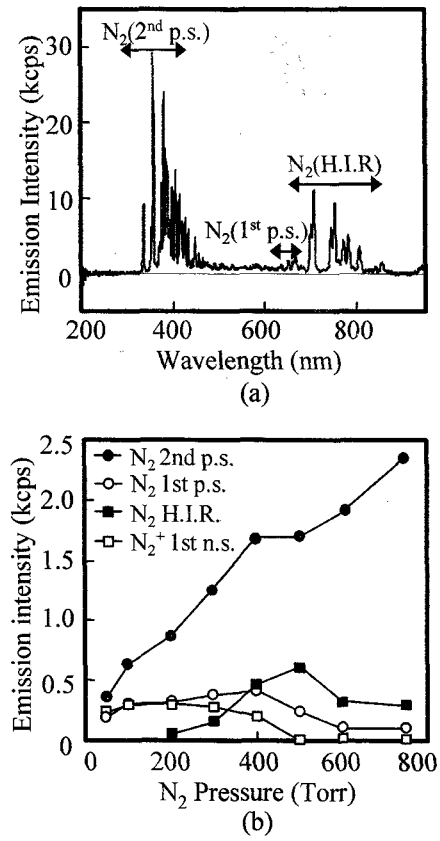

Fig. 2. (a) Optical emission spectrum observed from nitrogen plasma generated at 500 Torr and (b) nitrogen pressure dependence of optical emission intensities of N_2 2nd p.s., N_2^+ 1st n.s., N_2 H.I.R., and N_2 1st p.s., respectively.

The excited species generated through N_2 2nd p.s., N_2 1st p.s., and N_2 H.I.R. are effectively generated in the atmospheric pressure nitrogen plasma. Therefore, there is a possibility that several kinds of excited nitrogen species such as N_2 2nd p.s., N_2 1st p.s., and N_2 H.I.R. contribute to the formation of silicon nitride film in nitrogen plasma generated near atmospheric pressure.

Figure 2(b) shows the changes of emission intensities of N_2 2nd p.s. (380 nm), N_2 1st p.s. (773 nm), N_2 H.I.R (707 nm), and N_2^+ 1st n.s. (391 nm) against nitrogen pressure. As nitrogen

pressure increases, the emission intensity of N_2 2nd p.s. increases, while those of N_2 1st p.s. and N_2^+ 1st n.s. decrease and that of N_2 H.I.R has a maximum nitrogen pressure of 500 Torr.

Figure 3(a) shows the electron temperature obtained at pressures ranging from 50 to 700 Torr. The probe current increases with increasing nitrogen pressure. The electron temperature increases with increasing nitrogen pressure, as shown in Fig. 3(b).

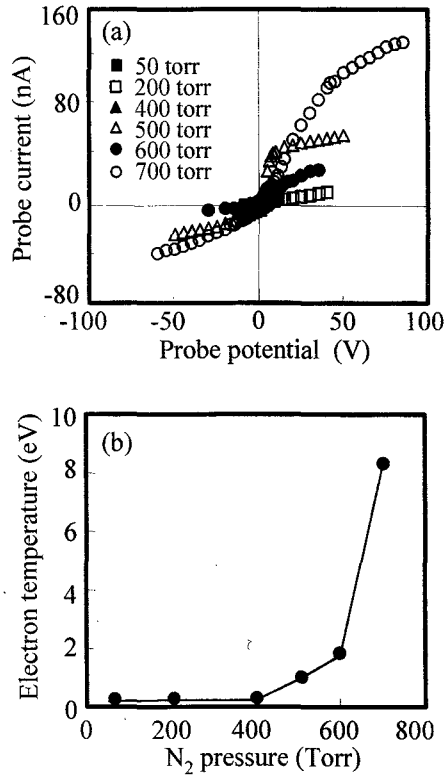

Fig. 3. (a) Double probe characteristics with different nitrogen pressure and (b) the electron temperature dependence of nitrogen pressure.

To study which excited species mainly contribute to nitridation in nitrogen plasma generated near atmospheric pressure, silicon nitridation using the nitrogen plasma generated was carried out. Nitrogen pressure and the nitridation temperature were varied from 50 to 700 Torr and from 25 to 500°C, respectively. The concentration of O_2 and H_2O impurities were reduced to less than 1 ppb by inserting the absorbing purifier.

Figure 4(a) and (b) show the XPS spectra of Si 2p and N 1s of the film prepared at 350°C and 500 Torr for 10 min. Chemically shifted Si 2p peak with a binding energy of 101.9 eV was observed at the surface of the film, which indicates that primarily a Si-N bond exists. A N 1s peak with a binding energy of 397.8 eV was also observed at the surface, which corresponds to a N-Si_3 bond. The peak corresponding to a Si-N bond does not shift along the film thickness of nitride film and a Si-N bond is homogeneous in the film. From the binding energy of the chemically shifted Si 2p peak, the composition of the film was calculated as $Si_3N_{3.5}O_{0.7}$.

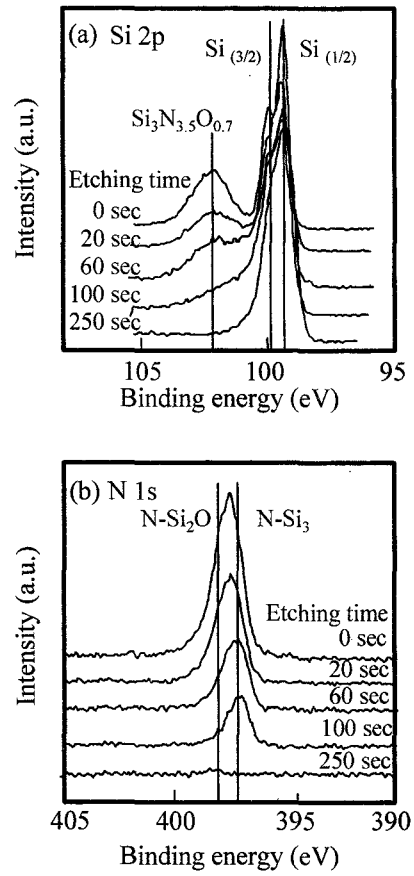

Fig. 4. X-ray photoelectron spectra of (a) Si 2p and (b) N 1s core level on the silicon nitride film fabricated at 500 Torr.

Figure 5(a) shows a change in the thickness, determined by using XPS against the nitrogen pressure. The nitridation was performed at 350°C. The thickness does not change by varying nitrogen pressures ranging from 400 to 700 Torr, and it decreases with decreasing pressure ranging from 50 to 400 Torr. The thickness change against nitrogen pressure corresponds well to the change of emission intensities of N_2 2nd p.s. in the OES. The excited molecular species generated through N_2 2nd p.s. in the nitrogen plasma generated by the plasma system should be responsible for the nitridastion of Si.

Figure 5(b) shows the relationship between the nitridation temperature and thickness. Exposure time was fixed at 10 min. The silicon nitride film with a thickness of 1.6 nm is formed even at 25°C and 700 Torr, and the thickness is independent of the nitridation temperature at pressures ranging from 50 to 700 Torr. The composition of the film fabricated at all nitrogen pressures is calculated to be $Si_3N_{3.5}O_{0.7}$. This

result shows that the nitridation process is limited by the amount of the excited molecular species generated though N_2 2nd p.s. and the thickness could be intentionally controlled by controlling the amount of excited species generated through N_2 2nd p.s.

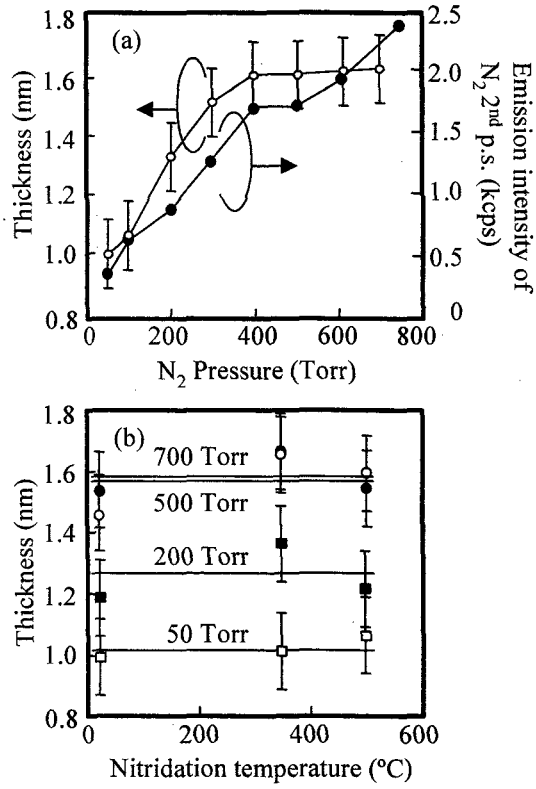

Fig. 5. Dependence of the thickness of the silicon nitride film and emission intensity of N_2 2nd p.s. on (a) nitrogen pressure and (b) nitridation temperature.

4. CONCLUSION

Silicon nitride films were fabricated at pressures by varying nitrogen pressure and the substrate temperature using the plasma system operated with pulsed voltage. The composition of the film was calculated to be $Si_3N_{3.5}O_{0.7}$ from XPS measurement. Although the film thickness, 1.6 nm, did not change by varying the nitridation temperature and the time, when the pressure was kept at above 400 Torr, the thickness decreases when decreasing the emission intensities of N_2 2nd p.s. at pressure ranging from 50 to 400 Torr. This supports the idea that the excited species generated through N_2 2nd p.s. in the nitrogen plasma generated by the plasma system contribute to the nitridation for silicon and the thickness could be controlled intentionally by the amount of the excited molecular species generated though N_2 2nd p.s.

5. REFERENCES

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