Effects of Pressure and Gas Mixture Composition on the Plasma Chemistry of $N_2/NH_3/SiH_4$ Inductively Coupled Plasma

K. –S. Seo, J. –H. Cha and H. –J. Lee

Department of Electrical and Computer Engineering, Pusan National University, Busan, Republic of Korea

Abstract: A fluid model of 2D axis-symmetry based on inductivel coupled plasma (ICP) reactor for hydrogenated silicon nitride (SiN_x: H) deposition has been developed. $N_2/NH_3/SiH_4$ gas mixture was used as the process gas. In total, 57 species (including electron, neutrals, ions, and excitation species), 195 chemical reactions, and 41 surface reactions were applied in this model. The effects of pressure and gas mixture ratio on the ions and active species density were analyzed. Also, the effects of dual antenna power on the compensation of the density non-uniformity were investigated.

Keywords: Fluid simulation, Inductively coupled plasma, Hydrogenated silicon nitride

1. Introduction

Hydrogenated silicon nitride (SiN_x: H) films are known to have high electrical insulation, chemical passivation and mechanical strength. Due to these characteristics, they are used for various industrial applications such as anti-reflection coating or surface passivation layer, encapsulation of organic light-emitting diodes (OLED) and passivation layer of semiconductor devices [1]. There have been many studies for SiN_x: H films deposition by PECVD process showing that properties of the films depend on the mixture gas composition and process conditions in various plasma sources [2,3]. Various precursors such as atomic nitrogen (N), excited N_2^* molecules, aminosilnae complexes ($SiH_x(NH_2)_y$), NH_x and SiH_x have been proposed to be involved in SiN_x: H films deposition. However, PECVD SiN_x: H deposition processes are not yet fully understood because the plasma chemistry is very complex. [1].

In this study, the effect of pressure and gas mixture ratio on the neutral and ion chemistry of large-area $N_2/NH_3/SiH_4$ ICP-PECVD reactor was investigated using two-dimensional axis-symmetric fluid model. Also, we report the effects of dual power operation to enhance uniformity under high pressure conditions.

2. Simulation conditions

Fig. 1 shows a schematic diagram and final meshes of ICP chamber used in this study. The 4 turn coil antenna 5 mm in radius located above the dielectric window which has a thickness of 20 mm. The wafer chuck (radius, 250 mm; height, 50 mm) located 15 cm below the window. The mixture gas is injected constantly at 100 sccm below the dielectric window and evacuated through the underside of the chamber. At the inlet, the gas mixture ratios were varied as follows: N_2 (60~90 %), NH_3 (5~20 %), and SiH_4 (5~20 %). The neutral gas temperature is fixed at 500 K. The pressure was varied from 10 to 50 mTorr and maintained constantly by the boundary condition of the gas outlet. The driving frequency was 13.56 MHz and the total input power was fixed at 1000 W in all conditions. In dual power modes, the power ratio between 2 inner coils and 2 outer coils were varied for optimization.

Ampere's law, continuity equation, Poisson's equation, and so on are used as the governing equations, and the gas flow in the chamber is considered using the Navier-Stokes equation. These equations were solved by using the commercially finite-element solver COMSOL Multiphysics [4].

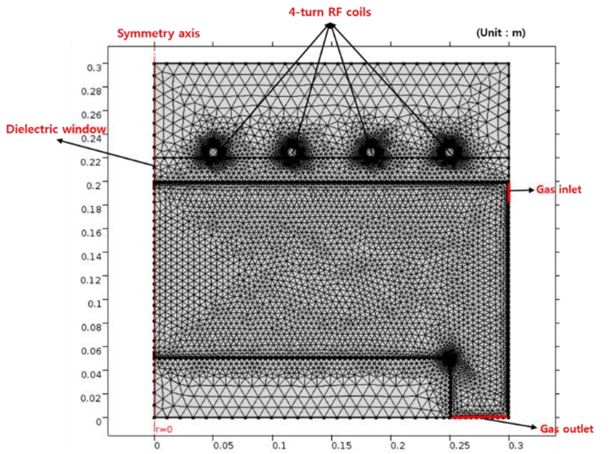

Fig. 1. Schematic diagram and final meshes of ICP chamber

3. Simulation results

Fig. 2 shows the electron density distributions with pressure variation from 10 to 50 mTorr. The gas mixture ratio is $N_2:NH_3:SiH_4$ = 80:10:10. The electron density increases with increasing neutral gas density and becomes more localized below the dielectric window with decreasing diffusivity.

Fig. 3 shows the maximum number density variations of important ions such as N_x^+, NH_x^+, and SiH_x^+ with pressure. Density distributions of these species show similar to electron density distribution at the same pressure. The N_x^+ species are the dominant ions simply because N_2 is the most abundant source gas. Electron impact ionization is important for both N^+ and N_2^+ generation. The N^+ ions density is observed much lower than that of the N_2^+ because of high threshold energy and two-step reaction nature. (electron impact reaction of N atoms from N_2 dissociation) [5]. The N_2^+ ions are dominantly generated not only electron impact ionization but also gas phase reaction between N_2 excited species (N_2 (a´) + N_2 (a´) $\rightarrow$ e + N_2 + N_2^+). The rate of this reaction increases with the pressure and is observed higher than electron impact reaction at 50 mTorr.

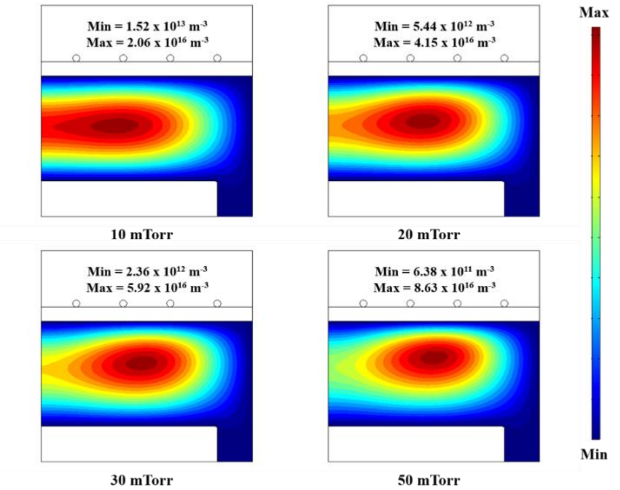

Fig. 2. Contour plots of the electron densities with the pressure (N_2:NH_3:SiH_4 = 80:10:10**)**

N_3^+ and N_4^+ ions are only produced by gas phase reactions such as ion-neutral or associative ionization reactions. Likewise, these two ions are observed to increase linearly with the pressure and become more important in high pressure conditions.

Most of ions generated from SiH_4 are SiH_2^+ and SiH_3^+, and their densities are higher than NH_x^+ ions as shown in Fig. 3. Main generation reactions of SiH_x^+ ions are electron impact ionization with the SiH_4. The SiH_2^+ has higher ionization rate than that of the SiH_3^+. However, the SiH_3^+ ions are also abundantly generated by gas phase reactions which consumes SiH_2^+ and N_2^+ ions. The reaction rates of these reactions have pressure dependency and the SiH_3^+ densities are observed higher than that of the SiH_2^+ at 20 mTorr or more. These results are similarly observed in many other studies [1,6].

The NH_3^+ density is higher than that of the NH_2^+ because of low threshold energy (NH_3^+ and NH_2^+ have ionization threshold voltages of 10.2 and 16.0 eV, respectively). When the pressure is higher than 30 mTorr, NH_4^+ ions become most abundant ions among the NH_x^+ species because they are mainly formed by ion-neutral reaction sand have no loss reactions besides electron attachment.

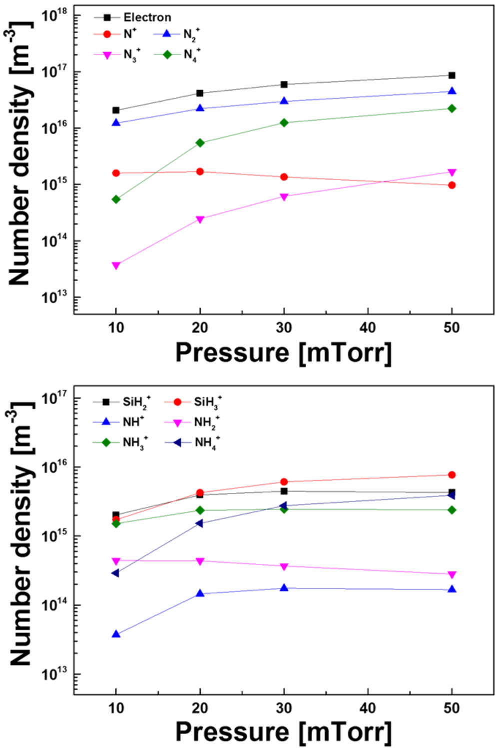

Fig. 3. Maximum density variations of important ions with the pressure (N_2:NH_3:SiH_4 = 80:10:10**)**

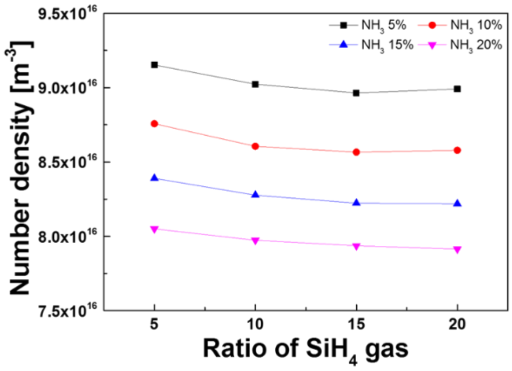

Fig. 4. Comparison of electron density with the gas mixture ratio (50 mTorr)

Fig. 4 shows comparison of the electron densities for the different gas mixture ratio. The pressure is fixed at 50 mTorr to investigate the dependence of the mixture gas ratio. It should be noted that the direct ionization rate of N_2 is lower than that of NH_3 or SiH_4. In spite of this fact, electron density decreases with decreasing N_2 mole fraction. The results come from that the N_2 gas is involved in producing a large amount of electrons by gas phase reactions between N_2 excited species as well as electron impact ionization. The gas reactions become more important as the pressure increases. NH_3 has a greater impact on the reduction of electron density than SiH_4.

As shown in Fig. 2, the higher the pressure, the uniformity of the plasma density worse. The variations of plasma uniformity in ICP are related to the electron energy relaxation length. When the electron relaxation length is shorter than the chamber length, the plasma is generated in the region of electron heating. It is referred to as local electron kinetics, and corresponds to a discharge in which a pressure is high or a magnetic field is applied [7]. For the relatively higher pressure conditions, it is important to optimize plasma heating zone for improving plasma density uniformity

Fig. 5 shows variation of radial plasma density distribution by dual zone antenna power ratio control. The figure corresponds to the electron density at the chamber center according to the power ratio of 2-inner and 2-outer coils. As the power ratio of the inner coils increases, the electron density becomes higher toward the center of the chamber. The case of center to outer antenna power dividing ratio 340/660W shows better density uniformity than single power case. Although not shown here, the uniformity of ions and neutrals density is also improved.

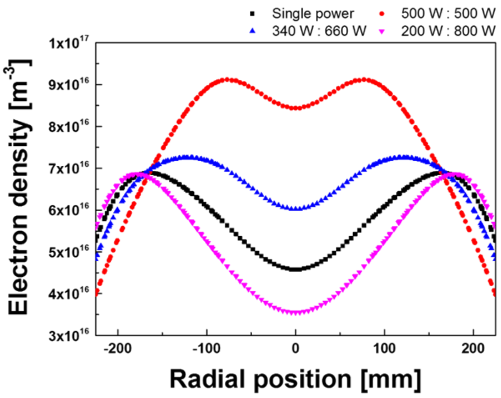

Fig. 5. Improvement of plasma density uniformity using by dual power driven (50 mTorr, N_2:NH_3:SiH_4 = 80:10:10)

4. Conclusion

In this study, the variation of plasma chemistry in $N_2/NH_3/SiH_4$ ICP PECVD system was investigated by using 2D fluid simulation. With increasing pressure, the electron density increases but distributions became more localized below the dielectric window. The ions that are mainly generated by electron impact ionization such as N^+, NH_3^+, NH_2^+, SiH_3^+ and SiH_2^+ show weak pressure dependence. On the other hand, the ions that are mainly generated by charge exchange reaction such as N_3^+, N_4^+, and NH_4^+ had high pressure dependence.

An increase in NH_3 and SiH_4 partial pressure or decrease in N_2 ratio resulted in electron density reduction. This results imply that ionization from exited N_2 species is important. The non-uniformity of neutrals density distribution increased with pressure due to the localized electron density distribution. It was shown that dual antenna power driven method is an effective way to compensate the non-uniformity of the ICP-PECVD in relatively high operation pressure conditions.

5. Acknowledgment

This work was supported by the National R&D Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (Grant No. NRF-2017R1A2B2011106).

6. Reference

[1] H. J. Kim, W. Yang, and J. Joo, J. Appl. Phys., **118**, 043304 (2015).

[2] D. Dergez, J. Schalko, A. Bittner, and U. Schmid, Appl. Surf. Sci., **284**, 348 (2013).

[3] S. P. Singh, P. Srivastava, S. Ghosh, S. A. Khan, and G. V. Prakash, J. Phys.: Condens. Matter, **21**, 095010 (2009).

[4] COMSOL User manual, *Comsol Multiphysics* v5.3a (2017)

[5] A. Bogaerts, Spectrochim. Acta Part B, **64**, 126 (2009)

[6] K. de Bleecker, D. Herrebout, A. Bogaerts, R. Gijbels, and P. Descamps, J. Phys. D: Appl. Phys., **36**, 1826 (2003)

[7] H. –C. Lee and C. –W. Chung, Phys. Plasmas, **20**, 101607 (2013)