Diagnosis of H₂-N₂ glow discharge plasma

H₂-N₂グロー放電プラズマの診断

<u>Hideki Nakada</u>, Kenichi Suda and Mitsuya Motohashi 仲田英起, 須田健一, 本橋光也

School of Engineering, Tokyo Denki University 2-2 Kanda-nishiki-cho, Chiyoda-ku, Tokyo 101-8457, Japan 東京電機大学工学部 〒101-8457 東京都千代田区神田錦町2-2

We evaluated the H_2 - N_2 glow discharge plasma by using the optical emission spectroscopy. When γ increased the emission intensity of the N_2^* and N_2^+ species increased, while the emission intensity of the H_2^* and H^* species decreased. The emission intensity of almost all species increased with the rf power. In this paper, we discuss the relationship between the emission intensities of all emission species. It was inferred that while the intensity of emission is decided by the energy level, the intensity is related to the internal reactions among species in the plasma discharge. Furthermore, it was found that the optical emission characteristics of the species change when the energy of the species is high (above approximately 13 eV).

1. Introduction

Plasma generated using the H₂-N₂ gas is widely used for the surface treatment of steel, resin and semiconductor materials [1]. There have been many studies on the surface modification of silicon-based materials, particularly because of the development of novel high-quality devices [2,3]. It is well known that the radicals and ions in the plasma play an important role in the surface treatment. Therefore, the analysis of these species (ions and radicals) is important. However, the diagnosis of the H₂-N₂ plasma is very difficult because the mechanisms of the decomposition and excited state reactions are very complicated. In previous studies, the plasma has been evaluated optical with the probe method, emission spectroscopy (OES), and mass spectroscopy. In particular, OES is more convenient method. Therefore, in this study, we evaluated the H₂-N₂ rf glow discharge plasma by using the OES. In addition, the decomposition and excited state reactions were studied.

2. Experimental method

Diode-type CVD and source gas separated plasma CVD (SSP-CVD) methods were used to generate H_2 - N_2 plasma. Fig.1 shows the structure of the electrode in the reaction chamber, and the OES apparatus used in the SSP-CVD method [4]. Between the anode and cathode, the reaction chamber was divided into three chambers—A, B, and C—by using an SS plate electrode with holes and an SS mesh electrode. N_2 and H_2 were introduced into the chambers A and B. RF power (13.56 MHz) was supplied to the cathode and mesh electrode by using two power supplies. Table 1



Fig.1 Electrode structure in the SSP-CVD reactor, and OES [4].

Table 1 Plasma conditions for SSP-CVD

Range	
Chamber A	Chamber B
99.998% N ₂	99.99999% H ₂
2-10 sccm	60 sccm
RFp = 5-25 W	RFq = 5 W
133 Pa (1 Torr)	
	Chamber A 99.998% N ₂ 2-10 sccm RFp = 5-25 W

 $1 \text{ sccm} = 1 \text{ cm}^3/\text{min}$ at 760 Torr, 20 °C

shows the plasma generation conditions. The gas flow rate ratio $\gamma [N_2/(H_2+N_2)]$ and the rf powers RFp and RFq were varied. In the case of the diode method, the plasma condition was almost the same as that in the SSP-CVD method. Fig.2 shows the potential energy levels of N₂, H₂, and H [5]. The emission species produced by the N₂* 1st positive system, N₂* 2nd positive system, N₂⁺ 1st negative system, H₂*, and H* (H_a and H_β) were observed. Then, the emission intensity of the species, I(N₂* 1st Pos.), I(N₂* 2nd Pos.), I(N₂⁺ 1st Neg.), I(H₂*), I(H_a), and I(H_β), was measured by OES.



3. Results and discussion

When γ increased, I(N₂* 1st Pos.), I(N₂* 2nd Pos.), and $I(N_2^+ \text{ 1st Neg.})$ increased, while $I(H_\alpha)$, $I(H_{\beta})$, and $I(H_{2}^{*})$ decreased in both methods. The emission intensity of almost all species increased with the rf power. From these results, we now discuss the relationship between the emission intensities of all species. Figs.3(a) and (b) show the relationship between $I(N_2^+ 1st Neg.)$ and $I(N_2^* 1st Pos.)$ and between $I(N_2^* 2nd Pos.)$ and $I(N_2^* 1st Pos.)$ Pos.). I(N₂* 2nd Pos.) and I(N₂⁺ 1st Neg.) increased with $I(N_2^* \text{ 1st Pos.})$. $I(N_2^+ \text{ 1st Neg.})$ in the diode CVD was greater than that of the SSP-CVD (Fig.3(a)). The relationship between $I(N_2* 1st Pos.)$ and I(N₂* 2nd Pos.) was the same in both SSP-CVD and diode CVD (Fig.3(b)). Figs.4(a) and (b) show the relationship between $I(H_2^*)$ and $I(H_a)$ and between $I(H_{\beta})$ and $I(H_{\alpha})$. $I(H_{\beta})$ and $I(H_{2}^{*})$ increased with $I(H_{\alpha})$. $I(H_{2}^{*})$ in SSP-CVD was greater than that in diode CVD (Fig.4(a)). Furthermore, the relationship between $I(H_{\alpha})$ and $I(H_{\beta})$ was the same in both methods (Fig.4(b)). From the energy levels of the species in Fig.2, it was found that the energy level of the N₂* 2nd positive was closer to that of



Fig.3 Relation between $I(N_2^+ \text{ 1st Neg.})$ and $I(N_2^* \text{ 1st Pos.})$ and between $I(N_2^* \text{ 2nd Pos.})$ and $I(N_2^* \text{ 1st Pos.})$.



Fig.4 Relation between $I(H_2^*)$ and $I(H_{\alpha})$ and between $I(H_{\beta})$ and $I(H_{\alpha})$.

the N_2^* 1st positive than to the energy level of the N_2^+ 1st negative. It was also found that the energy level of H_{β} was closer to that of H_{α} than to the energy level of H₂*. Hence, I suspect that the ratio of I(N₂* 2nd Pos.) to I(N₂* 1st Pos.) and the ratio of $I(H_{\beta})$ to $I(H_{\alpha})$ are constant regardless of the type of CVD reactor. $I(N_2^+ 1st Neg.)$ in diode CVD was greater than that in SSP-CVD (Fig.3(a)). $I(H_2^*)$ in SSP-CVD was greater than that in diode CVD (Fig.4(a)). In other words, while the intensity of emission is decided by the energy level, it is also related to the internal reactions among species in the plasma discharge. In addition, it was found that the optical emission characteristics of the species change when the energy of the species is high (above approximately 13 eV).

4. Conclusion

In the H₂-N₂ glow discharge plasma, the optical emission intensities of N_2^+ and H₂* depend on the type of chamber used. It was found that it is important to make observations in the range over about 13 eV for this plasma. Furthermore, it was inferred that the decomposition and exited state reactions of H₂ differed from those of N₂ gas. In a future study, the reaction process of H₂ and N₂ gases will be discussed.

References

- [1] H. Nagai, et al.: Jpn. J. Appl. Phys., Part 2, 42 (2003) L212.
- [2] L. T. Canham: Appl. Phys. Lett., 57 (1990) 1046.
- [3] V. Lehmann, et al.: Appl. Phys. Lett., 58 (1991) 856.
- [4] M. Motohashi, et al.: Electron. Comm. Jpn., Part 2, 90, 2 (2007) 9.
- [5] R. W. B. Pearse, et al.: *The Identification of Molecular Spectra* (Chapman and Hall, London, 1976) 4th ed., p.217.