# Relationship between properties of $SiN_x$ film and cluster incorporation using $SiH_4$+$N_2$ multi hollow discharge plasma CVD

Y. Sasaki[1], S.Nagaishi[2], K.Tanaka[2], H.Hara[2], S.Yamashita[2], K.Kamataki[2], N.Itagaki[2], K.Koga[2], and M.Shiratani[2]

[1]*Department of Electrical Engineering and Computer Science, School of Engineering, Kyushu University, Japan*

[2]*Graduate School and Faculty of Information Science and Electrical Engineering*

**Abstract:** We manufactured silicon nitride film to investigate the condition of cluster creation and the relationship between film quality and cluster content using $SiH_4$ + $N_2$ Multi Hollow Discharge Plasma CVD (MHDPCVD). These results were that the amount of cluster incorporation was changed by nitrogen flow rate. In addition, N/Si and the H contents in SiN film increased as the amount of cluster incorporation increased. On the other hand, refractive index and extinction coefficient decreased, and became constant as cluster incorporation increased.

**Keywords:** plasma CVD, silicon nitride, cluster incorporation

## 1. Introduction

In recent years, the Internet of Things (IoT) have rapidly became spread[1], and it is expected that the total number of them will be 125 billion over the world in 2020[2]. Improvements of productivity and quality of a semiconductor are required because of a rise of the total number and the variety of devices. Especially, a progress of silicon nitride (SiN) which is a main material of semiconductor must be vital.

SiN has following characters such as high resistance, dielectric constant, stability and density, and resists hydrofluoric acid etching well [3][4]. In addition, its electric character can be widely adjusted, by changing its construction [5][6]. For these points, SiN is used in precision equipments such as CMOS circuit [7].

SiN is manufactured in Thermal Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD), or Plasma CVD. In Thermal CVD method, there is a problem that substrate's construction is changed by high temperature in the process [4]. Furthermore, PVD method damages film because of particle collision [4]. In Plasma CVD method, film is deposited in low temperature room [4]. In fact, there are cases that high quality SiN film was manufactured by the plasma process. However, its deposition process is so complex that a relationship between its process and a quality of deposited film has not been cleared yet [5][8][9]. For certain manufacture of optimal film, it is needed to clear the relationship. Other laboratories have experimented about deposition rate, refractive index, or bond strength of various atoms, changing N/Si flow rate. They proved that flow rate of atoms of which plasma gas is consist effects film [10-16]. However, there are cluster and radical molecule in plasma gas, and it is suspected that their amount and rate also effect film.

Our laboratory's past study is to product solar cell whose photodegradation is least by MHDPCVD [17-19] method. In this study, deposition rate has been measured by using Crystal Oscillator Type Film Thickness Meter (QCM). QCM can measure deposition rate and composition rate of cluster by using a filter. The purpose of this study is to investigate the condition of cluster creation and how cluster effects on film.

## 2. Experimental Methods

Figure.1 shows the schematic of MHDPCVD device with QCMs. Plasmas were sustained in 79 holes of the electrodes. The diameter and length of the holes are 5.0 mm and 9.8mm. The powered electrode was connected to a 60MHz RF power source through a matching network. $SiH_4$ and $N_2$ were fed through the upper side of the reactor, then passed through the holes in the electrodes, and pumped out. The gas flow rate of $SiH_4$ was 10 sccm and of $N_2$ was set in a range of 30 to 120 sccm. The total pressure was 0.5 Torr. The substrate temperature was 55℃ (= 328K). The discharge power was 20 W. The deposition time is 1 hour. Nano-particles generated in plasmas were transported toward the downstream region by the gas flow, because their diffusion velocity was less than the gas velocity. Therefore, we can realize a cluster-rich condition in the downstream region.

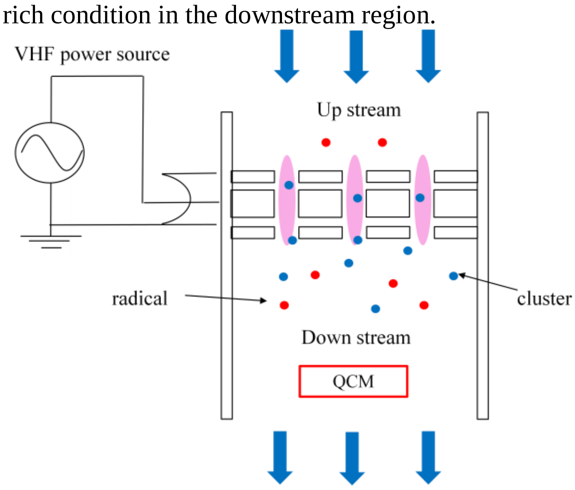


Fig. 1. Schematic of MHDPCVD device

Figure 2 shows system of QCM.

To measure deposition rate ($DR$) and the amount of cluster incorporated into SiN films, we employed three QCMs, which were set 20 mm below the lowest electrode. The resonance frequency of the quartz crystal decreases with increasing mass deposited on the crystal. The channel A of the QCM was used to measure the DR of radicals and SiN clusters ($DR_{total}$). The channel B of the QCM was appliedto measure the DR of radicals ($DR_{radical}$) by setting the cluster- eliminating filter above the microbalance. The channel C of the QCM was used as a reference sensor because the resonance frequency of the QCM depends on ambient temperature and pressure. The filter of channel B cuts off only all clusters, but also a certain percentage of radicals. $DR_{total}$ and $DR_{full\_radical}$, a deposition rate of all radicals, are expressed by the following equation. $Tr$ is a radical transmittance.

$$DR_{\mathrm{full\_radical}} = Tr \times DR_{radical} \tag{1}$$

$$DR_{total} = DR_{cluster} + DR_{full\_radical} \tag{2}$$

$$DR_{total} = DR_{cluster} + \frac{DR_{radical}}{Tr} \tag{3}$$

$V_f$, which is the cluster volume fraction, is defined as equation (4).

$$Vf = \frac{DR_{cluster}}{DR_{total}} \tag{4}$$

However, the value of $Tr$ in SiN is unknown, so a parameter $R$, which is expressed as equation (5), is used as the amount of cluster incorposition parameter instead of $Vf$. The relationship between $Vf$ and $R$ has a significant positive correlation.

$$\begin{aligned} R &= \frac{DR_{total}}{DR_{radical}} \\ &= \frac{DR_{total}}{Tr \times DR_{full\_radical}} \\ &= \frac{1}{Tr} \times \frac{DR_{total}}{DR_{total} - DR_{cluster}} \\ &= \frac{1}{Tr} \times \frac{1}{1 - \frac{DR_{cluster}}{DR_{total}}} \\ &= \frac{1}{Tr} \times \frac{1}{1 - Vf} \end{aligned} \tag{5}$$

The hydrogen content $H$ of the films was estimated from the absorption coefficient for the Si-H and N-H stretching modes through a FTIR measurement [a]. The refractive index $n$ and extinction coefficient $k$ of SiN films were obtained using an elipsometer. In addition, $N/Si$ was calculated from XRF.

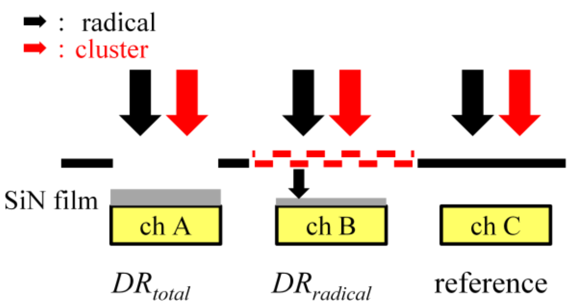


Fig. 2. Schematic of QCM

## 3. Results and Discussion

Figure 3 shows the deposition rate $DR_{total}$ and $DR_{radical}$ as a function of amount of cluster incorporation $R$. The $DR_{total}$ tends to increase as $R$ increasing. The $DR_{radical}$ is almost same. This result shows high $R$ means the high cluster volume fraction in SiN films.

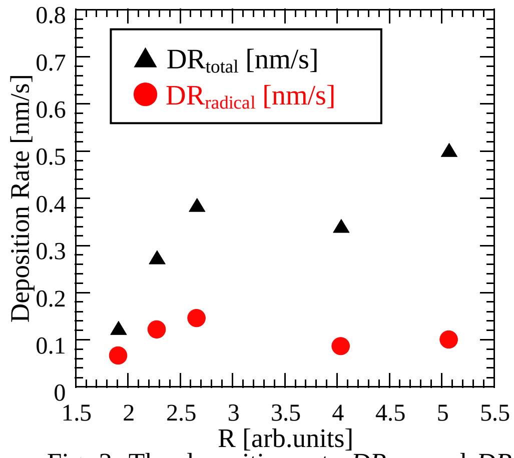


Fig. 3. The deposition rate $DR_{total}$ and $DR_{radical}$ as a function of $R$

Figure 4 shows nitrogen flow rate dependence of amount of cluster incorporation $R$. $R$ had a maximum value when $N_2$ flow rate was 50sccm. Figure 5 shows the $N/Si$ and as a function of $R$. The $N/Si$ tends to increase as R increasing.

This result suggests that deposited cluster has much nitrogen.

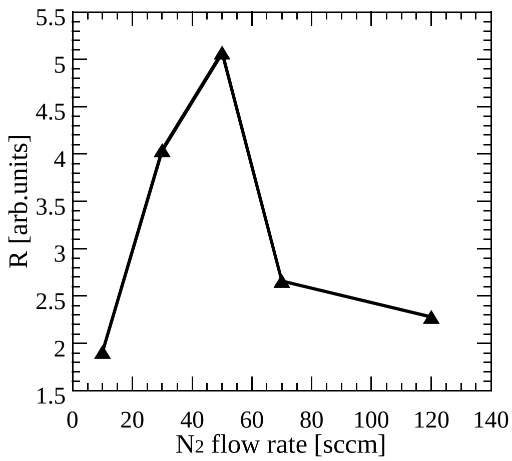


Fig. 4. Amount of cluster incorporation $R$ as a function of nitrogen flow rate

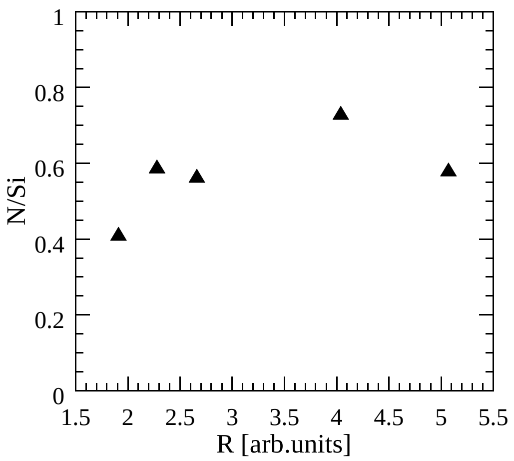


Fig. 5. *N/Si* as a function of *R*

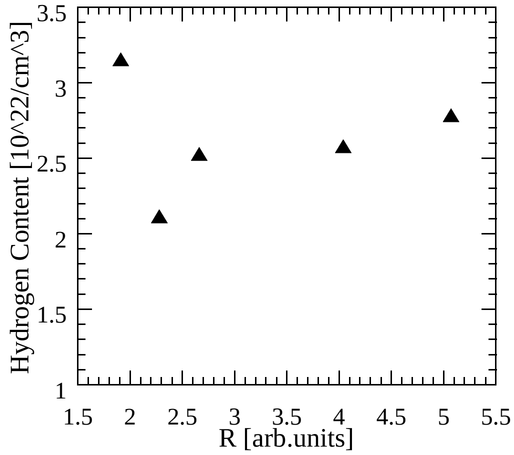


Fig. 7. The *H* content of SiN flms as a function of *R*

Figure 6 shows the refractive index *n* and extinction coefficient *k* as a function of *R*. The refractive index *n* and extinction coefficient *k* decrease from *R* = 1.9 to ~ 2.5 and are almost constant at *R* > ~ 2.5.

Figure 7 shows the relationship between hydrogen content *H* and *R*. The hydrogen content increases with increasing the amount of cluster incorporation *R*, except the condition of *R* ~ 1.9. The *H* content increase 1.3 times when the *R* increases from the value 2.3 to 5.0. This result shows the amount of cluster incorporated into film has positive correlation with the *H* content in the film. It implies that the bond of cluster has the hydrogen.

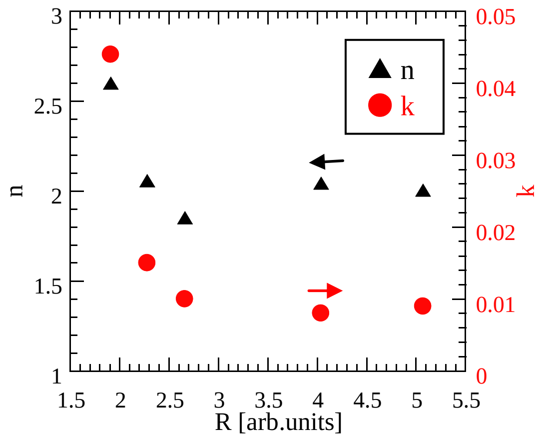


Fig. 6. Refractive index *n* and extinction coefficient *k* as a function of *R*

**4. Sammary**

The cluster incorporation *R* did not increase as nitrogen flow rate increasing. *R* had a maximum value when $N_2$ flow rate was 50 sccm. The amount of cluster incorporation was changed by nitrogen flow rate. In addition, *N/Si* and the *H* content in SiN film increased as the amount of cluster incorporation increased. On the other hand, refractive index and extinction coefficient decreased and became constant as cluster incorporation increased. It is suggested that the properties of SiN filoms are dependent of cluster incorporation.

**5. References**

[1] K.Inoue, Mini Special Issue “The Role of Service Science and Business Application for the Fourth Industrial Revolution”, **11**, 1 (2017)
[2] J.Howell (2017), HIS Markit TECHNOLOGY. https://technology.ihs.com/596542/number-of-connected-iot-devices-will-surge-to-125-billion-by-2030-ihs-markit-says
[3]Y.Mori, Confidentiality Engineering Journal, **70**, 2, (2004)
[4] M.Sawada, Characteristics of ECR plasma silicon nitride film, **30**, 3 (1987)
[5] M.Narita, Fuji Time, **78**, 4 (2005)
[6] S.Yasuda, Applied physics, **50**, 60 (1981)
[7]F.Otuka, Doctoral thesis from the University of Tsukuba (2009)
[8]H.Sakai, J-STAGE, **31**, 4 (1988)
[9]Z.Shao, Y.Chen, H.Chen, Y.Zhang and F.Zhang, Optics Express, **24**, 3 (2016)
[10]Y.Manabe and T.Mitsuyu, Journal of applied physics, **66**, 2475 (1989)
[11]H.P.Zhou, D.Y.Wei, L.X.Xu, Y.N.Guo, S.Q.Xiao, S.Y.Huang and S.Xu, Applied Surface Science, **264** (2013)
[12]Sang-Soo Han, Byung-Hyuk Jun, Kwangsoo No and Byeong-Soo Bae, Journal of The Electrochemical Society, **145**, 2 (1998)
[13]H.J.Stein, V.A.Wells and R.E.Hampy, Journal of The

Electrochemical Society, **126**, 10, (1983)
[14]T.Makino, Journal of The Electrochemical Society, **130**, 2 (1983)
[15]F.Ay and A.Aydinli, Optical Materials, **26**, 1 (2004)
[16]A.Elamrani, I.Menous, L.Mahiou, R.Tadjine and A.Lefgoum, Renewable Energy, **33**, 10 (2008)
[17]K.Koga, T.Inoue, K.Bando, S.Ieshita, M.Shiratani and Y.Watanabe, Journal of Applied Physics, **44**, 2 (2005)
[18]S.Toko, Y.Torigoe, K.Keya, H.Seo, N.Itagai, K.Koga and M.Shiratani, Japanese Journal of Applied Physics, **55**, 1S (2016)
[19]K.Keya, T.Kojima, Y.Torigoe, S.Toko, D.Yamashita, H.Seo, N.Itagaki, K.Koga and M.Shiratani, Japanese Journal of Applied Physics, **55**, 7S2 (2016)