Relationship between properties of SiN_x films and cluster incorporation studied using SiH_4+N_2 multi hollow discharge plasma CVD

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Abstract: To study relationship between properties of amorphous silicon nitride films and cluster incorporation, we deposited SiN_x films using SiH_4 + N_2 multi hollow discharge plasma CVD. The cluster incorporation amount depends considerably on N_2 flow rate. The atomic composition ratio, N/Si of films tends to increase with the cluster incorporation amount, whereas the H content in films is around 2-3x10^{22} cm^{-3} irrespective of the cluster incorporation amount. The refractive index and extinction coefficient decrease and become constant as the cluster incorporation amount increases. The cluster incorporation amount is one of the tuning knobs of the properties of SiN_x films.

Keywords: plasma CVD, silicon nitride, cluster incorporation

1. Introduction

In recent years, the Internet of Things (IoT) devices have rapidly become spread, and their total number of them is expected to be 125 billion over the world in 2020[1]. Semiconductor devices play central roles in IoT world. Among various fabrication processes of the semiconductor devices, plasma CVD of amorphous silicon nitride (SiN_x) films is one of the key processes especially for flexible devices [2-13].

SiN_x films have got wide applications as passivation insulting layer, interlayer dielectric, capacitor dielectric, etc. The properties of silicon nitride films can be widely adjusted by controlling the various process parameters such as deposition time, deposition temperature, pressure, reactants flow rate and substrate temperature during the fabrication [3]

SiN_x films are fabricated by various methods: Thermal Chemical Vapor Deposition (CVD), Physical Vapor Deposition (PVD), Plasma CVD, and so on. Among these methods, plasma CVD realizes low temperature deposition of high quality amorphous SiN_x films. Furthermore, PVD method damages film because of particle collision [4]. However, plasma CVD deposition process is so complex that a relationship between its process and properties of films has not been fully clarified yet [3, 5]. So far, most previous studies report relationship between the external process parameters and properties of films [7-13]. However, little study has been done to explore effects of deposition precursors such as radicals and clusters on the properties of SiN_x films deposited by plasma CVD.

To shed light on the relationship between deposition precursors on the properties of plasma CVD films, we have developed multi hollow discharge plasma CVD (MHDPCVD) method as well as an in-situ measurement method of cluster contribution to films by using three quartz crystal microbalances (QCMs) together with a cluster eliminating filter [14-19]. The purpose of this study is to investigate effects of cluster incorporation into SiN_x films on the film properties. For this purpose, we applied the MHDPCVD and QCM methods to SiN_x film deposition process.

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 that of N_2 was set in a range of 30 to 120 sccm. The total pressure was 0.5 Torr. The substrate temperature was 328K. The discharge power was 20 W. The deposition time was 1 hour.

Clusters generated in plasmas were transported toward the downstream region by the gas flow, because their diffusion velocity was less than the gas velocity. Therefore, cluster incorporation films were depositied in the downstream region.

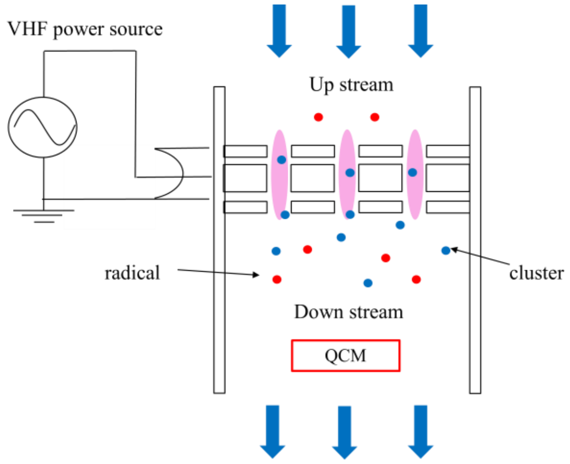

Fig. 1. Schematic of MHDPCVD device

Figure 2 shows the system of QCMs together with the cluster eliminating filter.

To measure deposition rate (*DR*) and the amount of cluster incorporated into SiN_x films, we employed three QCMs, which were set at 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 QCM was used to measure total DR due to radicals and clusters (DR_{total}). The channel B of QCM was applied to measure DR of radicals ($DR_{radical}$) by setting the cluster eliminating filter above the microbalance. The channel C of QCM was used as a reference sensor because the resonance frequency of the QCMs depends also on the ambient temperature and pressure. The filter of channel B cuts off not only above 99% cluster flux, but also a part of radical flux. DR_{total} and $DR_{full\_radical}$, a deposition rate of all radicals, are expressed by the following equation. *Tr* is a radical transmittance through the cluster eliminating filter.

$$DR_{\text{full\_radical}} = Tr \times DR_{radical} \quad (1)$$

$$DR_{total} = DR_{cluster} + DR_{full\_radical} \quad (2)$$

$$DR_{total} = DR_{cluster} + \frac{DR_{radical}}{Tr} \quad (3)$$

V_f, which is the cluster volume fraction in films, is defined as eq (4).

$$Vf = \frac{DR_{cluster}}{DR_{total}} \quad (4)$$

Since the value of *Tr* in SiN_x has not been determined yet, another parameter *R*, which is defined as eq (5), is used as the index of cluster incorporation amount instead of *Vf*. The relationship between *Vf* and *R* has a positive correlation as follows.

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

The hydrogen content *H* of films was deduced from the absorption coefficient for the Si-H and N-H stretching modes of FTIR absorption spectrs.

The refractive index *n* and extinction coefficient *k* of SiN_x films were obtained using an elipsometer.

In addition, the atomic composition ratio, *N/Si* was obtained by XRF.

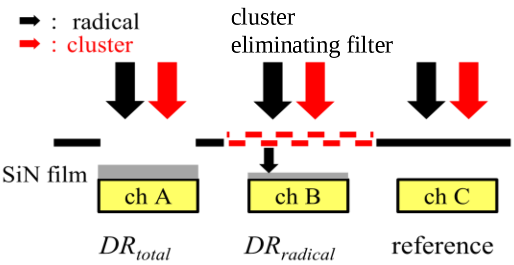

Fig. 2. Schematic of QCMs together with a cluster eliminating filter

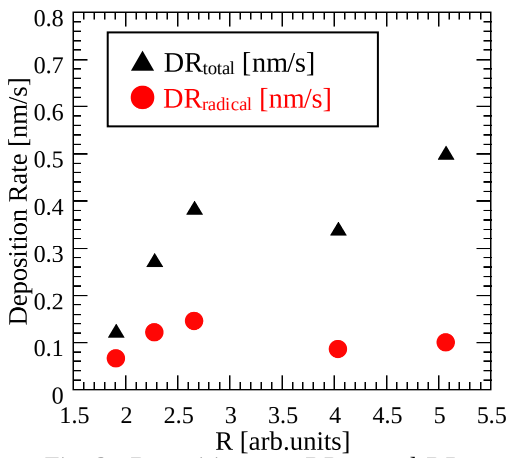

Fig. 3. Deposition rate DR_{total} and $DR_{radical}$ as a function of R

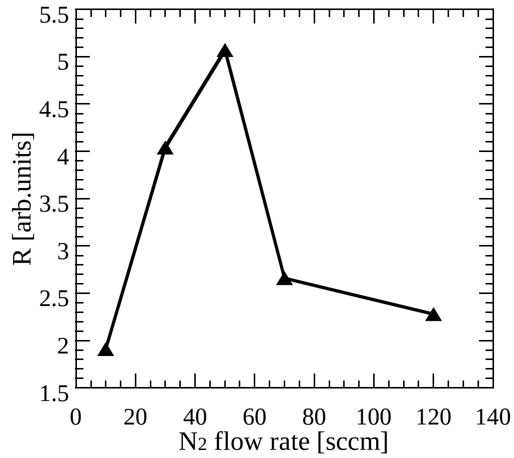

Fig. 4. Amount of cluster incorporation R as a function of N_2 flow rate

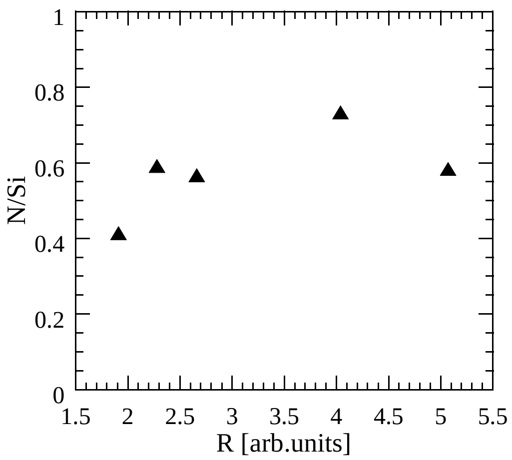

Fig. 5. *N/Si* as a function of R

3. Results and Discussion

Figure 3 shows the deposition rate DR_{total} and $DR_{radical}$ as a function of cluster incorporation amount *R*. The DR_{total} tends to increase with *R* whereas $DR_{radical}$ is almost the same. These results show that clusters are major film precursors for films $R > 2.3$.

Figure 4 shows N_2 flow rate dependence of the amount of cluster incorporation *R*. *R* depends on the N_2 flow rate in a convex way and it has a maximum value when N_2 flow rate is 50sccm. Figure 5 shows the *N/Si* and as a function of *R*. *N/Si* tends to increase with R. This tendency suggests clusters contain much nitrogen and deposition od such clusters enhances the N content in films.

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 around 2-3x10^{22} cm^{-3} irrespective of the cluster incorporation.

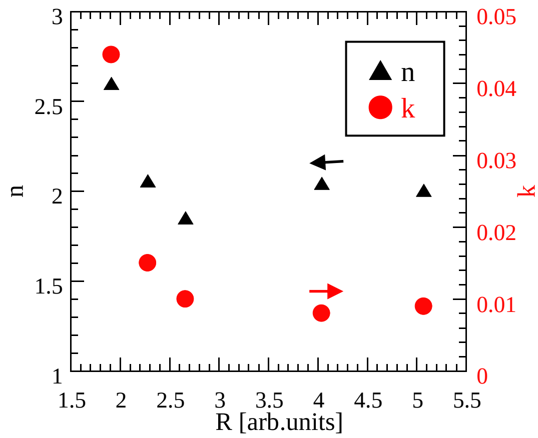

Fig. 6. Refractive index *n* and extinction coefficient *k* as a function of R

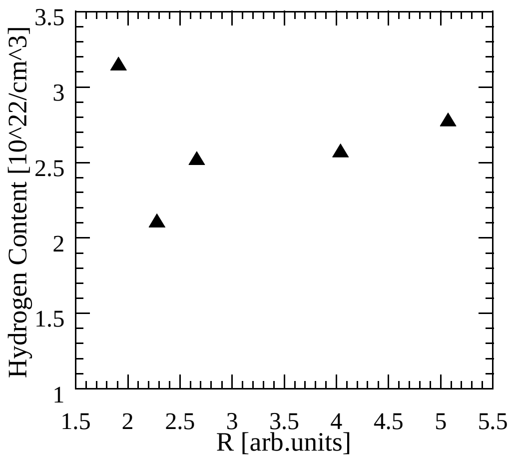

Fig. 7. The *H* content of SiN_x films as a function of R

4. Sammary

The cluster incorporation *R* depends on the N_2 flow rate in a convex way and it has a maximum value when N_2 flow rate is 50 sccm. The atomic composition ratio, *N/Si* of films tends to increase with the cluster incorporation amount, whereas the H content in films is around 2-3x10^{22} cm^{-3}. The refractive index and extinction coefficient decrease and become constant as the cluster incorporation amount increases. Therefore, the cluster incorporation amount is one of tuning knobs of the properties of SiN_x films.

5. References

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