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Effect of DC Bias Voltage on the Characteristics of Low Temperature Silicon–Nitride Films Deposited by Internal Linear Antenna Inductively Coupled Plasma Source

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1. Introduction

Silicon–nitride (SiN) films have been widely used in various important applications ranging from semiconductor devices to flat panel displays, such as passivation layers for diverse applications ranging from semiconductor devices to flat panel displays, silicon–nitride films have been widely used in various high density plasma sources, such as inductively coupled plasmas (ICPs), and electron cyclotron resonance (ECR), etc., have also been utilized. Especially, among the various high density plasma sources, ICP sources have been most widely used, due to their relatively simple source structure, in addition to their easier scalability to a larger area. In addition, as the source size becomes larger than a meter, the standing wave effect and capacitive coupling to the plasma becomes more significant. Therefore, in order to overcome these problems, many researchers have studied internal type ICP sources with various ICP source antenna configurations. For example, in the case of Wu et al., a traveling wave was introduced to overcome the standing wave problem caused by the long internal antenna length connected in series as well as to obtain uniform plasmas. In the case of Satsuhara et al., the low-inductance internal antenna configuration was used to suppress the electrostatic coupling and to obtain the high density plasma. However, even with the ICP-PECVDs, it is still difficult to obtain both high quality silicon nitride films required for the gate dielectrics at the deposition temperatures lower than 100 °C. In this study, to obtain high quality silicon nitride films at a low temperature (<100 °C), the dc biasing of the substrate was utilized during the deposition of the SiN thin film with an ICP source. For the extension of the ICP source to a larger area, an internal linear-type ICP, which is extendable to sizes larger than 2 m, was used with the reactant gases (NH₃/SiH₄) and the effects of the ratio of NH₃ to SiH₄ and dc biasing on the properties of the thin film were investigated.

2. Experimental Methods

A schematic diagram of the experimental setup consisting of an ICP-PECVD system with an internal linear U-type antenna used in this study is shown in Fig. 1(a). A square shaped substrate with dimensions of 175 × 175 mm² was installed in the cylindrical processing chamber having a diameter of 380 mm, and a U-type antenna module consisted of two internal linear antennas connected to each other (total length of the U-type antenna was 1650 mm and the distance between two linear antennas was 250 mm) was installed.
above the processing chamber. The inner conductor of each antenna was made of copper tube (10 mm in diameter) and was shielded by a quartz dielectric tube (33 mm diameter) to isolate it from the plasma. For the cooling of the antenna, water was flowed through the copper tube. The distance between the U-type antenna and the substrate holder was 150 mm. As shown in Fig. 1(b), one side of the U-type antenna was connected to a 13.56 MHz rf power supply through an L-type matching network and the other side of the antenna was connected to the ground. Also, a 12.56 MHz rf power supply was used to deliver the power to the substrate by the application of the 12.56 MHz rf power supply through an L-type matching network and the other side of the antenna was connected to the ground. Also, a 12.56 MHz rf power supply was used to deliver the power to the substrate for the formation of the dc bias voltage.

A gas mixture consisting of NH$_3$/SiH$_4$/Ar was fed to the chamber from the top of the chamber, where SiH$_4$ and NH$_3$ gases were used as the reaction gases and Ar gas as the ignition gas. The SiN$_x$ films were deposited on p-type (100) silicon substrates. The total gas flow rate of the NH$_3$/SiH$_4$/Ar gas mixture was maintained at 110 sccm and the operating pressure at 10 mTorr. The 13.56 MHz rf power supplied to the ICP source and the dc bias voltage supplied to the substrate by the application of the 12.56 MHz rf power were varied from 300 to 1000 W and from 0 to $-150$ V, respectively. While depositing the SiN$_x$ thin film, the substrate temperature was increased slowly with the increase of processing time due to the exposure to the plasma and ion bombardment, however, due to the cooling of the substrate holder during the processing, the substrate temperature could be maintained at the temperature below 100°C for all of the experimental conditions.

The compositions, binding states and refractive indices of the SiN$_x$ thin films were measured using a Fourier transform infrared spectrometer (FTIR; Bruker IFS-66/S) and an ellipsometer (J. A. Woollam M-2000, VASE Manager) at a wavelength of 632.8 nm, respectively. The ratio of Si/N in the deposited thin film was also investigated using X-ray photoelectron spectroscopy (XPS; Thermo VG MultiLab 2000, Mg K$_\alpha$ source). In addition, metal/insulator/semiconductor (MIS) capacitors having the structure of Al/insulator (deposited SiN$_x$)/p-Si were fabricated and their flat-band voltage and hysteresis voltage at a high frequency (1 MHz) were measured by the capacitance–voltage ($C$–$V$) method. The thicknesses of the Al layer and SiN$_x$ of the MIS capacitors were maintained at 100 and 300 nm, respectively. The $C$–$V$ curve measurement system consisted of a switch control unit (HP 3488A), voltage source (Keithley 230), capacitance meter (Boonton 17200) and programmable electrometer (Keithley 617). A step profilometer (Tencor Alphastep 500) was used to measure and adjust the thickness of the film.

### 3. Results and Discussion

Figure 2 shows the effect of the NH$_3$/SiH$_4$ ratio and rf power to the ICP source on the deposition rate of SiN$_x$. The operating pressure was maintained at 10 mTorr by keeping the Ar gas flow rate at 50 sccm and the flow rate of NH$_3$ + SiH$_4$ at 60 sccm. When the gas ratio of NH$_3$/SiH$_4$ was varied, the rf power was maintained at 500 W and when the rf power was varied, the gas ratio of NH$_3$/SiH$_4$ was kept at 2. As shown in Fig. 2, when the gas ratio of NH$_3$/SiH$_4$ was increased from 2 to 14, the deposition rate decreased from 62 to 15 nm/min, due to the decrease of in the proportion of the silicon source in the gas mixture. Also, when the ICP source power was increased from 300 to 1 kW, the deposition rate increased from 27 to 70 nm/min, although the increase of the deposition rate appears to slowly saturate from 500 W. The slow saturation of the deposition rate with increasing ICP power appears to also be related to the depletion of the silicon source in the gas mixture at a high deposition rate (that is, silicon precursor limitation). In Fig. 2, the effect of the dc bias voltage in the range from 0 to $-150$ V on the deposition rate is also shown for different
gas mixture ratios of NH₃/SiH₄. As shown in the figure, increasing the dc bias voltage to −150 V slightly decreased the deposition rate and, at −150 V, a decrease in the deposition rate of about 10% was observed for most of the gas mixtures. The decrease of the deposition rate with increasing dc bias voltage is believed to be related not only to the possible sputter etching during the deposition, but also to the increased density of the thin film deposited by the ion bombardment on the substrate.17,18)

For the SiNₓ thin films deposited using various gas mixtures at an ICP power of 500 W without a dc bias voltage, the chemical bonding states were investigated by FTIR and their FTIR broadband absorption spectra in the wavenumber range of 600–4000 cm⁻¹ are shown in Fig. 3(a). The SiNₓ thin films were deposited on p-type (100) silicon wafers and the thickness was maintained at 300 ± 20 nm. As shown in the figure, a strong Si–N band peak was observed at 880–900 cm⁻¹,19) and smaller peaks related to Si–O, Si–H, and N–H bonding were observed at 1170, 2190, and 3350 cm⁻¹, respectively.20) In addition, a small broad Si–O–Si bonding peak was also observed at about 1060 cm⁻¹ on the shoulder of the Si–N peak. As shown in Fig. 3(a), increasing the gas mixture ratio of NH₃/SiH₄ decreased the bonding peak intensity related to Si–H, while increasing the peak intensity related to N–H bonding. The decrease of the Si–H bonding peak and increase of the N–H bonding with increasing NH₃/SiH₄ ratio are believed to be related to the bonding of the excess N in the gas mixture with H in the film. The hydrogen in the silicon nitride film is known to affect its dielectric characteristics. By forming Si–H instead of N–H, it can remove the dangling bonds in the film and improve the electrical properties, while the increase in the amount of N–H bonds increases the interface trap density and forms local energy levels in the band gap, which degrade the electrical properties of the deposited silicon nitride.21) The oxygen related bonding peaks at 1060 and 1170 cm⁻¹, which may have originated from the background oxygen in the system, did not vary significantly with the gas mixture ratio. Increasing the gas mixture ratio of NH₃/SiH₄ caused the intensity of the Si–N bonding peak to be slightly increased, while shifting the peak position to the less silicon nitride-like bonding region.

Figure 3(b) shows the variation of the Si–N bonding peak position with the gas mixture ratio of NH₃/SiH₄ in Fig. 3(a) more clearly. In addition, the variation of the refractive index (n) of the deposited SiN thin film with the NH₃/SiH₄ ratio measured by an ellipsometer is also shown. As shown in Fig. 3(b), decreasing the NH₃/SiH₄ ratio from 14 to 2 decreased the peak wavenumber position from 907.5 to 883.3 cm⁻¹, bringing it closer to the more SiN-like bonding position at the expense of other bondings such as silicon oxide.22) The refractive index increased from 1.59 to 1.7 as the NH₃/SiH₄ ratio was decreased from 14 to 2, which is close to that of SiN. This also indicates the formation of more SiN-like bondings in the film. Therefore, by decreasing the NH₃/SiH₄ ratio to 2, a SiN-like thin film having a greater amount of Si–N bonding could be obtained.

In the case of an NH₃/SiH₄ ratio of 2 at an ICP power of 500 W, a dc bias voltage of up to −150 V was applied and the material characteristics were investigated. The FTIR absorption spectra for the Si–N bonding and the refractive index of the deposited SiNₓ measured as a function of the dc bias voltage are shown in Figs. 4(a) and 4(b), respectively. The thickness of the deposited SiNₓ thin films was also maintained at 300 ± 20 nm. As shown in Fig. 4(a), as the dc bias voltage applied to the substrate was increased, the Si–N bonding peak position shifted to a lower wavenumber, varying from 883.3 cm⁻¹ for no bias voltage to 864 cm⁻¹ for a dc bias voltage of −150 V, although no significant shift of the wavenumber was observed at dc bias voltages higher than −100 V. In addition, the intensities of the Si–O bonding related peaks, such as those at 1060 cm⁻¹ and 1170 cm⁻¹, decreased with increasing dc bias voltage. Therefore, it is believed that increasing the dc bias voltage during the deposition of the thin film increased the bonding ratio of Si–N/Si–O in the deposited film and made it more silicon nitride-rich.23) The refractive index measured as a function of the dc bias voltage in Fig. 4(b) increased from 1.7 at no bias voltage to 1.83 at a dc bias voltage of −150 V, which also indicates the formation of a silicon nitride-rich thin film. Kuo et al.18) reported that the refractive index of the silicon nitride gate dielectric layer showing the lowest threshold voltage (Vth) of an MIS device is in the range of 1.8–1.9.

The Si/N ratio and the hydrogen concentration in the deposited film were estimated using an XPS and FTIR spectra in Fig. 3(a), respectively,24,25) and the results are shown in Fig. 5. The Si/N ratio and the hydrogen concen-
Hydrogen concentration and Si/N ratio of the films as a function of the dc bias voltage for a gas ratio of NH$_3$/SiH$_4$ = 2 and an rf ICP source power of 500 W.

MIS capacitors composed of Al (100 nm)–SiN$_x$ (300 nm)–p-type (100) silicon were fabricated with the SiN$_x$ thin films deposited at different dc bias voltages on the substrate. The interface between SiN$_x$ and silicon is the hysteresis voltage, $V_{fb}$. Also, these are slow traps, because the response of the trapped carriers depends not only on the gate voltage, but also on the time of the voltage sweep. The amount of charge ($Q$) trapped in the slow interface trap level tends to shift the threshold voltage ($V_{th}$) of the TFT devices. As shown in Fig. 6, as the dc bias voltage was increased from 0 to $-150$ V, the shift of threshold voltage ($\Delta V_{th}$) caused by decreasing the hysteresis voltage was decreased from 8.1 to 1.8 V. Therefore, a lower interface trap charge density is believed to be obtained under higher dc bias voltage conditions.

Using the $C$–$V$ characteristics shown in Fig. 6 and an ellipsometer, the interface trap charge density of the MIS capacitors and the dielectric constant of the deposited silicon nitride thin films were obtained as a function of the dc bias voltage for NH$_3$/SiH$_4$ = 2 and an ICP power of 500 W and the results are shown in Fig. 7. The trap charge density in the film was mostly due to the $N$–$H$ bonding compared to Si–H bonding, and the hydrogen concentration was decreased with the increase of dc bias voltage possibly due to the removal of hydrogen from the $N$–$H$ bonding in the film by the ion bombardment. The decrease of hydrogen content in the SiN$_x$ thin film is believed to increase the film density and is also related to the change of the film properties shown in Figs. 4(a) and 4(b) with SiN$_x$ and the change of refractive index, respectively. In the case of the Si/N ratio in the film, as shown in the figure, it decreased with the increase of dc bias voltage, therefore, the film became more nitrogen-rich SiN$_x$ thin film with the increase of dc bias voltage.

MIS capacitors were fabricated with the SiN$_x$ thin films deposited at various dc bias voltages, as shown in Fig. 4, and their high frequency (1 MHz) $C$–$V$ characteristics were measured and the results shown in Fig. 6. As shown in Fig. 6, the $C$–$V$ characteristics showed hysteresis under all dc bias voltage conditions, possibly due to the local distribution of the interface charge trap density at the interface between the silicon and SiN$_x$. The hysteresis is due to the differences in the gate voltages during the trapping and escaping of the carriers (electrons or holes) at the interface between SiN$_x$ and silicon. Also, these are slow traps, because the response of the trapped carriers depends not only on the gate voltage, but also on the time of the voltage sweep. The amount of charge ($Q$) trapped in the slow interface trap level tends to shift the threshold voltage ($V_{th}$) of the TFT devices. As shown in Fig. 6, as the dc bias voltage was increased from 0 to $-150$ V, the shift of threshold voltage ($\Delta V_{th}$) caused by decreasing the hysteresis voltage was decreased from 8.1 to 1.8 V. Therefore, a lower interface trap charge density is believed to be obtained under higher dc bias voltage conditions.
of $-100\,\text{V}$, the trap density was decreased to $2 \times 10^{11}\,\text{cm}^{-2}$. Further increasing the dc bias voltage up to $-150\,\text{V}$ slightly increased the trap charge density. A high trap charge density degrades the electrical properties of the fabricated MIS devices by forming an internal electric field. The interface trap density is related to structural defects at the insulator/silicon interface, and its effect on the film properties was also investigated.

4. Conclusions

Using an internal-type ICP source, SiN thin films were deposited at the temperature lower than $100\,\text{°C}$ at various $\text{NH}_3/\text{SiH}_4$ ratios and rf powers applied to the ICP source and the effects of these parameters on the film properties were investigated, in order to evaluate their potential use as the inorganic gate dielectric for organic devices and flexible display devices. In addition, to improve the characteristics of the deposited SiN thin film, a dc bias voltage was applied and its effect on the film properties was also investigated.

Increasing the rf power increased the SiN deposition rate, although the deposition rate at a fixed $\text{NH}_3/\text{SiH}_4$ ratio became nearly saturated at high rf powers, due to the limitation of the silicon source in the gas mixture. Increasing the $\text{NH}_3/\text{SiH}_4$ ratio at a fixed total gas flow rate also decreased the deposition rate, due to the limitation of the silicon source in the gas mixture. The SiN thin film deposited with a gas mixture ratio of $\text{NH}_3/\text{SiH}_4 = 2$ showed the lowest amount of N–H bonding and the largest amount of Si–N bonding. The further improvement of the properties of the deposited SiN film could be obtained by the application of a dc bias voltage of up to $-150\,\text{V}$ during the deposition process. Under deposition conditions of $\text{NH}_3/\text{SiH}_4 = 2$ and a dc bias of $-150\,\text{V}$, the refractive index was 1.83, which is close to that of silicon nitride (2.02). And, under these conditions, the interface trap charge density measured for the fabricated MIS capacitors was the lowest, with a value of $2 \times 10^{11}\,\text{cm}^{-2}$ being obtained compared to the value of $1 \times 10^{13}\,\text{cm}^{-2}$ in the case where no bias voltage was applied. Therefore, it is believed that high quality SiN thin film potentially applicable to flexible display devices can be fabricated at the temperature lower than $100\,\text{°C}$ using an internal-type $\text{NH}_3/\text{SiH}_4$ ICP with the application of a small dc bias voltage to the substrate.

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