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Silicon Nitride Films with Low Hydrogen Content, Low Stress, Low Damage and Stoichiometric Composition by Photo-Assisted Plasma CVD

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We have developed a photo-assisted plasma CVD method to deposit high quality silicon nitride films with low hydrogen content of 3-7 atm%, the density of 2.9-3.3 g/cm^3, the tensile stress of 0.5-3.0x10^9 dyn/cm^2 and the Si/N composition of 0.75 at 300 ^{0}C. N_2 gas was excited in a high density plasma kept apart from a wafer. The excited species were effectively transported to the deposition chamber under the Knudsen pressure region. SiH_4 gas introduced directly to the deposition chamber reacted with the excited nitrogen to generate intermediates. The adsorbed intermediates on the wafer were photo-excited to produce silicon nitride film.

1. INTRODUCTION

Silicon nitride (SiN) film has various advantages over silicon oxide film becauce of high density, high dielectric coefficient, hardness and high reliability of passivation for moisture, ion and thermal shock.

SiN films for the protection layers in LSI and TFT are required to be deposited at a low temperature below 300 ^{0}C. RF plasma CVD (P-CVD) using SiH_4 and NH_3/N_2 has been used for low temperature deposition.[1,2] However, the P-CVD method has the following problems: (i) The hydrogen content in SiN films is high (15-40 atm%). The hydrogen ions cause the V_{th} shift of MOSFET in LSI.[3] The density is low (2.1-2.9 g/cm^2). (ii) The peening effect due to high energy ions induces strong compressive stress in the films (1-8x10^9 dyn/cm^2), which causes the stress migration effect.[4] (iii) Incident ions with high energy onto the wafer induce the damage of MOSFET. And (iv) Si/N composition in the films tend to be Si-rich (0.8-1.2), because SiH_4 is decomposed more readily than NH_3 or N_2 in the plasma, and relatively high Si content in the SiN films degrades the insulating property and the transparency.

By the ECR P-CVD method,[5] the film quality is superior to that by P-CVD, but the step coverage is not conformal due to an anisotropic particle incident to the wafer. By photo-CVD method,[6,7] SiN films with low damage and conformal coverage are obtained, but the deposition rate is low.

The poor film quality by the P-CVD is considered to be caused by the inadequate reaction. Because the reaction is occured mainly in a vapor phase, the hydrogen atoms are easily incorporated into the film. If the surface reaction such as hydrogen extraction is realized at low temperature, the film quality can be improved. We have developed the hybrid-excitation CVD method, in which the source gas is excited through plasma in a vapor phase and the surface reaction is induced by UV irradiation.[8]

The aim of our study is deposition of high quality SiN film with low hydrogen content, low stress, low damage and stoichiometric composition below 300 ^{0}C by photo-assisted plasma CVD (PAP-CVD) method.

2. PAP-CVD METHOD

The main points of idea of SiN film deposition by PAP-CVD are as follows: (i) N_2 gas is excited in a high density plasma which

is kept apart from the wafer. (ii) Excited species such as nitrogen atoms are effectively transported to the deposition chamber under the Knudsen pressure region, because the mean-free path of nitrogen under the Knudsen pressure region is about 0.01-0.3 of the chamber dimension. (iii) SiH_4 gas, which decomposes and deposits more easily than N_2 gas, is separately introduced into the deposition chamber and reacts with the excited nitrogen to generate reactive intermediates such as $SiNH_x$. And (iv) adsorbed intermediates on the wafer are photo-excited to produce SiN film through photochemical and thermal reactions.

3. EXPERIMENTAL

Figure 1 shows the schematic of the PAP-CVD apparatus. The RF (13.56 MHz) plasma was generated in a quartz tube (33 mmØ and 210 mm length) with C-coupled electrodes. The RF power was 100-300 W. The high density plasma with an electron density of 2×10^{10} cm^{-3} was confined in the quartz tube. The after-glow plasma with low electron density of 1×10^{9} cm^{-3} was generated near the wafer, and the sheath potential between plasma and wafer was low.

The Xe illuminator (Cermax, LX-800UV) was used as a light source. The emission peak was 400 nm. The light from the illuminator was absorbed by the reactive intermediates as shown in the next section (Fig. 2). The illumination intensity on the wafer was 0.6 W/cm^2, where the wafer surface was heated to 300 ^{o}C. The illumination window was more than 200 mm apart from the powered electrode and the pipe ring for introducing SiH_4 gas in order to reduce the contamination on the window.

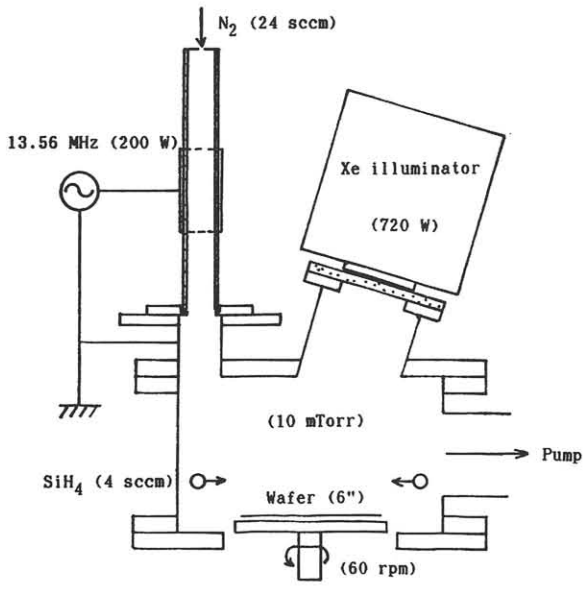

Fig.1. Schematic of PAP-CVD apparatus.

SiH_4 and N_2 were used as the source gases. The N_2 gas was used in order to reduce hydrogen incorporation and to eliminate a photo-absorption in a vapor phase. SiH_4 gas was introduced near the wafer without passing through the plasma generated in the quartz tube. The flow rate of SiH_4 and N_2 were 1-24 sccm and 3-100 sccm, respectively. The operating pressure was 2-50 mTorr.

4. RESULTS AND DISCUSSIONS

Figure 2 shows the emission spectrum of the Xe illuminator and the absorption spectrum of the reactive intermediates deposited on the quartz wafer without Xe illuminator irradiation. The both spectra overlapped with each other, and thus the reactive intermediates were effectively excited by the irradiation of the Xe illuminator. On the other hand, the Xe emission spectrum did not overlap with the absorption spectra of the source gases, and thus the photochemical vapor reaction which might cause the contamination on the window was reduced.

Figure 3 shows the Si/N composition ratio vs. SiH_4/N_2 flow ratio. The Si/N composition ratio in the film was measured with AES and IR spectroscopies. The Si/N stoichiometric

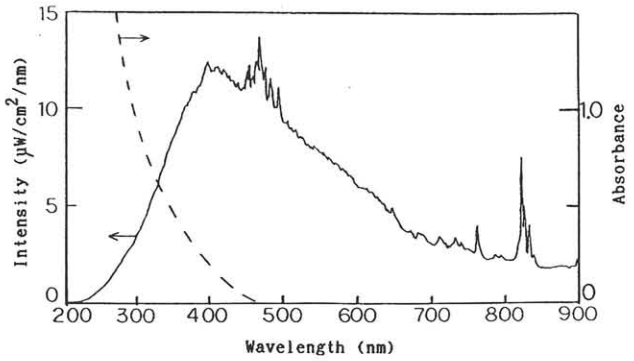

Fig.2. Emission spectrum of Xe illuminator (——) and absorption spectrum of reactive intermediates(- - -).

composition in the film was easily obtained at a SiH_4/N_2 flow ratio of 0.1-0.7.

Figure 4 shows the hydrogen content vs. SiH_4/N_2 flow ratio. The flow ratio which produced the minimum hydrogen content was nearly equal to that of the stoichiometric composition. The minimum hydrogen content was obtained as low as 3-7 atm%.

Figure 5 shows the hydrogen content vs. wafer temperature. The hydrogen content with the irradiation was about a quarter of that without the irradiation, and was 30-50 % of that at 300 ^{0}C with resistive heating. It was confirmed that a photochemical surface reaction was effective to extract hydrogen atoms from an reactive intermediates adsorbed on the wafer surface.

Figure 6 shows the refractive index vs. composition ratio. The film density was obtained from the Lorentz-Lorenz relation.[9]

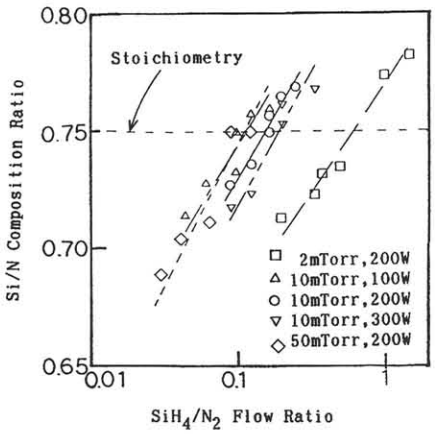

Fig.3. Si/N composition ratio vs. SiH_4/N_2 flow ratio.

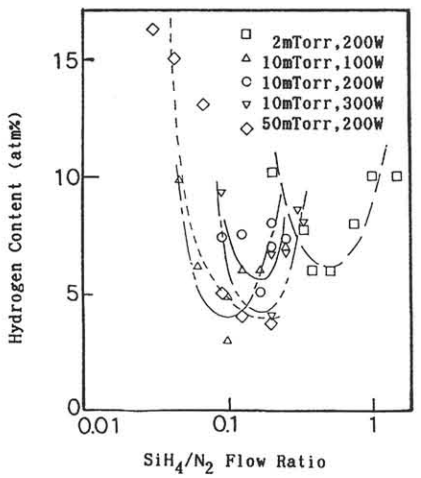

Fig.4. Hydrogen content vs. SiH_4/N_2 flow ratio.

The film density was 2.9-3.3 g/cm^3, which was higher than that of the usual P-CVD SiN film (2.0-2.9 g/cm^3).

Figure 7 shows the stress in the film vs. RF power. The stress in the film was observed with the stress gauge (Ionic Systems, WDG). The tensile stress of 0.5-3.0x10^9 dyn/cm^2 was induced in PAP-CVD SiN films. The value of the tensile stress was smaller than that of 1.2-1.8x10^{10} dyn/cm^2 induced in the conventional LP-CVD SiN films. The compressive stress of about 3.0x10^9 dyn/cm^2 was induced without the irradiation. The stress of PAP-CVD film can be controlled to be zero by adjusting the illumination intensity.

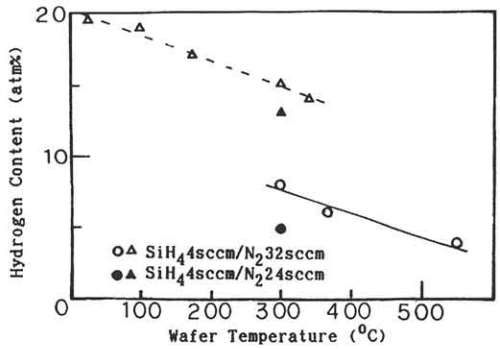

Fig.5. Hydrogen content vs. wafer temperature with Xe irradiation(——) or resistive heating(- - -).

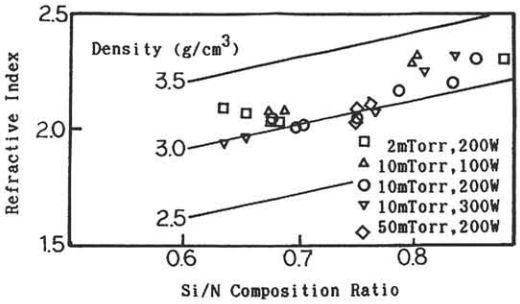

Fig.6. Refractive index vs. Si/N composition ratio.

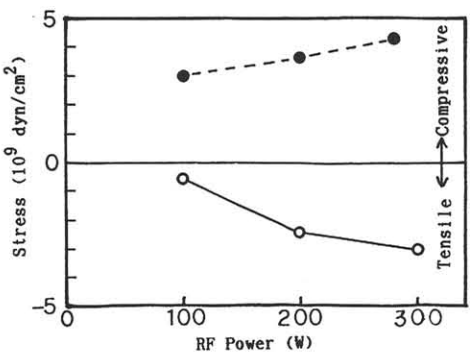

Fig.7. Stress vs. RF power with(——) or without(- - -) irradiation.

Figure 8(a) shows SEM photograph of cross-sectional view of the film. The SiN film was deposited on Al line and space pattern formed on SiO_2 layer. A mouse-ear-like cross section of the SiN film by the PAP-CVD was similar to that of P-CVD SiN film. Figure 8(b) shows a photograph of the cross-sectional view of the PAP-CVD film etched by buffered fluoric acid (BHF) for 10 min. The cross-sectional view was not changed even slightly after BHF etching. In the conventional P-CVD film, the film deposited on the side wall of Al line was etched faster than that deposited on the top of Al line. It should be remarked that the film deposited both on the side wall and the top of Al line was not etched even slightly in the PAP-CVD.

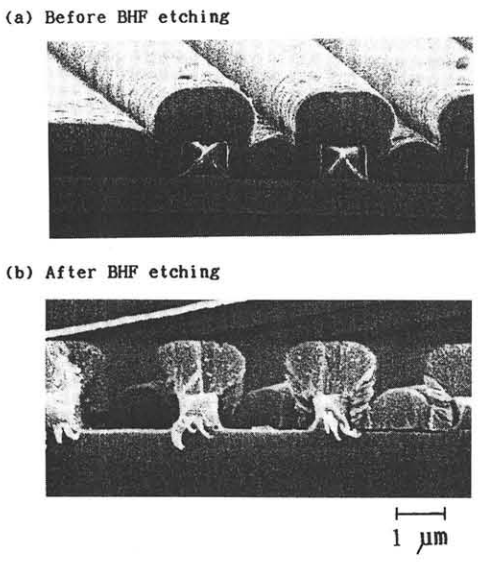

Fig.8. SEM photographs of cross-sectional view (a)before and (b)after BHF etching.

The typical deposition rate was 12 nm/min. for 4 sccm of SiH_4, 24 sccm of N_2, 10 mTorr of pressure and 200 W of RF power, and the largest deposition rate at the present time was 46 nm/min.

Since the N_2 gas was effectively excited in the high density plasma kept apart from the wafer and the adsorbed intermediates were excited by the Xe illuminator irradiation, the SiN film with low hydrogen content, low stress and stoichiometric composition was obtained at the temperature as low as 300 ^{0}C. The quality of the PAP-CVD film was superior to that of the conventional P-CVD film. The step coverage by PAP-CVD was superior to that by ECR P-CVD, because the particle incident to the wafer was isotropic in the case of PAP-CVD. The deposition rate was larger than that of the photo-CVD, because the deposition rate was dominated by the plasma excited reaction.

Using the PAP-CVD, the high quality SiN film comparable to that of the low-pressure CVD was obtained at 300 ^{0}C whose temperature was extreamely low comparing 800 ^{0}C of LP-CVD.

5. CONCLUSION

We have developed the photo-assisted plasma CVD (PAP-CVD) method. Silicon nitride film with low hydrogen content, low stress and stoichiometric composition was deposited at low temperature. The silicon nitride film by PAP-CVD is the most suitable to the protection layers of many devices and can be widely used in many other applications.

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