Ultra-Low-Temperature Formation of Si Nitride Film by Direct Nitridation Employing High-Density and Low-Energy Ion Bombardment

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Abstract
High-integrity silicon nitride films can be obtained at a temperature of 430 °C by using high-density (>10¹⁰cm⁻³) plasma featuring low ion bombardment energy (7eV). The electrical properties of silicon nitride films are equivalent to those of thermally grown nitride film. Moreover, the hysteresis width of C-V curve attributed to charge traps and leakage current of nitride film can be decreased dramatically by irradiating Ar/N₂/H₂ plasma after Ar/N₂ plasma nitridation.

Introduction
As semiconductor devices are scaled down to smaller dimensions, conventional processing temperature such as 900 °C will be incompatible with the desired device structure. For example, conventional high-temperature gate insulator formation process changes the impurity profile previously formed in the substrate. Moreover, it is necessary to introduce metal substrate SOI device for future high speed (>1GHz) ULSI device. To realize the metal substrate SOI device, all of manufacturing processes have to be done at below 550 °C. Thus gate insulator must also be formed below 550 °C. Moreover the requirements to replace silicon oxide by high dielectric-constant films, for example Ta₂O₅ and Si₃N₄, increase more and more in order to overcome scaling limit of silicon oxide. Therefore lowering growth temperature of high-integrity silicon nitride film is a key for future metal substrate SOI device fabrication. In our previous study, we found that controlling ion bombardment energy less than 9eV and the ion flux density higher are essential to obtain high-integrity silicon oxide films at 450 °C [1]. On the other hand, in our recent research, we found that ion bombardment energy decreases as low as 7eV and ion flux density is 1.5 orders of magnitude higher in microwave excitation high-density plasma than that in conventional parallel plate type RF excitation plasma [2]. The purpose of this paper is to improve electrical properties of silicon nitride films formed by employing high-density and low-energy ion bombardment.

Experimental
Fig.1 illustrates a newly-developed microwave-excitation plasma system featuring radial line slot antenna (RLSA) [3]. This system is characterized by low ion bombardment energy less than 7eV, high plasma density above 10¹² cm⁻³ and low electron temperature below 1.3eV. Silicon nitride films were formed by this system at 430°C. The thickness was measured by spectro-ellipsometry. MIS [Al/Si₃N₄/Cz n-type Si(100) with resistivity 3-5Ω·cm] capacitor was fabricated to evaluate electrical properties.

Results and Discussion
Fig.2 shows Si2p X-ray photoelectron spectroscopy (XPS) spectrum of silicon nitride film formed by high-density plasma. XPS spectrum of thermally grown oxide is also shown in Fig.2 as a reference. The shape and position of chemically shifted Si2p peak shows that the silicon nitride film is stoichiometric and SiO₂ bond does not exist in the silicon nitride film at all.

Fig.3 shows N/Si ratio and optical emission intensity of N₂⁺ (λ=391nm) in plasma dependence on Ar/N₂ mixing ratio. Stoichiometric silicon nitride film (N/Si=1.33) can be obtained when Ar/N₂ mixing ratio is 5-6%. This result suggests that N/Si ratio strongly depends on emission intensity of N₂⁺.

Fig.4 shows hysteresis width of C-V curve attributed to charge traps in silicon nitride film. Hysteresis width decreases by irradiating Ar/N₂/H₂ plasma after Ar/N₂ plasma nitridation (Ar/N₂/H₂ anneal).

Fig.5 shows J-V characteristics of nitride films formed by high-density plasma. It was found that the leakage current was dramatically decreased by Ar/N₂/H₂ anneal.

Figs.6 (a) (b) show N1s XPS spectra of silicon nitride films formed by Ar/N₂ plasma and Ar/N₂ plasma with Ar/N₂/H₂ anneal, respectively. In the spectrum of nitride film formed by Ar/N₂ plasma with Ar/N₂/H₂ anneal, NH bond was identified. On the other hand, NH bond was not identified in the spectrum of nitride film formed by Ar/N₂ plasma. The results of Fig.4-6 suggest that dangling bonds in silicon nitride film are terminated by hydrogen.

Conclusion
Direct nitridation of silicon surface can be realized at 430°C by employing high-density plasma featuring low ion bombardment energy. The electrical properties of nitride films formed by this high-density plasma are improved by irradiating Ar/N₂/H₂ plasma after Ar/N₂ plasma nitridation. These technologies become very promising for fabricating feature metal substrate SOI devices and silicon nitride gate MISFET. The possibility of silicon nitride gate MISFET for future ULSSI device was confirmed.

Reference
Microwave (8.3GHz)  
Radial Line Slot Antenna  
Coaxial Wave Guide  
Si Wafer  
Quartz Shield  
Al Chamber

Fig. 1  Schematic diagram of newly-developed microwave-excitation plasma process equipment

![Graph]

Fig. 2  XPS spectrum of silicon nitride film formed by high-density plasma at 430°C

![Graph]

Fig. 3  N/Si ratio of silicon nitride film and optical emission intensity of $N_2^+$ ($\lambda=391$nm) as a function of Ar/N$_2$ mixing ratio

![Graph]

Fig. 4  Hysteresis width of C-V curve of nitride films formed by Ar/N$_2$ plasma and Ar/N$_2$ plasma with Ar/N$_2$/H$_2$ anneal

![Graph]

Fig. 5  J-V Characteristics of silicon nitride films formed by high-density plasma at 430°C

![Graph]

Fig. 6  N1s XPS spectra of silicon nitride film formed by Ar/N$_2$ plasma and Ar/N$_2$ plasma with Ar/N$_2$/H$_2$ anneal