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Incorporated Nitrogen Behavior in Plasma-nitrided Silicon Oxides Formed by Chemical Vapor Deposition Method

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Abstract

Behavior of N atoms in plasma-nitrided CVD silicon oxides was characterized by physical analyses and electrical properties. N_2 molecular are incorporated into CVD silicon oxides by the plasma nitridation. NH species are generated by O_3 oxidation from these N_2 molecular. Since NH species have a high diffusivity, they easily diffuse in plasma-nitrided CVD silicon oxides even at a lower temperature than the plasma nitridation below 500˚C.

1. Introduction

Nitrogen (N) incorporation into chemical vapor deposited silicon oxides (SiO_2) film has been widely used in a number of critical applications in semiconductor devices, such as gate dielectrics, spacers, and impurity-diffusion barriers. Incorporation of N atoms into SiO_2 films was carried by many different ways such as plasma nitridation, thermal nitridation, and ion-implantation followed by annealing[1-4]. The plasma nitridation at a low temperature is useful technique because of a low damage on the surface. Until recently, many studies on plasma nitridation of thermally grown SiO_2 films have been conducted[2-4]. However, incorporated N behavior of plasma-nitrided SiO_2 formed by chemical vapor deposition (CVD) method is not yet fully understood.

This paper describes the distribution of N atoms and chemical bonds of plasma-nitrided SiO_2 formed by CVD method. The results of physical analyses are consistent with electrical properties for metal oxide semiconductor(MOS) capacitors.

2. Experimental Procedure

Blanket SiO_2 films with thickness of 10nm were formed on Si (001) substrate by CVD below 500˚C. Nitridation was then performed at a substrate temperature below 500˚C with remote Ar-N_2 plasma discharge at a pressure lower than 0.2 Torr. For comparison, the following 2 processes were performed. One is nitridation annealing over 900˚C in N_2. The other is deposition of capping oxide films using CVD with O_3-oxidant below 350˚C.

To characterize the chemical bonding of N atoms in the plasma-nitrided SiO_2 CVD layers, x-ray photoelectron spectroscopy (XPS) spectra were obtained with monochromatized AlKα radiation. Depth profiles of N in SiO_2 were obtained by secondary ion mass spectrometry (SIMS) with Cs^+ as the primary ion. In order to investigate SiO_2 film quality, bonding states were obtained fourier transform infrared spectroscopy (FT-IR).

3. Results and Discussion

Figure 1(a) shows the XPS N 1s spectrum taken at photoelectron take-off angle of 90˚ for the plasma nitrided SiO_2 CVD layer. From the spectral deconvolution, 3 different N-bonding states were resolved. The peaks at 399.3 eV, 400 eV and 404.5 eV are due to N-Si_3, N-Si_2O, and N_2, respectively[3,4]. But in contrast, the signal intensity derived from the molecular N_2 was reduced by the subsequent nitridation annealing at temperature higher than 900˚C as shown in Fig. 1(b). Figure 2 shows the depth profiles of N atoms in SiO_2 CVD layers. The N atoms in SiO_2 decreased significantly with the annealing. These results indicate that the molecular N_2 atoms easily diffuse out during the high temperature annealing over 900˚C.

Figure 3 shows the FT-IR spectra of silicon oxides with no additional process, with plasma nitridation only, and with plasma nitridation combined with annealing over 900˚C. Each spectrum was normalized with main peak intensity indentified as Si-O bonding at 1060 cm^{-1}[5]. The adsorption of Si-O stretching vibration with plasma nitridation shifted to lower wavenumber compared with that of the as-grown CVD film, as indicated in Fig. 4(a). This suggests that incorporation of the molecular N_2 by plasma nitridation generated defects (e.g., dangling bond) in silicon oxides[6]. At the same time, as shown in Fig. 4(b), FT-IR absorption intensity at 920 cm^{-1} by plane vibrations of N-Si-O bond increased[7,8]. Furthermore, the adsorption of Si-O stretching vibration shifted to higher wavenumber by the subsequent nitridation annealing over 900˚C, while absorption intensity at 920 cm^{-1} had a slight difference. It is considered that annealing induced the relaxation of strain in the silicon oxides network by out diffusion of molecular N_2.

It is interesting to note that the subsequent oxide film deposition using O_3-oxidant has a marked influence in the atomic bonding of plasma-nitrided silicon oxides formed by CVD method. Figure 5 shows N1s XPS spectrum for plasma-nitrided CVD-SiO_2 with subsequent oxide deposition. The peak of 402 eV associated with H_2NSiO_3 was produced by deposited subsequent oxide film as indicated in Fig. 5. It is considered that O_3-oxidation during depositing oxide film dissociated molecular N_2 into NH species in CVD-SiO_2 having a large amount of H incorporating. Furthermore, it should be noted that N concentration increased in the interface of SiO_2/Si substrate during depositing subsequent oxide film at a low temperature below 350˚C, as shown in Fig. 6 where the depth profiles of N in plasma-nitrided CVD SiO_2 measured by SIMS. It is because N and NH species have higher diffusivities in SiO_2 as compared with NO and N_2[9]. The changes in distribution and atomic bonding of N atoms have a marked effect on flat band voltage shifting of MOS capacitors. The process flow for polycrystalline-Si gate MOS capacitors is illustrated in Fig. 7. Fig. 8 shows the flat band voltage of the MOS capacitors as a function of N concentration in plasma-nitrided SiO_2 which is determined by SIMS. In the subsequent oxide deposited MOS capacitor, the flat band voltage markedly shifted toward negative though N concentration was independent of the oxide deposition. It was considered that the NH species with a high diffusivity, which were dissociated from the molecular N_2, reached at the interface of SiO_2/Si substrate and promote to generate interface traps such as $(Si=NH-Si)^+$[10].

4. Conclusions

In the plasma-nitrided SiO_2 formed by CVD method, molecular N_2 easily move in the network of silicon oxides during annealing at higher than 900˚C. It is considered that desorption of molecular N_2 induced recovering the extent of structural distortion in CVD SiO_2 film. Furthermore, it is clarified that the O_3 oxidation during depositing subsequent oxide film dissociates molecular N_2 into NH species even at a low temperature below 350˚C. In addition, the diffusion of N atoms toward substrate and the significant flat band voltage shifting in MOS capacitors are clearly observed. This can be interpreted in terms that the NH species with the higher diffusivities in SiO_2 as compared with NO and N_2 SiO_2/Si interface traps by depositing subsequent oxide film.

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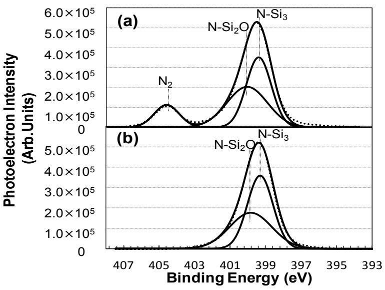

Fig.1 N 1s XPS spectra for CVD-SiO_2 layers with **(a)** plasma nitridation only and with **(b)** plasma nitridation combined with annealing over 900˚C, which were taken at a photoelectron take-off angle of 90 ˚. The thickness of CVD-SiO_2 was 10 nm.

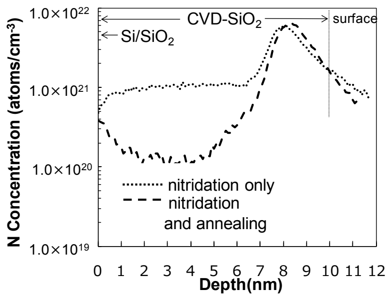

Fig.2 Depth profiles of N in CVD-SiO_2 layers with plasma nitridation only and with plasma nitridation combined with annealing over 900˚C.

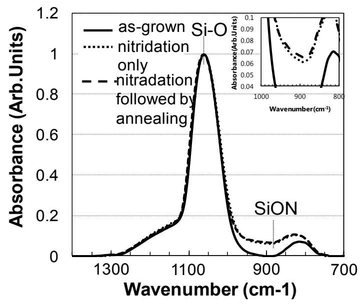

Fig.3 IR spectra for CVD-SiO_2 layers with no additional process, with plasma nitridation only, with plasma nitridation combined with annealing over 900˚C. Each spectrum was normalized with the Si-O peak intensity at 1060 cm^{-1}.

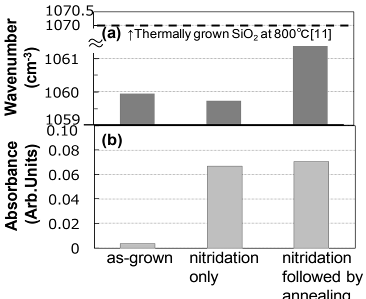

Fig.4 **(a)**Position of Si-O stretching vibration and **(b)** adsorption intensity at 920 cm^{-1} for CVD-SiO_2 layers with no additional process, with plasma nitriding only, and with plasma nitridation combined with annealing over 900˚C.

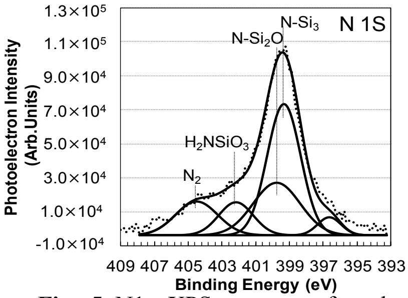

Fig. 5 N1s XPS spectrum for plasma nitrided CVD-SiO_2 film with subsequent oxide deposition using O_3-oxidant below 350˚C. The photoelectron take-off angle was set at 90 ˚.

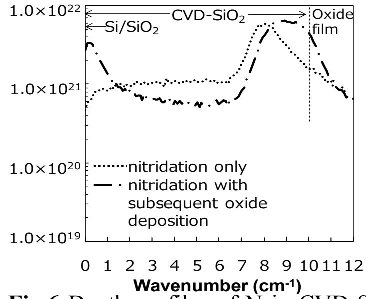

Fig.6 Depth profiles of N in CVD-SiO_2 layers with with plasma nitridation only and plasma nitridation combined with oxide deposition using O_3-oxidant below 350˚C.

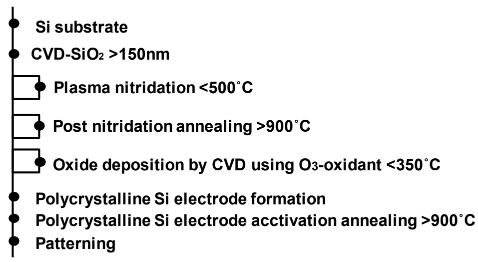

Fig.7 Process flow for polycrystalline-Si gate MOS capacitors.

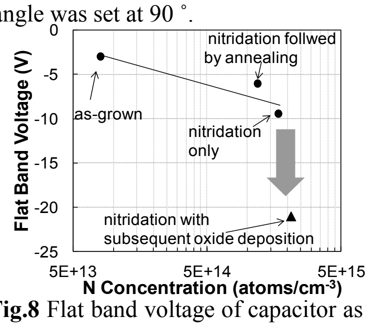

Fig.8 Flat band voltage of capacitor as function of N concentration in CVD-SiO_2 layer which is determined by SIMS measurement.