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Formation of Silicon Oxynitride Films with High Nitrogen Concentration at Low Temperatures

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1. Introduction

Silicon oxynitride films have been attained much attention for the use of next-generation gate dielectric materials because incorporated nitrogen atoms suppress the diffusion of boron from the gate electrode [1] and improve the interfacial characteristics such as hot-electron immunity [2]. For the formation of oxynitride films by the reaction of Si (or SiO_2) with N_2O or NO, high temperature heating around 1000 ℃ is necessary [3-7]. Even with such high temperature heat treatments, the concentration of nitrogen atoms is less than a few percents, and hence, the effective improvement of the electrical characteristics is not achieved [8]. In the present study, a new method for the formation of silicon oxynitride films at low temperatures (i.e., 25 ~ 700 ℃) is developed using technique of plasma generated by low energy electron impact [9].

2. Experimental

After cleaning p-type Si(100) wafers of ~1 Ωcm resistivity, a ~6 nm-thick oxide layer was formed by heating the wafers at 850 ℃ in an oxygen plus hydrogen atmosphere. Then, the specimens were introduced in a UHV chamber for the plasma treatment. For generating nitrogen plasma, a tungsten filament was heated at 1400 ℃ in a 0.02 mbar nitrogen atmosphere. Electrons emitted from the filament were accelerated by applying a bias voltage between 25 and 50 V to the grid with respect to the filament. The oxide-covered Si specimens were exposed to nitrogen plasma for 1 h at temperatures between 25 and 700 ℃. During the plasma treatment, a bias voltage between −15 and 20 V was applied to the specimen with respect to the grid.

3. Results and discussion

Figure 1 shows the XPS spectra in the N 1s region observed after nitridation of the silicon oxide layers by nitrogen plasma generated by low energy electron impact at 25 ℃. After the nitridation, a N 1s peak was observed for all the specimens, indicating that the nitridation occurred even at room temperature [spectra (a) ~ (c)]. The intensity of the N 1s peak was increased by applying a negative bias voltage to the specimen, showing that nitrogen ions (N^+ and N_2^+) played an important role in the nitridation. The atomic nitrogen concentration ratio [N/(N+O)] in the surface region was 8 % for 0 V [spectrum (a)], 19 % for −10 V [spectrum (b)], and 27 % for −15 V [spectrum (c)]. These concentrations are much higher than those for oxynitride films produced by the reaction of Si (or SiO_2) with NO or N_2O molecules at high temperatures around 1,000 ℃ (i.e., less than ~5 % [3-6]).

The N 1s spectra for the 25 ℃-nitridation were resolved into two peaks at 397.9 and 399.2 eV. From the binding energies, the former and latter peaks are attributed to nitrogen atoms bound to three Si atoms each (i.e., stoichiometric species, $N\equiv Si_3$) [3,5] and N^+ ions bound to two Si atoms each (i.e., $N^+{=}Si_2$). For nitridation above 450 ℃, on the other hand, only one peak due to the stoichiometric species was observed [spectrum (d)].

Figure 2 shows the depth profiles of the nitrogen concentration for the oxide layers nitrided at 25 ℃. For both the layers nitrided at 0 V and −15 V applied to the specimens, the nitrogen concentration is high in the surface and interfacial regions. The ratio in the nitrogen concentration of the bulk (the concentration at the depth of 3 nm) to that at the surface became higher when a negative bias voltage was applied to the specimen.

On the bias of these results, we propose a following mechanism for the nitridation of silicon oxide by nitrogen plasma (cf. Fig. 3). The strong bias dependence (Fig. 1) shows that the reacting species is nitrogen ions. In the nitrogen plasma, N_2^+ ions and possibly N^+ ions are present. It is reported that N^+ ions react with Si but N_2^+ ions do not [10]. Therefore, we think that the reacting species with SiO_2 is N^+ ions present in nitrogen plasma or formed on the oxide surface by the decomposition of N_2^+ ions. N^+ ions replace oxygen atoms at the surface, forming $N^+{=}Si_2$. Then, the place exchange between N^+ and the

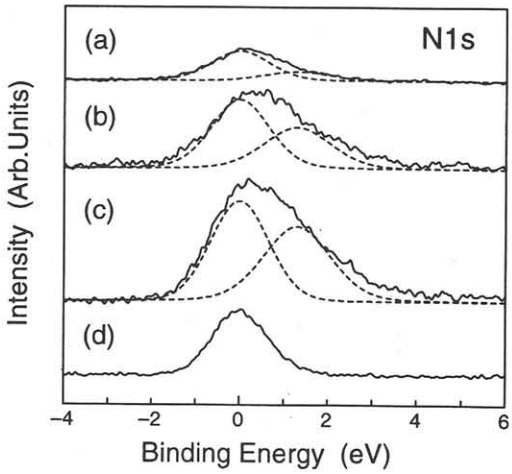

Fig. 1 XPS spectra in the N 1s region for the silicon oxide layers nitrided by nitrogen plasma generated by low energy electron impact at the following temperatures and the bias voltage applied to the specimen: (a) 25 ℃ and 0 V; (b) 25 ℃ and −10 V; (c) 25 ℃ and −15 V; (d) 700 ℃ and 0 V.

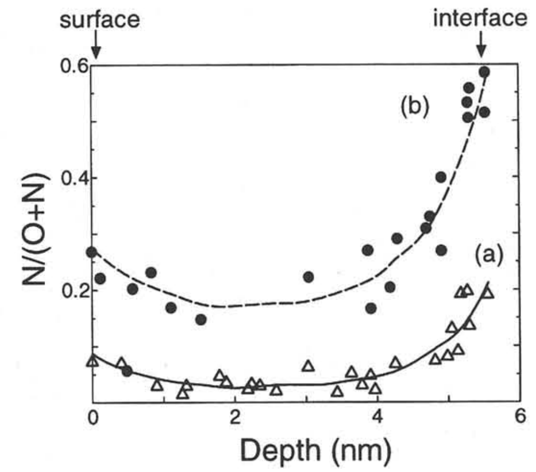

Fig. 2 Depth profiles of the nitrogen atomic concentration ratio [N/(O+N)] for the silicon oxide layers nitrided by nitrogen plasma at 25 ℃ under the following bias voltage applied to the specimen: (a) 0 V; (b) −15 V.

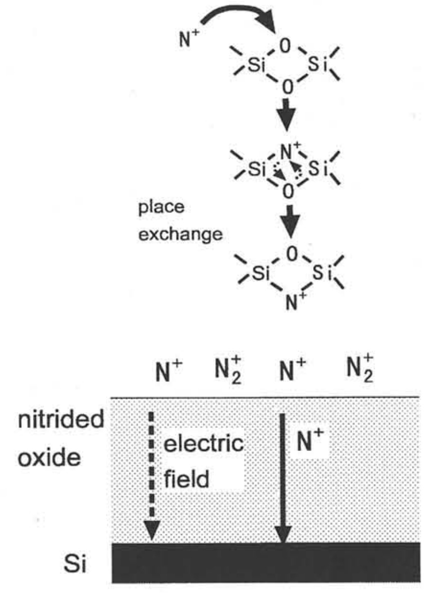

Fig. 3 Mechanism of the nitridation of silicon oxide layers by nitrogen plasma.

underlying oxygen atom occurs. Similar place exchange reaction is proposed in the mechanism of the Si oxidation at low temperatures [11]. It is likely that the activation energy for the place exchange is considerably reduced by electric field induced by N^+ and N_2^+ ions on the surface [11]. The inward movement of N^+ is also enhanced by the electric field. The enhancement of the migration of N^+ by electric field is supported by the experimental result that the relative nitrogen concentration in the bulk to that at the surface increases by applying the negative bias voltage to the specimen (Fig. 2). When N^+ obtains a sufficiently large energy to go over the potential hill of the activation energy, the $N{\equiv}Si_3$ species is formed.

The bond energies of N-O, Si-O, and Si-N are 151, 191, and 105 kcal/mol, respectively [12], and thus, the reaction of NO with SiO_2 does not occur. On the other hand, the Si-Si bond energy is 78 kcal/mol, and therefore, NO molecules can react with Si, leading to the accumulation of nitrogen atoms in the interfacial regions when the nitridation is carried out by the reaction with NO or N_2O [3,13]. (In the case of oxynitridation by N_2O, NO formed by the decomposition of N_2O is the reacting species [14].) In the present nitridation method using nitrogen plasma generated by low energy electron impact, on the other hand, N^+ ions can directly react with SiO_2, leading to the high nitrogen concentration in the surface region as well as in the interfacial region. Another reason for the inclusion of a large amount of nitrogen atoms may be due to the absence of atomic oxygen which removes nitrogen atoms in the oxide layers [15]. High concentration nitrogen atoms in the surface region effectively prevent the diffusion of boron from the gate electrode, and those in the interfacial region improve the interfacial characteristics. Therefore, the nitrogen distribution with the high density in the surface and interfacial regions is ideal for the gate-dielectric materials of MOS devices.

4. Conclusions

Silicon oxide layers can be nitrided at low temperatures (25 ~ 700 ℃) by nitrogen plasma generated by low energy electron impact. The nitrogen concentrations in the surface and interfacial regions are high (10 ~ 40 %). The nitrogen concentration increases by applying a negative bias to the specimen during the nitridation. It is concluded that the reacting species is N^+ ions which can directly react with SiO_2 and easily migrate with the assistance of electric field in the dielectric layers.

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