Low Dielectric Constant Non-Porous Fluorocarbon Films for Inter-Layer Dielectric
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Introduction
Development of Low-k dielectrics for inter-metal layers is one of the emergency issues for high performance ULSI devices. Recently, the porous low-k materials, such as SiO2, SiOC, etc. have been reported[1]. However, for applying of the porous material to inter-layer dielectric, there are many difficulties for device integrations, such as CMP process and cleaning process due to its characteristics of weak mechanical strength and absorbency. On the other hand, the non-porous fluorocarbon films formed by electron cyclotron resonance (ECR) plasma source has been reported [2]. However, good characteristics of the films using plasma enhanced chemical vapor deposition (PECVD) technology has not been obtained so far because conventional plasma equipments induce excess decomposition of material gases resulting from high electron temperature (∼3eV) and hence original characteristics of material gases cannot be used well.

In this paper, we describe new fluorocarbon films with low dielectric constant of about 2.0 or less realized by suppressing the excess decomposition of the material gas (C2F6) using a new microwave-excited low electron temperature (1~2eV) and high-density plasma equipment with a dual shower plate structure[3,4].

Experimental
Fig. 1 shows the schematic view of the new microwave-excited low electron temperature and high-density plasma equipment with the dual shower plate structure (for 33mm wafer). Microwave (2.45 GHz) was introduced into the chamber through the dielectric upper shower plate of Al2O3. Plasma excitation gas (Ar) was introduced uniformly into the plasma excitation region using the upper shower plate. As a result, high-density plasma (~1015 cm-3) was excited in the plasma excitation region. The lower shower plate for the supply of material gas (C2F6) is set at the diffusion plasma region with low electron temperature (~2.0 eV). Therefore, the excess decomposition of material gases can be suppressed. The lower shower plate have many small gas injection holes supplies material gases toward the wafer. In some cases, rf power (13.56MHz) was supplied to the wafer electrode in order to obtain energy of bombarding ions to the wafer. Since the plasma excitation region is limited to the space immediately below the upper shower plate, the CVD process region is completely separated from the plasma excitation region. As a result, rf power can be supplied without disturbing the plasma excited by the microwave.

Results and discussions
Fig. 2 shows 13C-NMR spectra of the fluorocarbon films formed by (c)the new equipment, (b)the conventional ECR plasma source, and (a)a controlled sample of polytetrafluoroethylene (PTFE). The structure of the fluorocarbon films formed by the new equipment is obviously different from both that formed by ECR and PTFE. The fluorocarbon film formed by the new equipment contains much more (-C-C-) structure [64 ppm (C-C]< : tetra carbon structure) and 98 ppm (C-C,F : triple carbon structure)], while (-C-C-) structure is not observed for the cases of that formed by ECR and PTFE. The structure (-C-C) is related to hardness of films, adhesion with metal and heat-resistance characteristics. The results clearly demonstrate advantages of the use of the new equipment, where the excess decomposition can be suppressed. Fig. 3 shows thermal desorption spectroscopy - atmospheric pressure ionization mass spectroscopy (TDS-APIMS) spectra of the fluorocarbon films. Case (a) indicates that fluorocarbon film is stable although the film is exposed to air after the film is annealed at 400 °C. In addition, post treatment of Ar/N2 plasma can increase heat-resistance of the film as shown in Fig. 3(b).

Fig. 4 shows the k-value of the film as a function of Ar flow rate. The k-value can be reduced as Ar flow rate increases, and the value at Ar flow rate of 480 sccm reaches 1.9 [pressure : 9.3 Pa, microwave power : 900 W (2.6 W/cm2)]. The result suggests that diffusion of CF3 into plasma excitation region can be suppressed in case of sufficient Ar gas flow from the upper shower plate, and at the same time, the excess decomposition of CF3F8 can also be suppressed.

Figs. 5(a) and 5(b) show the SEM (Scanning Electron Microscope) images and AFM (Atomic Force Microscopy) images of the fluorocarbon films at 120 sccm and 480 sccm of Ar flow rate. The non-porous structure for both cases is observed from the SEM image. However, the surface roughness for fluorocarbon film of 480 sccm of Ar flow rate is larger than that of 120 sccm (Ra = 1.4 nm at 120sccm, and 5.3 nm at 480sccm). The surface smoothness should be improved for realizing fine device integrations.

For improving the surface smoothness, microwave power was increased, and the rf power of 10 W (1.2 W/cm2) was applied to the wafer substrate in order to obtain energy of bombarding ions to the wafer. In case of 1800W of microwave power and 10 W of rf power, the film with k-value of 2.0 can be obtained. The SEM image and AFM image for this condition are shown in Fig. 5(c). Excellent surface smoothness is achieved (Ra = 1.5 nm). The results suggest that high ion energy generated by applying rf power to the wafer promotes the migration of depositing molecular on the surface during the process, indicating that both microwave power for plasma excitation and rf power for obtaining energy of incident ions are useful parameters to improve film properties. The J-E characteristic of this fluorocarbon film is shown in Fig. 6. The leakage current density of 6.9 x 10^-6 A/cm2 at 1 MV/cm can be realized. The typical characteristics of the film are shown in Table 1.

Conclusions
We have successfully developed the formation of the non-porous fluorocarbon film using the new microwave-excited low electron temperature and high-density plasma equipment with the dual shower plate structure. The equipment can suppress the excess decomposition of material gases. The fluorocarbon film formed by the new equipment has the low dielectric constant (k = 2.0), low leakage current density (J < 1 x 10^-6 A/cm2 @ 1 MV/cm), and superior flat surface (Ra = 1.5 nm) as well as characteristics of stable and excellent mechanical strength. Fig. 7 shows our proposed structure of the inter layer using non-porous low-k fluorocarbon films. This technology is the key to realize high performance ULSI devices for next generation.

References
microwave (2.45 GHz)

Figure 1 Schematic view of high-density plasma equipment

Figure 2 $^{13}$C-NMR spectra show the fluorocarbon films

Figure 3 TDS-APIMS spectra of the fluorocarbon films

(a) without post treatment
(b) with post treatment of Ar/N$_2$ plasma

Figure 4 k-value as a function of Ar flow rate

Figure 5 the SEM images and AFM images of the fluorocarbon films

(a) Ar 120 sccm : $k = 2.1$, $Ra = 1.4$ nm
(b) Ar 480 sccm : $k = 1.9$, $Ra = 5.3$ nm
(c) rf bias power applied : $k = 2.0$, $Ra = 1.5$ nm

Figure 6 J-E characteristics of fluorocarbon film

Table 1. The typical characteristics of the fluorocarbon formed by Ar/C$_5$F$_8$ plasma

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Conventional</th>
<th>Advanced</th>
<th>Future</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ value</td>
<td>$k_{eff} &gt; 3$</td>
<td>$k_{eff} = 2.2$</td>
<td>$k_{eff} = 1.9$</td>
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<tr>
<td>Adhesion</td>
<td>$k = 4.0$</td>
<td>$k = 4.0$</td>
<td>$k = 5.0$</td>
</tr>
<tr>
<td>Modulus</td>
<td>$&gt; 8$ GPa</td>
<td>$&gt; 8$ GPa</td>
<td>$&gt; 8$ GPa</td>
</tr>
<tr>
<td>Adhesion</td>
<td>$6.9$ J/m$^2$</td>
<td>$6.9$ J/m$^2$</td>
<td>$6.9$ J/m$^2$</td>
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Figure 7 proposed structure of the inter layer