Formation of SiOF Films by PECVD Using (C$_2$H$_5$O)$_2$SiF

H.Kito, M.Muroyama, M. Sasaki, M.Iwasawa* and H.Kimura*

Process Division, Semiconductor Company, Sony Corporation
4-14-1, Asahi-cho, Atsugi-si, Kanagawa-ken, 243 Japan
*Center for Computational Science, Research Center, Sony Corporation
*134, Goudo-cho, Hodogaya-ku, Yokohama-si, 240 Japan

A new PECVD method using (C$_2$H$_5$O)$_2$SiF: tris-ethoxy-fluoro-silane (TEFS) for a interlayer dielectric film was proposed based on the consideration of gas chemistry. RF power dependence of the film formed of TEFS was investigated and it was clarified that the relative dielectric constant increased with increasing RF power and was about 3.5 over 700W. Fluorine stability was also improved with increasing RF power. Moisture absorption of the film formed of TEFS at 900W was comparable to that of the SiO$_2$ film formed of TEOS/O$_2$ using PECVD

1. Introduction

Requirements of low dielectric constant of interlayer dielectric films are increasing as well as the demand of high gap-filling capability. Because multi-level metalization suffers from increased wiring capacitance which affects operation speed of the ULSI devices. SiOF is a promising low dielectric material because of suitability to LSI process, however, it has the difficulty of moisture absorption.1) This difficulty comes from instability of F included in the SiOF film by conventional RF plasma enhanced chemical vapor deposition (PECVD). Dual frequency PECVD method was proposed to reduce the unstable F in the film but the films formed with this method have tendency to hold moisture.2) On the other hand, to improve the film quality, SiOF films by high density PECVD were also proposed.3) 3) In this work, we tried to utilize conventional parallel plate PECVD equipment. New gas chemistry to form a stable SiOF film using (C$_2$H$_5$O)$_2$SiF:tris-ethoxy-fluoro-silane (TEFS) was proposed to realize a low dielectric constant and good film quality.

2. Gas Chemistry

We investigated chemistry of TEFS as an organic source gas which includes a Si-F bond. Figure 1 shows the molecular structure of TEFS. It is expected that stable Si-F bond using the molecular orbital calculations on the bond energies of TEFS by a semi-empirical Austin Model 1(AM1) method. Table 1 shows the results of AM1 calculation on TEFS. The two center energies of bonds in (C$_2$H$_5$O)$_2$SiF were in the order of Si-F > Si-O > O-C > C-C. This result suggests that TEFS is decomposed with remaining the Si-F bond. It was also expected that the film using TEFS has good gap-filling capability, because the molecular structure of TEFS is similar to that of tetra-ethoxy-silane (TEOS). Thus, TEFS seems suitable source gas for SiOF deposition.

Table 1 Two center bond energies calculated by AM1 method

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-F</td>
<td>-19.43</td>
</tr>
<tr>
<td>Si-O</td>
<td>-16.24</td>
</tr>
<tr>
<td>C-C</td>
<td>-14.26</td>
</tr>
<tr>
<td>C-O</td>
<td>-14.48</td>
</tr>
</tbody>
</table>

(C$_2$H$_5$O)$_2$SiF

3. Experiment

In the experiment, a parallel-plate plasma enhanced CVD reactor was used. A source gas for the growth was TEFS. TEFS was picked-up by helium and introduced into a reaction chamber. RF power (13.56 MHz) was applied to the upper electrode, and a SiOF film (TEFS-SiOF) was deposited on a wafer at the lower electrode. The RF power was varied from 300W to 900W. TEFS/He gas flow rate was 1000 sccm, gas pressure was 1.1 kPa, and deposition temperature was 400°C. The TEFS-SiOF film structure was investigated by FT-IR (Fourier Transform Infrared Absorption Spectroscopy). Desorbed gas was analyzed with thermal desorption spectroscopy (TDS), where the samples were heated to 1000°C (1°C/s). To measure fluorine concentration, Rutherford backscattering spectrometry (RBS) was used. Dielectric constant was measured using Capacitance-Voltage measurement.
4. Result and Discussion

FT-IR spectra of the TEFS-SiOF films are shown in Figure 2. The films are deposited at various RF powers. All measurements were done as deposited. Absorption peaks at around 1100 cm⁻¹ and 810 cm⁻¹ correspond to Si-O bonds, and an absorption peak at around 930 cm⁻¹ corresponds to Si-F bonds. These peaks are observed in all conditions. On the other hand, the absorption peak at around 2900 cm⁻¹ which corresponds to C-H bonds is not observed in any conditions. From the FT-IR spectra, any particular differences between deposition conditions are not seen.

Figure 3 shows a RBS spectrum of the TEFS-SiOF film deposited at 900W. We can see that F and C are contained in the film. The concentration of fluorine in the films measured by RBS is shown in Figure 4. The concentration of the fluorine increases with increasing RF power.

In order to clarify characteristics of the TEFS-SiOF films, the films were analyzed using TDS.

Figure 5 shows CO₂ desorption (M/Z=44) of the films deposited at various RF powers. The appearance of CO₂ around 350°C means that CO₂ is produced from remaining ethoxy groups (C₂H₅O⁻) in the film. Because ethoxy groups were decomposed into mainly H₂O (M/Z=18), C₂H₄ (M/Z=28) and CO₂ (M/Z=44). The CO₂ desorption, which corresponds to hydrocarbon concentration in the film, is smallest at 500W. Considering the bond-energies in Table 1, we speculate the RF power dependence of the hydrocarbon content as follows:

1) At RF power of 500W, TEFS is decomposed into precursors of the film and stable by-products, and the by-products are rapidly evacuated from the reaction chamber resulting in the smallest C content in the film.
2) At higher RF power, TEFS is decomposed into small pieces and by-products are incorporated into the films.

RF power dependence of the relative dielectric constant is
increasing RF power to 700W, and is about 3.5.

Figure 7 shows TDS spectra of F (M/Z=19) in the TEFS-SiOF films deposited at various RF powers. Broad peaks are observed over about 300°C in all conditions. Fluorine desorption increases with decreasing RF power during deposition. This indicates that fluorine in the film becomes more stable with increasing RF power.

In order to investigate film stability, moisture absorption and instability of F were analyzed by TDS. Figure 8 shows the F desorption spectra of the 900W sample 30 minutes and 7 days after deposition. Though F desorption is slightly increased after 7 days, the increase is not so significant. Moisture desorption after 7 days from deposition was comparable to that of the SiO2 film formed of TEOS/SiO2 using PECVD. These results indicate that TEFS-SiOF film deposited with high RF power has potential for application to interlayer dielectric.

References
2) H. Miyajima, R. Katsumata, N. Hayasaka and H. Okano: Dry Process Symposium (1994) 133