A Fluorinated Organic-Silica Film with Extremely Low Dielectric-Constant

Yasutaka Uchida, Kohshi Taguchi and Masakiyo Matsumura

Dept. of Electronics and Information Science, Teikyo University of Science and Technology, Uenohara-machi, Kitatsuru-gun, Yamanashi 409-0193, Japan. Phone:+81-554-63-4411, Fax:+81-554-63-4431, E-mail: uchida@ntu.ac.jp

1. Introduction

For the purpose of continuing steady improvement of ULSI performances in the next century, low dielectric-constant, k, insulating films for inter-metal-dielectrics are strongly requested[1]. Although many low-k materials have been proposed [2-5], no one satisfies simultaneously conditions requested from a practical viewpoint, which include a sufficiently low k value, good moisture-tolerance, oxidation-tolerance and adhesion characteristics.

We have proposed OH-free and fluorinated organic-silica films [6]. They could be prepared by low-temperature CVD of organic silica films using a mixture of cyanate-silanes and tri-methyl amine[7], and successive fluorination [8]. The proposal was based on the following chemical features: (1) since C-H bonds are strong, the source gas mixture is quasi H-free. (2) since CH3-Si bonds are not broken by amines, the deposited film contains CH3 groups. And (3) cyanate groups remained intentionally in the as-deposited film can be replaced to F by a post-fluorination. Since F and CH3 in the film have complementary properties with each other, such as against moisture and oxygen, the fluorinated organic-silica film has potentially all desirable properties mentioned above. We could not show, however, satisfactorily that the film really has these properties, due to the insufficient CH3 content, and due to the undesirably low deposition and post-fluorination temperatures. Here we have improved the CVD and post-fluorination parameters. The film had k of as low as 2.1 and sufficient moisture-tolerance.

2. Effects of amine

CVD characteristics depend strongly on type of amines[8]. This is because generation rate of precursors and their residence time on the surface change with number of CH3 groups in amines and molecular weight of amines. Better source gas combination will improve CVD characteristics, resulting in the good film properties. Thus, we have added di-methyl ethyl amine [DMA: N(CH3)2C2H5] to the current CVD source gas. Standard CVD parameters are tabulated in Table I. These values were used in this study unless otherwise mentioned. A deposition system has been described elsewhere[6,7]. The deposition rate G is shown in

**Table I** Standard deposition conditions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH3)2Si(NCO)2</td>
<td>0.13sccm</td>
</tr>
<tr>
<td>Si(NCO)4</td>
<td>0.007sccm</td>
</tr>
<tr>
<td>N(CH3)3</td>
<td>60sccm</td>
</tr>
<tr>
<td>N(CH3)2C2H5 (DMA)</td>
<td>60sccm</td>
</tr>
<tr>
<td>Total gas flow rate</td>
<td>300sccm</td>
</tr>
<tr>
<td>Pressure</td>
<td>760Torr</td>
</tr>
</tbody>
</table>

![Fig.1](image1.png) G as function of 1/T for the film deposited with or without DMA.

![Fig.2](image2.png) G and C to Si ratio as a function of DMA flow rate.

![Fig.3](image3.png) C to Si ratio as a function of 1/T for the film deposited with or without DMA.
Fig. 1 as a function of reciprocal temperature, 1/T. G increased by addition of DMA, but the activation energy did not change. G and the relative C content with respect to the Si content evaluated by AES are shown in Fig. 2 as a function of the DMA flow rate. They enlarged with increasing the flow rate, since DMA can decompose organo cyanate-silanes more effectively.

The C ratio is shown in Fig. 3 as a function of T. The ratio in case of no DMA is also shown in the figure as a reference. The ratio enlarged with reducing T, and took 0.43, at 100°C, which is twice as high as that in case of no DMA.

3. Post-fluorination and dielectric constant

A post-fluorination system was described elsewhere[9] and process conditions are tabulated in Table II. Relative F content with respect to Si was typically 9%. K is shown in Fig. 4 by open marks for the post-fluorinated film as a function of T. Results are also shown in the figure by closed marks for the film deposited without DMA. K was as low as 3.2 for the film deposited at 150°C even without post-fluorination. By fluorination, K reduced abruptly by about 0.6. And by annealing at 500°C, K reduced further by about 0.4. The K value was as low as 2.1, that is, to the best of our knowledge, the minimum value reported to date for the silica-based film.

<table>
<thead>
<tr>
<th>HF(N2 carrier gas) flow rate</th>
<th>20sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(50%HF acid)</td>
<td></td>
</tr>
<tr>
<td>Total gas flow rate</td>
<td>200sccm</td>
</tr>
<tr>
<td>Temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Post-fluorination time</td>
<td>5min</td>
</tr>
</tbody>
</table>

Fig. 4 as a function of deposition temperature for the film with or without post-fluorination.

Insulating characteristics were improved also by adding DMA, and further improved by post-fluorination and vacuum annealing. The breakdown field strength defined at the current density of 1μA/cm² was as high as 5.7MV/cm and the low-field resistivity $\rho$ defined at 100kV/cm was about 10^16Ωcm after the 500°C vacuum-annelling for the post-fluorinated film.

4. Long-term stability

Figure 5 shows k and $\rho$ by open marks for the film deposited with DMA as a function of storage time in air. Results are also shown in the figure by closed marks for the film deposited without DMA. Both films were post-fluorinated and vacuum-annealed at 500°C. It is clear that DMA improves long term stability. K was stable for 150 hr and then increased very gradually from 2.3 to 2.4 with elongating the storage time to 580 hr. (Note that the film was deposited at 200°C) $\rho$ was constant for 400 hrs and then decreased, but only gradually, from 10^16Ωcm.

5. Conclusion

Addition of DMA in the current CVD source gas improves the deposition characteristics of the organic silica films and also enlarges the C content in the deposited film. Both of them are effective for the better electronic and chemical characteristics of the film aiming at inter-metal-dielectrics applications. This OH-free and fluorinated organic-silica film was confirmed to have a satisfactorily low k value and a good long-term stability.

Acknowledgement
Authors would like to thank Showa-Denko Corp. for providing cyanate-silanes.

References