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

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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 CH_3-Si bonds are not broken by amines, the deposited film contains CH_3 groups. And (3) cyanate groups remained intentionally in the as-deposited film can be replaced to F by a post-fluorination. Since F and CH_3 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 CH_3 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 CH_3 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: $N(CH_3)_2C_2H_5$] 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

$(CH_3)_2Si(NCO)_2$ flow rate	0.13sccm
$Si(NCO)_4$ flow rate	0.007sccm
$N(CH_3)_3$ flow rate	60sccm
$N(CH_3)_2C_2H_5$ (DMA) flow rate	60sccm
Total gas flow rate	300sccm
Pressure	760Torr

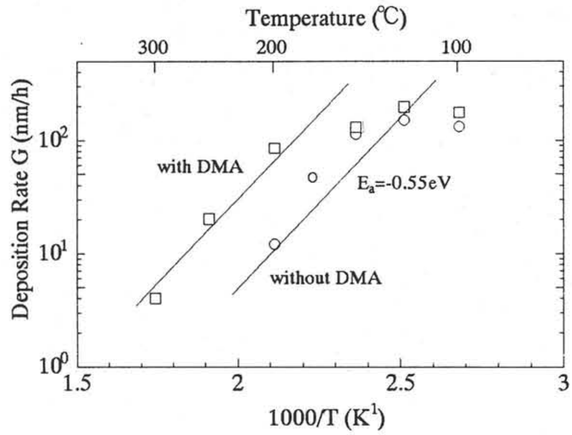

Fig.1 G as function of 1/T for the film deposited with or without DMA.

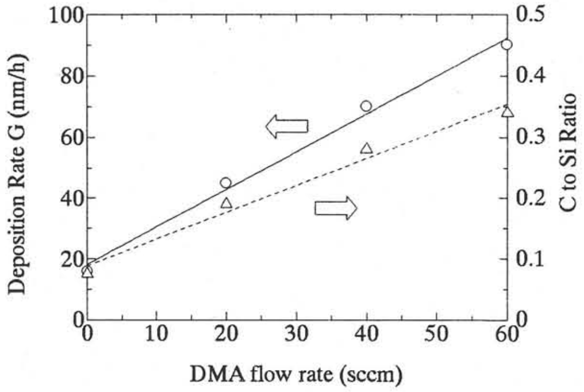

Fig.2 G and C to Si ratio as a function of DMA flow rate.

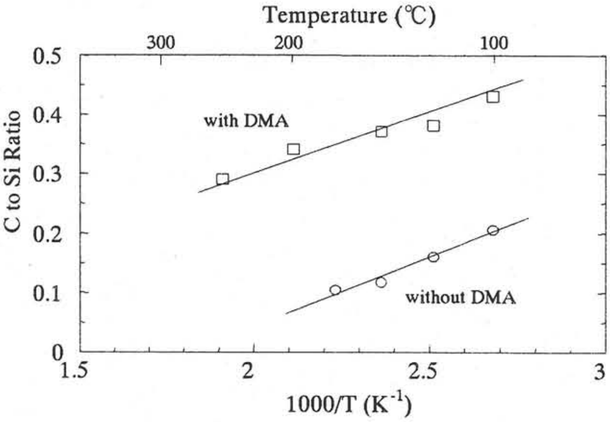

Fig.3 C to Si ratio as a function of 1/T for the film deposited with or without DMA.

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 II Post-fluorination conditions

HF(N_2 carrier gas) flow rate (50%HF acid)	20sccm
Total gas flow rate	200sccm
Temperature	250°C
Post-fluorination time	5min

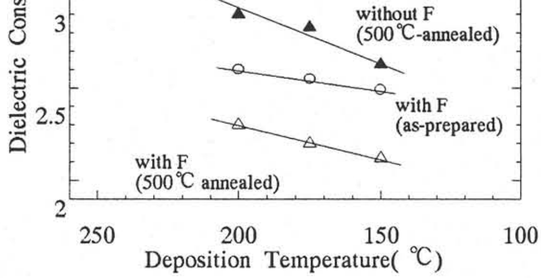

Fig.4 k as a function of deposition temperature for the film with or without post-fluorination.

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 $1\mu A/cm^2$ was as high as 5.7MV/cm and the low-field resistivity ρ defined at 100kV/cm was about $10^{16}\Omega cm$ after the 500°C vacuum-annealing for the post-fluorinated film.

4. Long-term stability

Figure 5 shows k and ρ 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.) ρ was constant for 400 hrs and then decreased, but only gradually, from $10^{16}\Omega cm$.

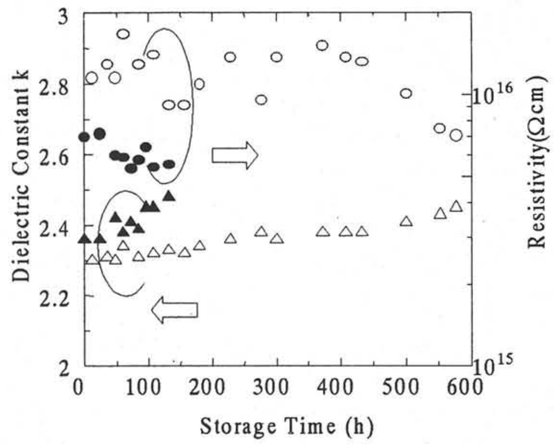

Fig.5 k and ρ as a function of storage time for the film deposited with or without DMA.

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

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