Preparation of Low-k Porous SiO_2 Films by SiO_2/Organic Hybrid Chemical Vapor Deposition

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Abstract

Low dielectric constant materials of the interlayer film are required for the reduction of the RC delay time in the future of ULSI. The dielectric constant of porous silica films can be less than 2. We have proposed that the SiO_2/Organic hybrid film was deposited by CVD and after deposition organic groups were removed from the film by annealing. SiO_2 films were deposited by the dehydration reaction between tetra-isocyanate silane (TICS: $Si(NCO)_4$) and water, and organic films were deposited by the biuret reaction between diisocyanate and water. Isophorone diisocyanate (IPDI: 3-Isocyanatomethyl-3, 5, 5-trimethylcyclohexyl Isocyanate) was used as a diisocyanate source. After annealing, the refractive index was from 1.05 to 1.43, and the porosity obtained from the film density was from 0 to 95 % between TICS pressure of 0.1 to 1. Pores from SEM in porous silica films were observed, but the pore sizes seemed to minute. At the refractive index of 1.05 the dielectric constant and the resistivity were 1.4 and 10^{12} Ωcm, respectively.

1. Introduction

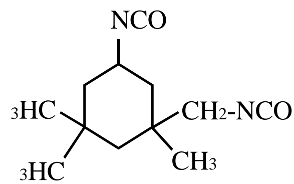
In the future of ULSI, for the purpose of reducing the delay time and the power dissipation caused by increasing capacitance lower dielectric constant films for inter-metal dielectrics (IMD) are strongly required[1]. Recently a variety of low dielectric constant films, such as SiOF films[2], MSQ films[3], a-CF films[4], organic films[5], etc., are being actively studied. Porous silica films are the desirable IMD materials, since they have several advantages in comparison with other lower dielectric materials. SiOF films are unable to decrease the dielectric constant 3.5 due to their moisture absorption. The dielectric constant of MSQ films is as low as 2.7, but they do not have sufficient oxidation resistance to oxygen plasma and ozone. Also, the dielectric constant of a-CF films is as low as 2.1, but the thermal stability is less than 300℃, and the adhesion of a-CF films and organic films is poor. Therefore, the process suitability of those films is poor. On the other hand, porous silica films have the structure of which SiO_2 films have lots of pore. As a result, the dielectric constant decreases with the increasing porosity and the value can be less than 2. Since properties of porous silica films are essentially as the same as those of SiO_2 films, the thermal stability is high and the adhesion is good. In addition, the damage of oxygen plasma is none. These films are compatible with the present and well-refined technology. Recently, porous silica films have been already fabricated by spin on glass (SOG)[6]. However, there are some problems in the fabrication process related to porous silica films by SOG. One of the problems is whether narrow spaces between interconnections are completely deposited or not. Another problem is the size of large pore with less than 0.1 μm process. Furthermore, the problem essentially lies the emission of much waste in the solution in the coating process. Therefore, we tried to prepare porous silica films by Chemical Vapor Deposition so that the CVD might have the feasibilities to get over their problems.

In this paper we have proposed that SiO_2/Organic hybrid films were deposited by CVD and that porous silica films were fabricated by removing organic groups. The properties of porous silica films were evaluated by optical and electrical measurements.

2. Experimental

SiO_2 films were deposited by the dehydration reaction between tetra-isocyanate silane (TICS: $Si(NCO)_4$) and water[7]. On the other hand, organic films were deposited by the biuret reaction between diisocyanate and water. In this study, isophorone diisocyanate (IPDI: 3-Isocyanatomethyl-3, 5, 5-trimethylcyclo-hexyl Isocyanate) was used as a diisocyanate source. IPDI is the structure as shown in Fig. 1, and the melting point, the boiling point and the flash point are -60°C, 158°C/10 Torr and 163°C, respectively.

The deposition systems were used atmospheric hot-wall type. CVD parameters are tabulated in Table Ⅰ. NH_3 was used as a catalyst for the deposition of organic films. TICS and IPDI were introduced by bubbling with the N_2 carrier gas. Water and NH_3 was supplied by bubbling of N_2 with the ammonia solution (28%), and water and NH_3 pressure were fixed at 5 and 100 Torr, respectively. If ammonia was not added, organic films were not deposited.



IPDI (isophrone diisocyanate)

Fig. 1 Structure of IPDI

Table Ⅰ Deposition condition

TICS pressure 0～1Torr
H_2O pressure 5Torr
NH_3 pressure 100Torr
IPDI pressure 0～1.5Torr
Deposition temperature 120°C
Total gas flow rate 200sccm
Total pressure 760Torr

3. Results and discussion

3.1 Deposition properties

Figure 2 shows the Fourier Transfer Infrared spectra of the deposited film. Both TICS and IPDI pressure were 0.5 and 0.5 Torr, respectively. Absorption peaks around 1080, 800 and 450 cm^{-1} corresponding to the Si-O bond were observed. Peaks around 1560, 1620 and 1660 cm^{-1} corresponding to the -CO-NH- bond and the $-CO-NH_2$ bond were observed. Peaks related to the C-H bond around 3000 cm^{-1} and those related to the N-H bond around 3200 cm^{-1} were clearly observed, too. Therefore, we succeeded in depositing SiO_2/Organic hybrid films. Furthermore, peaks related to the Si-OH bond around 975 cm^{-1} and those related to H_2O and the OH bond around 3360 and 3500 cm^{-1} were observed. A large amount of water, the Si-OH bond and the -C-OH bond were contained in the film.

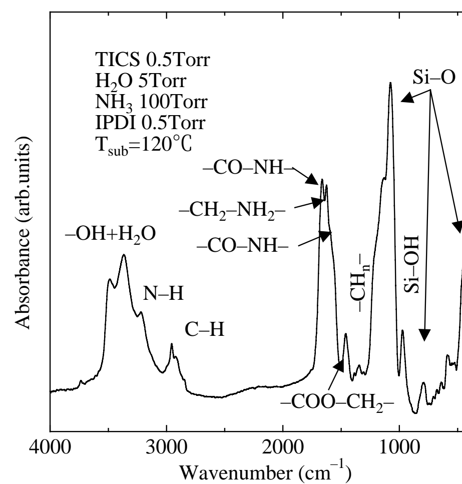


Fig. 2 FT-IR spectra of the hybrid film

Since there were no absorption peaks corresponding to the -NCO bond around 2300 cm^{-1}, TICS and IPDI were completely eliminated by H_2O.

Figure 3 shows the FT-IR spectra as a function of IPDI pressure. The film without IPDI was SiO_2 that contained a large amount of H_2O and the Si-OH bond. The peak strength around 1080 cm^{-1} related to the Si-O bond decreased. On the contrary, the strength around 1500~1700 cm^{-1} related to the biuret bond increased with IPDI pressure increasing. Similarly, the peak strength of the C-H bond (3000 cm^{-1}) and the N-H bond (3200 cm^{-1}) increased. Therefore, peaks of organic groups in the hybrid film increased with IPDI pressure increasing, and got saturated at more than 1 Torr.

Then, IPDI pressure was fixed at 1.5 Torr, and TICS pressure was changed. Figure 4 shows the FT-IR spectra as a function of TICS pressure. As is expected, the peak strength related to the Si-O bond increased with TICS pressure increasing, and the strength related to the biuret bond decreased. On the contrary, the peak strength related to the Si-O bond decreased with TICS pressure decreasing. At TICS pressure of 0.05 Torr, the peak strength of the Si-O bond reached 1~2% of the thermal oxide. Assuming simply, the porosity of the film may reach 98~99 %. Therefore, the porosity may be controlled freely by varying TICS pressure.

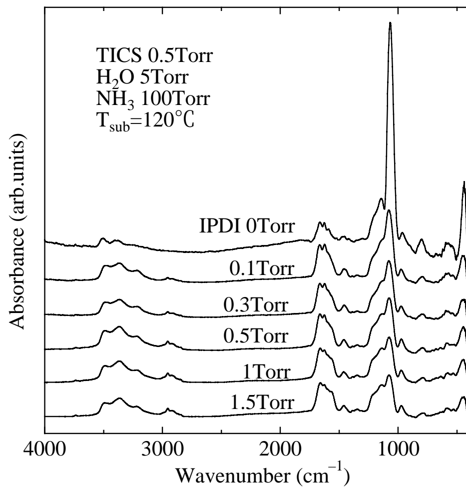


Fig. 3 FT-IR spectra as a function of IPDI pressure

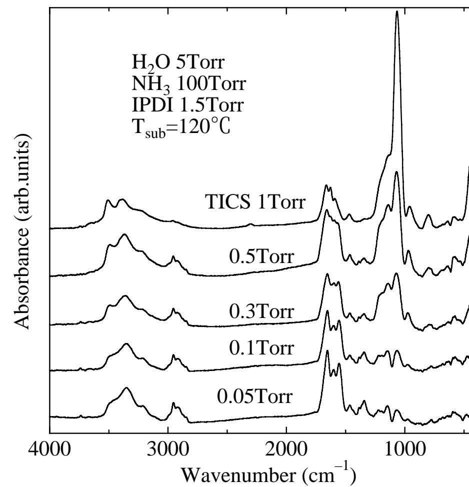


Fig. 4 FT-IR spectr as a function of TICS pressure

3.2 Removal of organic groups

To fabricate porous silica films, organic groups must be removed from the hybrid film. It was suggested that organic groups were removed by thermal annealing in nitrogen ambient. Organic groups consisted of the biuret bond, and this structure was as the same as the urethane polymer. Since the heat resistance of the urethane polymer is less than 300°C, it is expected that organic groups can be decomposed at more than 300 °C. To decompose them completely, the hybrid film was annealed at 400°C for 30 minutes. Figure 5 shows the FT-IR spectra after annealing. The upper of the figure is the as-deposited film at TICS pressure of 0.5 Torr. The middle of the figure is the spectra of the film after annealing in nitrogen ambient.

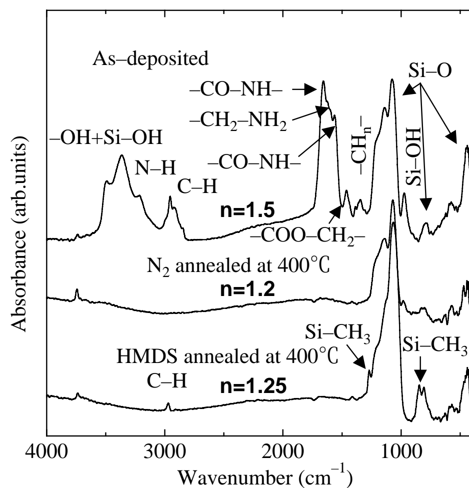


Fig. 5 FT-IR spectra after annealing in N_2 and HMDS ambient

After annealing, peaks around 1080, 800 and 450 cm^{-1} related to the Si-O bond remained completely, but those around 1500~1700 cm^{-1} related to the biuret bond and those of the C-H bond (3000 cm^{-1}) and the N-H bond (3200 cm^{-1}) disappeared completely. Hence, organic groups could be removed. Then, the refractive index of the film decreased from 1.5 to 1.2. Therefore, we succeeded in fabricating porous silica films. However, after annealing in nitrogen ambient peaks around 985 cm^{-1} related to the Si-OH bond was confirmed. The Si-OH bond has a large dipole moment. As a result, it has a large orientation polarization and hence the dielectric constant increases. To remove the Si-OH bond, annealing in hexamethyldisilazane (HMDS) ambient is effective. The overall reactions between the Si-OH bond and HMDS occur as follows[8]:

$$2\equiv\text{Si-OH}+\text{H}_2\text{N-Si(CH}_3)_3\rightarrow 2\equiv\text{Si-O-Si(CH}_3)_3+\text{NH}_3\uparrow . \quad (1)$$

Since the surface of the film is terminated at the Si-CH_3 bond, it is hydrophobic and hence it is expected that the film does not absorb water. The lower of Fig. 5 is the spectra of the film annealed in HMDS ambient for 30 minutes at 400°C. After annealing, peaks around 985 cm^{-1} related to the Si-OH bond disappeared. Peaks of the stretching mode (1270 cm^{-1}), the bending mode (810 and 850 cm^{-1}) of the Si-CH_3 bond and those around 3000 cm^{-1} related to the C-H bond newly appeared. Therefore, the residual Si-OH bond replaced to the Si-CH_3 bond, and the film got hydrophobic. Although the film was revealed in the air exposure for a week, the FT-IR spectra did not change and the film did not absorb water. Similarly, after annealing in HMDS ambient, the refractive index increased from 1.2 to 1.25. This is because the Si-O-Si bond is newly formed by the above-mentioned reactions and the film density increases only a little.

3.3 Porosity and refractive index

Figure 6 shows the refractive index after annealing. The refractive index decreased with TICS pressure decreasing. However, there was a problem. After annealing the refractive index was different in the film of 1500 Å and 4500 Å at TICS pressure of less than 0.3 Torr. The refractive index at 4500 Å decreased more than that at 1500 Å. The film shrinkage at 1500 Å was larger. Although we can not understand why it occurs, we assume that during annealing the film thickness can not be maintained. Furthermore, at for the film thickness 4500 Å another problem occurred. After annealing in nitrogen ambient, the surface of the film got a little muddy. Observing at SEM micrograph, many holes with several micrometers were confirmed on the surface. It was assumed that because of a large amount of gases such as CO_2, NH_3 and H_2O, which came out due to decomposition during annealing, many holes were formed on the surface. Furthermore, it was assumed that at 400°C of the annealing temperature, those holes were formed by destroying the film partly due to its shrinkage. To solve this problem, in the barrel type the film was annealed, and annealing conditions were 0.5 Torr, 100 W and at the room temperature. After annealing the surface was lapping and no cracks. Thus, since only O radical decomposes organic groups, it was assumed that the film was not destroyed and those organic groups were removed. Therefore, oxygen plasma in the barrel type was effective for the purpose of removing organic groups from the hybrid film.

Figure 7 shows the porosity and the refractive index as a function of TICS pressure after annealing. The porosity was calculated based on the film thickness from ellipsometry and the thermal oxide density of 2.2 g/cm^3. The porosity increased with TICS pressure decreasing and was 95 % at 0.1 Torr. Similarly, it decreased with TICS pressure increasing and was 5 % at 1 Torr. Therefore, by varying TICS pressure, the porosity could be controlled freely from 0 to 95 %. However, at TICS pressure of 0.05 Torr, the film shrinkage is large, so that the control of the porosity was very difficult. The refractive index could be changed from 1.04 to 1.43.

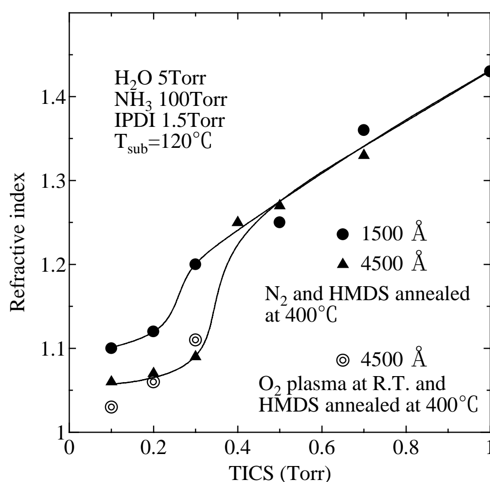


Fig. 6 Refractive index as a function of TICS pressure after annealing in 1500 Å and 4500 Å

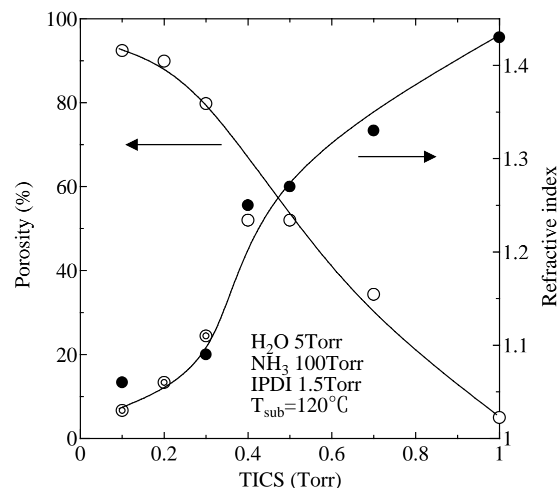


Fig. 7 Porosity and refractive index as a function of TICS pressure after annealing

3.4 Cross sectional SEM micrograph of porous silica films

SEM micrograph of porous silica films is shown in Fig. 8. Pores were observed, but the pore sizes seemed to be minute.

3.5 Dielectric constant and resistivity

Figure 9 shows the dielectric constant and the resistivity of porous silica films. Aluminum dots were deposited on porous silica films about 4500 Å with Si substrates. The dielectric constant was obtained from a MIS capacitance under the strong accumulation conditions. The resistivity of the film was defined by the leakage current density with the electric field 0.1 MV/cm. The X-axis on the bottom indicates the refractive index. The dielectric constant decreased with the refractive index decreasing and was 1.4 at the refractive index of 1.05. Similarly, the resistivity decreased with the refractive index decreasing and was 10^{12} Ωcm at 1.05.

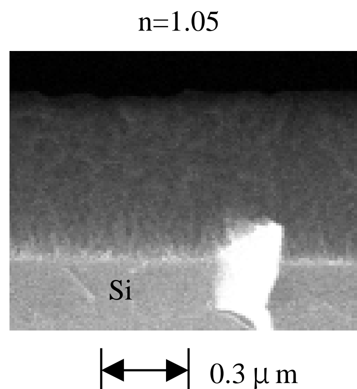


Fig. 8 cross-sectional SEM micrograph

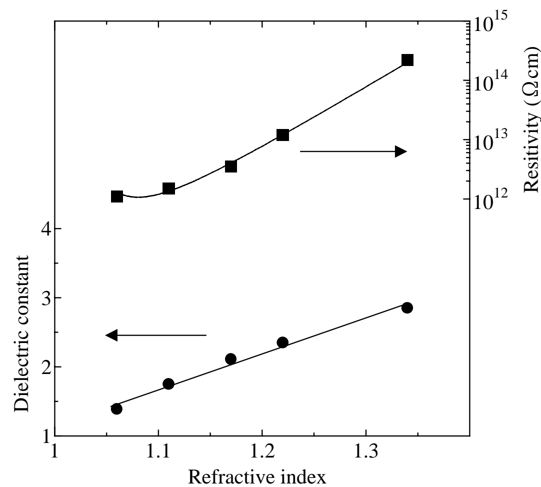


Fig. 9 Dielectric constant and resistivity

4. Conclusions

We prepared porous silica films by depositing SiO_2/Organic hybrid films and removing organic groups. SiO_2 films were deposited by the dehydration reaction using TICS and H_2O. Organic films were deposited by the biuret reaction using IPDI and H_2O. O_2 plasma in the barrel type was effective for the purpose of removing organic groups. By varying deposition conditions, the porosity could be controlled freely from 0 to 95 %. The dielectric constant was minimum of 1.4. The pore sizes from SEM seemed to be minute.

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