A silica-based inter-metal-insulator with low dielectric-constant and high thermal conductivity

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ABSTRACT

Silica films with an $O_{3/2}$-Si-R-Si-$O_{3/2}$ network were deposited by a CVD method from a mixture of silicon-chlorides and water. And film properties were evaluated comparatively for those with R=-CH_2-, -C_2H_4- and -C_3H_6-, by means of AES, FTIR and TPD methods. Thermal conductivity and electrical characteristics were also studied comparatively. The methane film (R=-CH_2-) is concluded the most attractive for an inter-metal-insulator application.

INTRODUCTION

The product of interconnection line resistance and line capacitance is becoming the dominant limiting factor for circuit delay and power consumption in LSIs[1]. Considerable efforts have been thus made to develop inter-metal-insulators with a dielectric constant, k, much lower than that (=4.1) of the CVD SiO_2 film[2]. One of promising ways to reduce the k value is the modification of the silica film by organic groups[3,4]. Present organic silica films, such as the silica film with dense CH_3 groups [5], however, has the fatal shortcoming of low thermal conductivity, because a continuous Si-O-Si network in the pure silica film is interrupted frequently by CH_3 groups, and thus thermal vibration of atoms can not propagate along the network smoothly. We have proposed a group of new organic silica films where a part of O atoms in the pure silica film are replaced by alkylene groups, R, such as -CH_2-, -C_2H_4-, -C_3H_6- and so on, as schematically shown in Fig. 1[6,7]. Since thermal vibration of C atoms in R having delivered from the adjacent Si atom can be transferred to the Si atom at the other side of R, the proposed film will have high thermal conductivity. And the film will have a low dielectric constant by the effects of R. Since these properties will change with number of C atoms in R and also with geometrical structure of R, we have deposited the films having various kind of R and evaluated comparatively electrical properties and thermal properties of these films.

EXPERIMENTAL

One of desirable source materials for growing such organic silica films is of Si-chloride compounds having alkylene groups as listed in Table I. Si-Cl bonds can be oxidized by H_2O to Si-OH groups by a hydrolysis reaction, and a dehydration reaction between Si-OH precursors results in formation of the Si-O-Si network at low temperatures such as 100^oC. Si-C bonds, C-C bonds and C-H bonds, on the other hand,

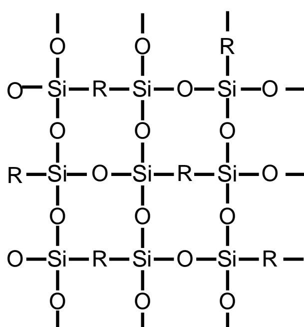


Fig.1. Schematic of new silica films

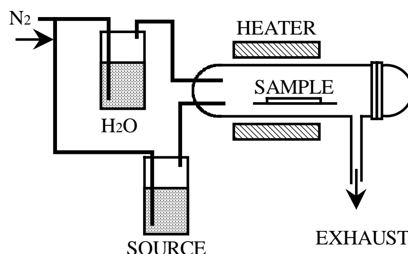


Fig.2. CVD system

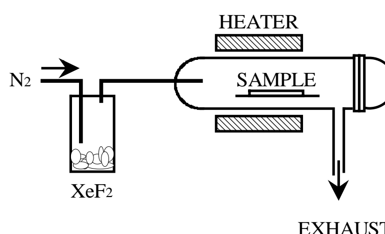


Fig.3. XeF_2 dehydration system

Table I   Source compounds

Film name	Source compound
Methane film	$Cl_3SiCH_2SiCl_3$
Ethane film	$Cl_3SiC_2H_4SiCl_3$
Propane film	$Cl_3SiC_3H_6SiCl_3$

are hardly broken by H_2O under such low temperature conditions. Thus the proposed films can be grown from a mixture of bis(trichlorosilyl)alkanes (Cl_3Si-R-$SiCl_3$) and H_2O. Hereafter in this paper, the films grown from alkanes having R=-CH_2-, -C_2H_4- and -C_3H_6- were referred as the methane, ethane and propane films.

Although these source molecules are liquid, they have relatively high vapor pressures and thus we have used a normal pressure CVD method for the film growth using a system schematically shown in Fig.2. The Si-chloride source materials and H_2O were carried by N_2 gas into the chamber of hot wall type under normal pressure conditions. As an example, CVD parameters for the methane film growth are listed in Table II.

Composition of grown films was evaluated by auger electron spectroscopy (AES). Their chemical structure was analyzed by Fourier-transform infrared spectroscopy (FTIR) and their thermal stability by temperature-programmed desorption spectroscopy (TPD). Electrical properties and thermal properties were also evaluated for the film grown on Si wafers. The film contained dense H_2O molecules and OH groups under as-grown conditions, and they deteriorated the film properties drastically as given later. Thus we have dehydrated the film at low temperatures in a XeF_2 ambient by using a simple annealing system shown schematically in Fig.3.

FILM COMPOSITION AND STRUCTURE

AES spectra are shown in Fig.4 for the methane, ethane, and propane films under as-grown conditions. Dominant AES signals were at 90eV, 270eV and 490eV from Si, C and O atoms, respectively, and signals from Cl and N atoms were under the detection limit. The O to Si concentration ratio was around 1.5 for all films, and the C to Si concentration ratio was changed linearly in proportion to that in the Si-chloride sources. FTIR spectra are shown in Fig.5 for as-grown films. The main signals for all films were around $1100cm^{-1}$, $1080cm^{-1}$ and $830cm^{-1}$, respectively, meaning that the dominant chemical bonds were of the Si-O form, but that a cyclo-tetra-siloxane structure $(-O-Si-O-)_4$, had not formed satisfactorily. (1) There were signals from Si-R-Si bonds in a narrow range from 1100 cm^{-1} to $1400cm^{-1}$, (2) a signal for C-H bonds was detected around $2950cm^{-1}$, (3) there were a signal at $900cm^{-1}$ and a sharp signal around $3700cm^{-1}$ coming from Si-OH bonds, and a broad signal around $3500cm^{-1}$ from H_2O molecules

in

Table II Deposition parameters for methane film

Deposition temperature	80 °C
Net source molecule flow rate	1.0 sccm
Net H_2O flow rate	60 sccm
Total flow rate	400 sccm

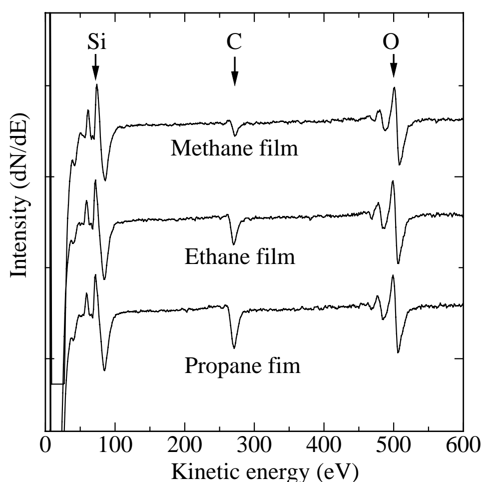


Fig.4. AES spectra for as-grown films

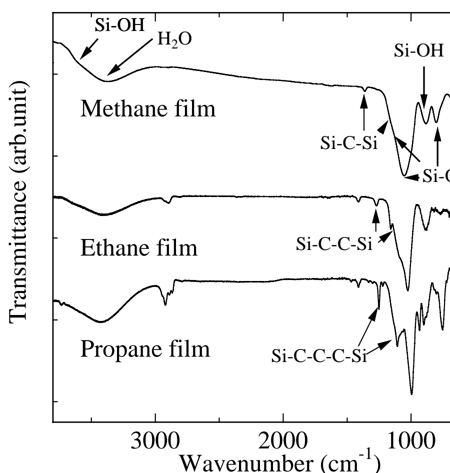
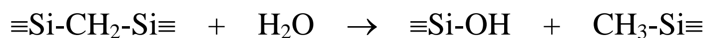


Fig.5. FTIR spectra for as-grown films

the film. We have concluded that the entire Si-R-Si configuration in the chloride source molecules remains in the as-grown films, and that the films can be written as $O_{3/2}$-Si-R-Si-$O_{3/2}$, as schematically shown in Fig.1.

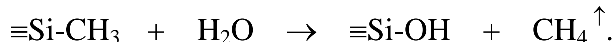
THERMAL STABILITY

Narrow range FTIR spectra are shown in Fig.6 after the vacuum annealing for 30min. For the methane film, the main signal caused from the Si-CH_2-Si configuration at around 1360cm^{-1} could keep its original intensity only till 300 °C, and the signal from Si-CH_3 bonds appeared clearly at 1280cm^{-1} at 400°C as shown in (a). For the ethane film, there were two characteristic signals from the Si-C_2H_4-Si configuration at 1160cm^{-1} and 1270cm^{-1}, respectively, under as-grown conditions as shown in (b). These signals did not change clearly after the 400°C vacuum annealing. For the higher temperature annealing, however, these signals decreased in intensity and the new signal from Si-CH_3 bonds appeared as in case of the methane film. For the propane film, original signal around 1250cm^{-1} from the Si-C_3H_6-Si configuration decreased a little in intensity at 400°C, and the new signal from Si-CH_3 groups around 1280cm^{-1} appeared TPD spectra are shown in Fig.7 for as-grown films. TPD measurement indicated that dominant desorption species were CH_4 with the mass number of 16 for all films.. The ethane and propane films had simple Gaussian-like-shaped desorption waveforms starting from around 400°C. On the other hand, the methane film had at least two signal components; the lower one started at less than 300°C and took the peak value around 500 °C. The upper one took the peak value at 700 °C. The methane film was thermally less stable than the ethane and propane films! We have speculated that the origin of this interesting feature is in the HO-related reaction of Si-C bonds as:



$$\equiv Si\text{-}CH_2\text{-}Si\equiv \; + \; H_2O \; \rightarrow \; \equiv Si\text{-}OH \; + \; CH_3\text{-}Si\equiv$$

and



$$\equiv Si\text{-}CH_3 \; + \; H_2O \; \rightarrow \; \equiv Si\text{-}OH \; + \; CH_4\uparrow.$$

There were dense H_2O molecules and Si-OH bonds in the as-grown film as shown in Fig.4, and then above-mentioned reactions are found thermodynamically favorable for all R. However, for the ethane and propane films, due to strong hydrophobic properties of higher alkylene groups in the film, H_2O molecules cannot approach Si-C bonds, resulting in the better stability of the film. Since better stability is also expected for the methane film, from above discussion, by dehydration, we have carried out the low-temperature dehydration annealing using XeF_2. The FTIR signal relating with Si-CH_2-Si configuration for the methane film did not change even at the 500°C vacuum annealing. TPD spectra for CH_4 are shown in Fig.8 for several temperatures of the successive vacuum annealing after XeF_2 dehydration. The lower desorption branch in the TPD spectra for the as-grown methane film disappeared, and the desorption started from 550°C. The critical temperature was thus improved for more than 200 °C compared with that of the as-grown film. The critical temperature for the ethane film was also improved from 400 °C to 450 °C, but the propane film showed no change in the critical temperature by dehydration. Amount of the improvement depended strongly on the hydrophobic properties of the alkylene groups as expected. Experimental results are summarized in Table III.

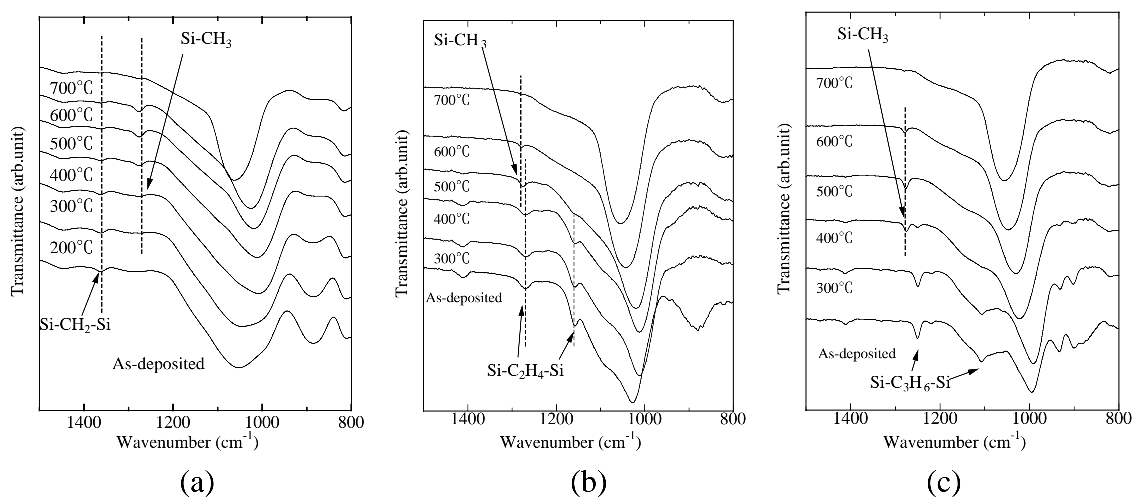


Fig.6. FTIR spectra after vacuum annealing

Table III   Thermal stability

Film name	Maximum acceptable temperature	
	As-grown film	Dehydrated film
Methane film	300°C	550°C
Ethane film	400°C	450°C
Propane film	400°C	400°C

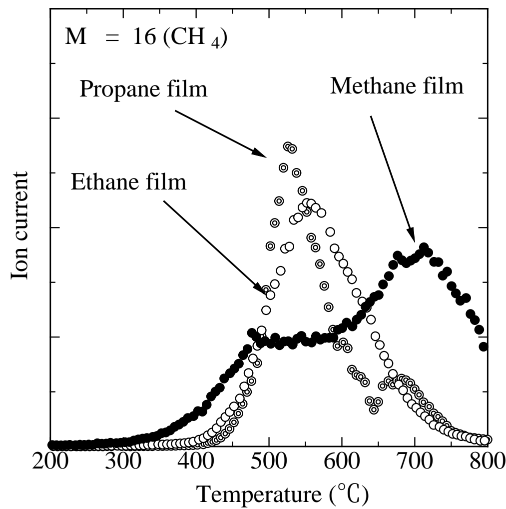


Fig.7. TPD spectra for as-grown films

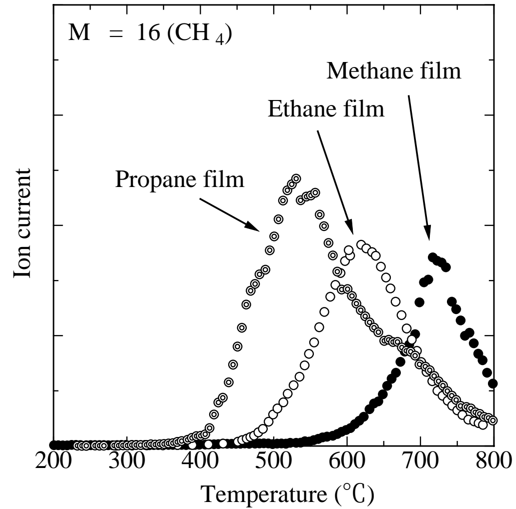


Fig.8. TPD spectra for dehydrated films

ELECTRICAL PROPERTIES

Leakage characteristics were investigated by the metal-insulator-semiconductor structure. All films showed unsatisfactory insulating properties under as-grown conditions, because they have a lot of Si-OH groups and H_2O molecules in the film. After XeF_2 dehydration, however, they had good insulating properties as shown in Fig.9. Resistivity, ρ, defined at 100kV/cm, and the breakdown field strength, E_{BD}, at 1μA/cm^2 were $2\times10^{15}\Omega$cm and 3.3MV/cm, respectively. For the methane film after the successive vacuum annealing at 500°C, dielectric constant was 2.8. The ethane and propane films had also good insulating properties, but did not have a low dielectric constant, maybe, due to the fact that H_2O molecules and Si-OH bonds could not be removed satisfactorily from the film due to their insufficient thermal stability.

THERMAL CONDUCTIVITY

Thermal conductivity has been evaluated for the methane film. It was about 95%

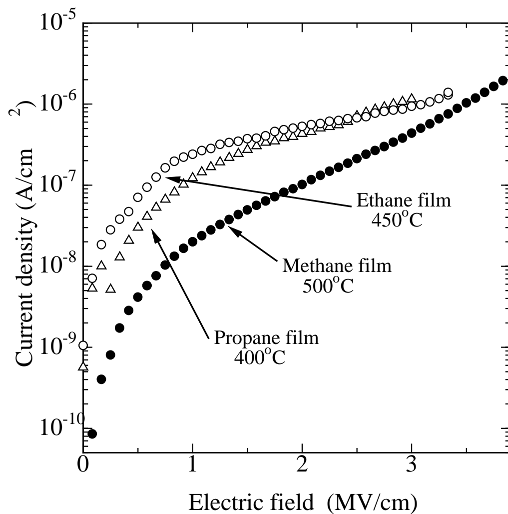


Fig.9. Leakage characteristics

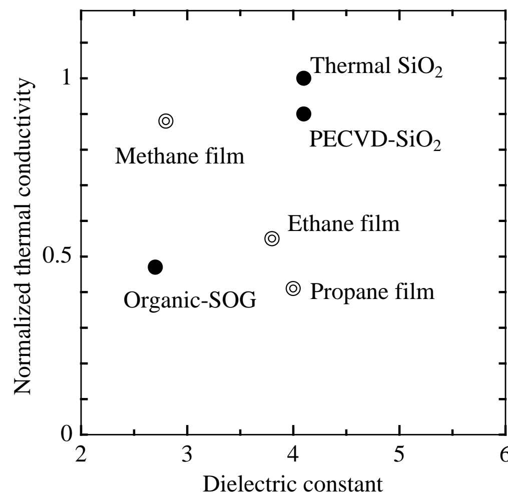


Fig.10. Thermal conductivity vs. dielectric constant

of that for the PECVD SiO_2 film. For the ethane and propane films, however, the thermal conductivity was as low as that for the organic SOG film and about one-half of that for the PECVD SiO_2 film. The thermal conductivity is plotted as a function of dielectric constant for several silica films in Fig.10. There is a room of improvement in the dielectric constant for the ethane and propane films by sufficient dehydration. However, thermal conductivity will not be improved by dehydration. Thus only the methane film is promising for a low-k and thermally conductive insulator aiming at LSI inter-metal-insulator application.

CONCLUSION

Silica films modified by dense alkylene groups have been CVD-deposited from a mixture of bis(trichloro-silyl)alkanes. Only the dehydrated methane film grown from bis(trichloro-silyl)methane was satisfactorily stable. The film has a dielectric constant as low as the organic-SOG film and a thermal conductivity as good as the PECVD SiO_2. If we define the quality factor Q as thermal conductivity versus excess dielectric constant (i.e., dielectric constant minus unity), then Q for the methane film was about twice as good as that for the organic SOG film, the representative low-k film and 1.8 times as god as that for the PECVD SiO_2 film. Since good thermal conductivity for the methane film comes from a strong chemical bonding between Si and C atoms, we can expect that the film is also mechanically strong. Thus the methane film is very promising for inter-metal-insulators in LSIs. The ethane and propane films are not promising in their original form due to their fatal shortcoming on the thermal conductivity. There is, however, a room for dramatic improvements in these films by replacing H atoms to F atoms in R groups, since C-F bonds can modify the chemical strength of the Si-C and C-C bonds.

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