J. of Basic Sciences, Cheju Nat. Univ.
8(1), 115~121, 1995.

기초과학연구 제주대학교
8(1), 115~121, 1995.

Formation and Characterization of SiOF Thin Films by LPCVD Method

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Abstract

An investigation on the deposition of SiOF films was undertaken to form an IMD by using a low pressure chemical vapor deposition (LPCVD) for the submicron multi level metallization. The films have been characterized by using FTIR spectroscopy and AES. Two SiOF thin film samples are not glassy. In the FTIR spectra for these samples, there are some absorption peaks, corresponding to Si-O stretching mode, Si-F stretching mode, Si-O bending mode, and Si-OH bond at $1108.9cm^{-1}$, $894cm^{-1}$, $820cm^{-1}$, and $966.7cm^{-1}$, respectively. Another SiOF thin film sample is glassy. In the spectrum for this sample, the position of absorption peaks corresponding to Si-F stretching mode and Si-O bending mode are same those of previous samples. But the absorption peak positions corresponding to Si-O stretching mode and Si-OH are at $1098.2cm^{-1}$ and $946.7cm^{-1}$, respectively. Electrical properties such as dielectric constant, dielectric breakdown and leakage current are also investigated using C-V and I-V measurements with MIS capacitor structure. The relative dielectric constant was~3.2. The dielectric breakdown voltage and leakage current are 1.02MV/cm and $3.5\times10^{-9}A/cm^2$, respectively.

Introduction

New intermetal dielectric (IMD) material formation technology is essential for multilevel interconnection fabrication in ULSI devices. Present aluminum interconnects with silicon dioxide as IMD layers will result in high parasitic capacitance and crosstalk interference in high density devices[1,2].

SiO_2 films have the values of dielectric constants, 3.9-5.0 according to growing methods. But it is necessary to reduce the dielectric constant.

One of the most promising IMD materials that provides a modest reduction in the dielectric constant but retains many of the properties of silicon dioxide is fluorinated silicon dioxide[3,4].

The dielectric constant of the material is dependent on the extent of permanent polarized bonding and the angles between chemical bonds. A less polarizable dielectric material will have a lower dielectric constant.

Fluorine is the most electronegative and the least polarizable element on the periodic table. Incorporation of fluorine reduces the number of polarizable Si-OH bonds and also causes changes in the network of silicon dioxide to a less polarizable geometry[5]. These changes results in lowering the polarizability of the F_xSiO_y film itself, thus lowering the dielectric constant.

In this study, fluorinated silicon oxide film was fabricated by using low pressure chemical vapor deposition (LPCVD) method and its chemical, physical, and electrical properties were investigated. The deposition technique utilized fluorotriethoxysilane [FTES, $FSi(OC_2H_5)_3$] and water vapor as gas source.

Experimental

SiOF film deposition was carried out with a low pressure CVD system, as shown Fig. 1. Fluorotriethoxysilane and pure water were vaporized by N_2 bubbling in the thermostatic chambers. These gases were transported separately and injected into the reactor, followed by mixing, where the gas lines were kept at the same temperature as the thermostatic chambers. The deposition conditions of SiOF films are shown in Table 1.

Chemical, physical, and electrical properties of the SiOF film, such as film composition, chemical bonding structure, dielectric break down voltage, leakage current, and dielectric constant were investigated.

The film composition was analyzed Auger Electron Spectroscopy (AES). To study the chemical bonding structure, Fourier transform infrared (FTIR) measurement was performed. The electrical properties such as dielectric constant (1MHz) were also investigated using MIS (Al/980nm thick film/p-Si) structure.

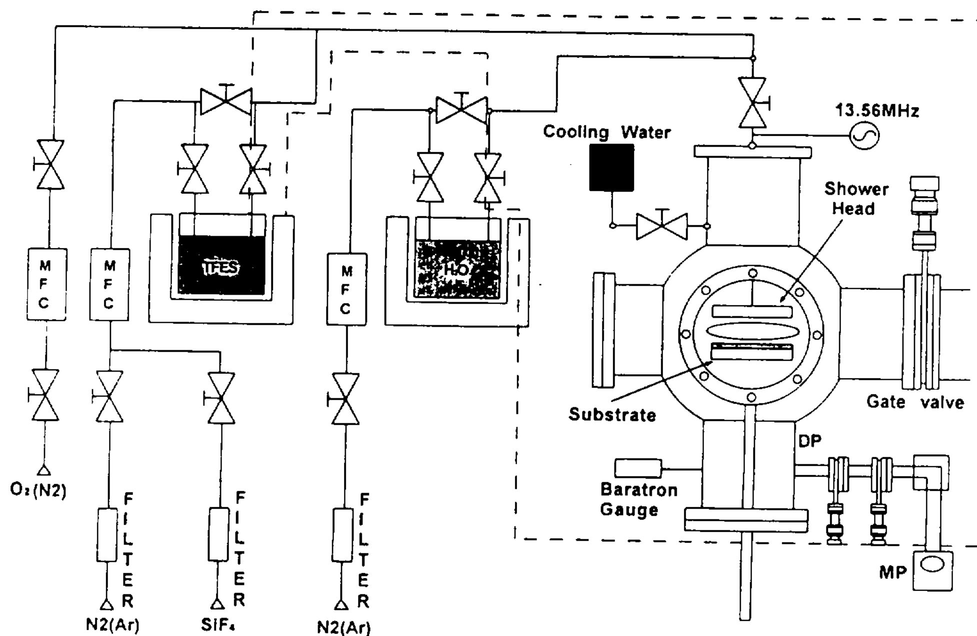


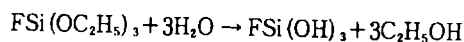
Fig. 1. The cross sectional view of the experimental apparatus for low pressure CVD system

Table 1. Deposition conditions for the SiOF thin film by FTES/H_2O-LPCVD

Parameter	Value	Unit
Initial pressure	3×10-6	Torr
Working pressure	12~40	Torr
Gas line and reaction chamber temp.	50	℃
Substrate temperature	RT~400	℃
Gas flow rates		
FTES	100~200	sccm
H_2O	75~150	sccm
Bubbler temperature	50	℃

Results and Discussions

The SiOF film deposition mechanism is considered as being according to the following reactions, which generally represent hydrolysis and polymerization reactions, respectively.



$$FSi(OC_2H_5)_3 + 3H_2O \rightarrow FSi(OH)_3 + 3C_2H_5OH$$

$$n[FSi(OH)_3] \rightarrow [FSiO_3/_2]_n + 3n/2\ H_2O$$

These reactions occur even at room temperature, because the fluorine contained in the FTES acts as a catalyst for these two reactions[2].

The FTIR spectra of the SiOF films deposited in various conditions are shown in Fig. 2. In the spectra of sample (a) and (b) of Fig. 2, the absorption peaks corresponding to Si-O stretching mode, Si-

F stretching mode, and Si-O bending mode are at 1108.9cm^{-1}, 894cm^{-1}, and 820cm^{-1}, respectively. There is another peak at

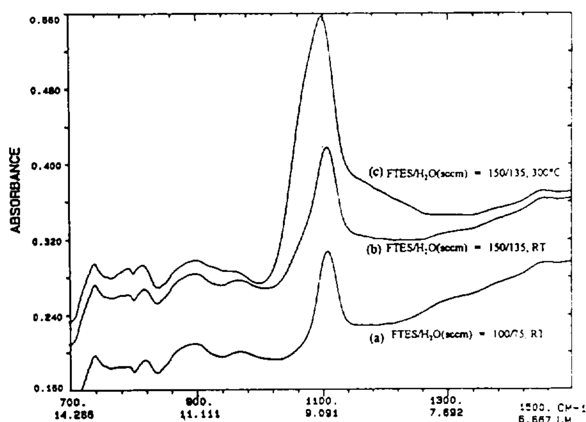


Fig. 2. FTIR spectra of SiOF thin film formed by FTES/H_2O-LPCVD

966.7cm^{-1}, it is identified as the absorption peak corresponding to Si-OH bond. Generally, the absorption peak corresponding to the Si-F stretching mode in the SiOF thin film is at around 930cm^{-1}. But the peak position of Si-F stretching mode in these samples are shifted to lower wave number. This shift may be due to the mixing of Si-OH or non-crystallization of SiOF thin film.

In the spectrum of sample (c) which was formed at the substrate temperature of 300℃ the absorption peak at 1098.2cm^{-1}, is identified as the absorption peak corresponding to the Si-O stretching mode.

Fig. 3, 4, and 5 are the depth profiles

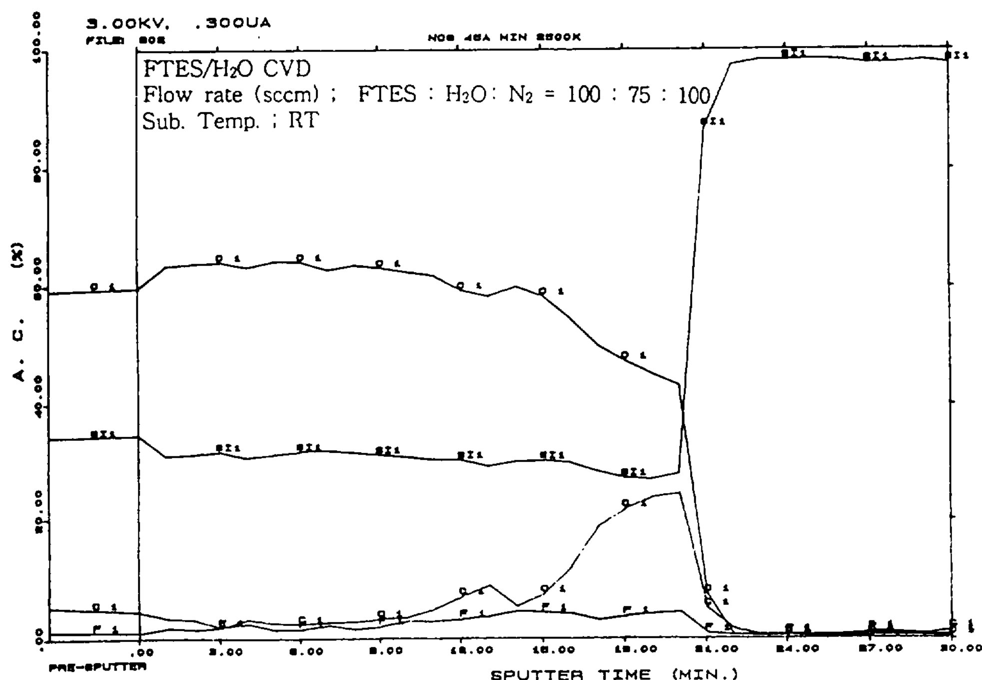


Fig. 3. AES depth profile for SiOF thin film formed by FTES/H_2O LPCVD

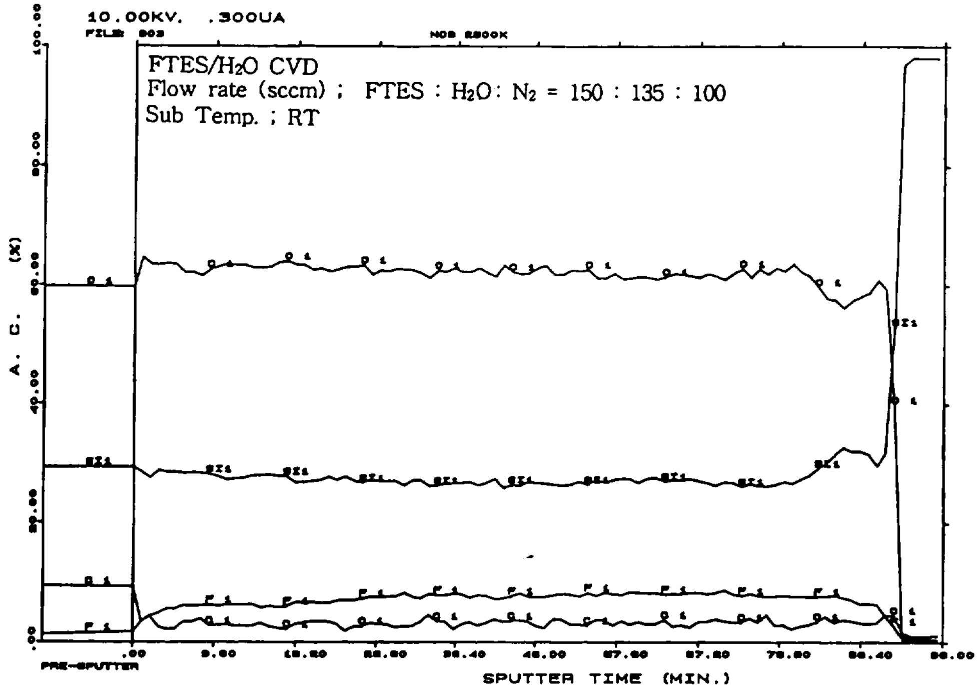


Fig. 4. AES depth profile for SiOF thin film formed by $FTES/H_2O$ LPCVD

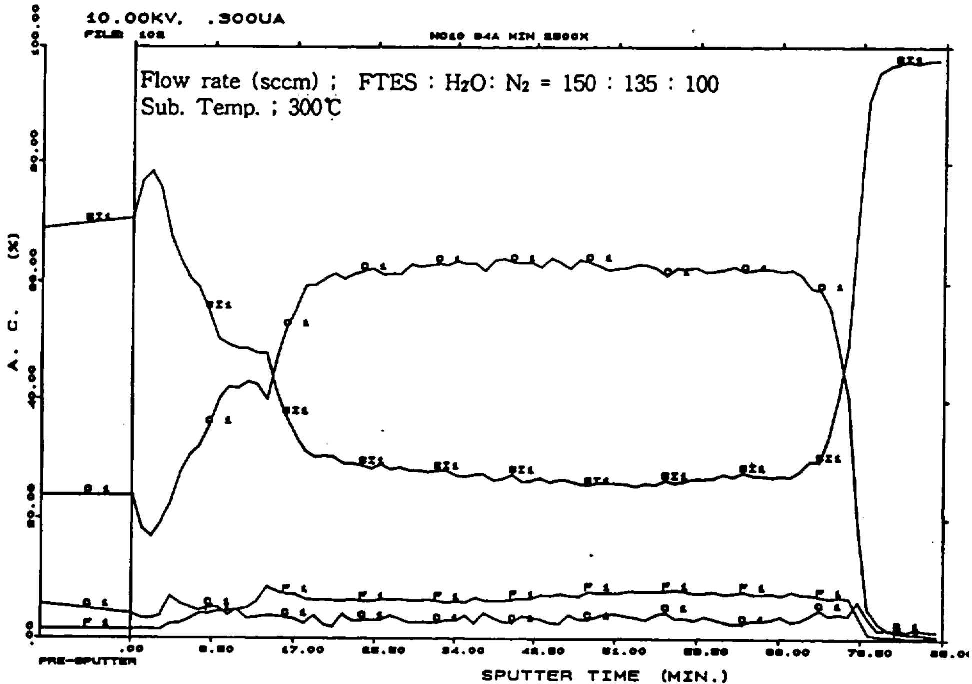


Fig. 5. AES depth profile for SiOF thin film formed by $FTES/H_2O$ LPCVD

of sample (a), (b), and (c) by AES in the chemical reaction of FTES and H_2O, respectively. In the Fig. 3 and 4, the atomic ratios of sample (a) and (b), Si : O : F, are 3.2 : 6.4 : 0.1 and 2.6 : 6.2 : 1.2, respectively. From this ratios, the chemical formulas of SiOF film in sample (a) and (b) are $F_{0.05}SiO_2$ and $F_{0.5}SiO_{2.4}$, respectively. A comparison of the depth profiles, the concentration of F in sample (b) is 11% larger than that in sample (a). this indicates that the concentration of F is depend on the flow rate of FTES. Fig. 5 shows the atomic ratio of sample (c), Si : O : F, is 2.64 : 6.32 : 0.8. From this ratio, the chemical formula of FTES film in sample (c) is $F_{0.3}SiO_{2.4}$. The difference in deposition condition between sample (b) and (c) is only the substrate temperature. From the results of depth profile of sample (b) and (c), the concentration of SiOF film formed at higher substrate temperature is smaller than that at lower substrate temperature. This fact may be due to the diffusion of F atoms to the outside of SiOF film by heating of substrate.

The electrical properties of SiOF thin films were investigated only on the sample (c). Because the SiOF thin film of sample (a) and (b) were not glassy but that of sample (c) was glassy.

Fig. 6 shows C-V plot of MIS(Al/980nm SiOF/p-Si) capacitor of sample (c). From

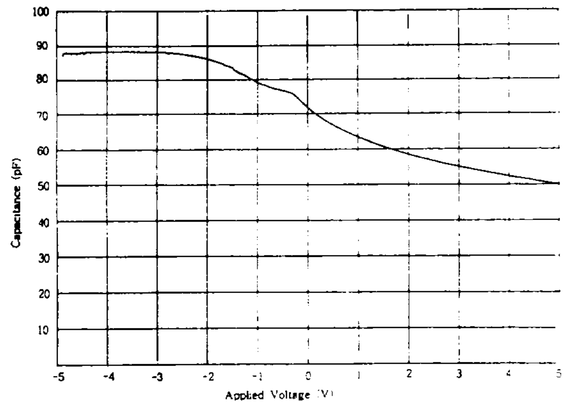


Fig. 6. C-V plot for SiOF thin film formed by FTES/H_2O LPCVD

C-V plot, relative dielectric constant was 3.2 that is a value lower than that of the oxides by other methods[3].

The dielectric breakdown voltage and leakage current are 1.02MV/cm and 3.5×10^{-9}A/cm^2, respectively.

Conclusion

In the FTIR spectra of three samples of SiOF thin films deposited using LPCVD, the absorption peak corresponding to Si-OH stretching mode is at around 965cm^{-1}. From the results of depth profile of three samples using AES, the concentration of F atom is depend on the flow rate of FTES and H2O and substrate temperature. The dielectric constant of the SiOF thin film which was formed at substrate temperature of 300℃, and flow rate of

FTES and H_2O are 150sccm and 135sccm, respectively, is 3.2. The obtained dielectric breakdown voltage and leakage current are 1.02MV/cm and $3.5\times10^{-9}A/cm^3$.

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