Preparation and Characterization of Thin Films by Plasma Polymerization of Hexamethyldisiloxane

Sang Hee Lee, Duck Chool Lee
Department of Electrical Engineering, Inha University
253 Yonghyun-dong, Nam-gu, Inchon 402751, South Korea

Abstract

Plasma polymerized hexamethyldisiloxane (PPHMDSO) thin films were produced using an electrode capacitively coupled apparatus. Fourier transform infrared spectroscopy analysis indicated that the thin film spectra are composed not only of the corresponding monomer bands but also of several new bands. Auger electron spectroscopy analysis indicated that the permeation depth of aluminum into the films is ca. 30 nm when top electrode is deposited by evaporation aluminum. The increase of relative dielectric constant and decrease of dielectric loss tangent with the discharge power is originated from high cross-link of the films.

Key words : Plasma processing and deposition; Fourier transform infrared spectroscopy; Auger electron spectroscopy; Dielectric properties

1. Introduction

The production of thin polymer films on solid surfaces has received considerable attention for many years. The formation of these films from the monomers can be accomplished by numerous techniques such as electron bombardment, ultraviolet radiation, photolysis, evaporation, and glow-discharge polymerization. Among these methods, glow-discharge or plasma polymerization is widely used since polymer films prepared by this method are pin-hole free, highly cross-linked, insoluble and heat resistant, and generally have excellent chemical, mechanical, electrical, and thermal properties [1]. Further, the materials formed by plasma polymerization are vastly different from conventional polymers and constitute a new kind of material.

One of the characteristic features of plasma polymerization is the ability to initiate polymerization of organic compounds which will not form polymers under normal polymerization conditions. Among the very wide range of possible monomers for plasma polymerized films (aromatic hydrocarbons [2], aliphatic hydrocarbons [3], organosilicones [4-6], and others), the organosilicones appear to hold much promise : Not only are these films quite stable at elevated temperature, but they are a priori more readily compatible with silicon-based integrated circuits in electronic applications [7]. Plasma deposits of organosilicone compounds can be used as coating for scratch and corrosion protection, as well as in gas diffusion membranes/barriers [8].

Recently, considerable attention has been devoted to the plasma polymerization of organosilicon monomers, particularly hexamethyl-disiloxane (HMDSIO). These monomers are of interest because of high deposition rates and the ability to control structure and properties by varying deposition conditions [9].

Kashiwagi *et al.* reported the study for the formation process by which to fabricate oxide insulation films with ease, and the electrical

properties of HMDSO hybrid films formed by the plasma process [6].

Cai *et al.* fabricated HMDSO films by means of an inductively coupled electrodeless glow discharge, and reported that the effect of different chemical bonds in the monomer structure on monomer reactivity was investigated through the determination of monomer polymerization kinetics [10].

Also, hexamethyldisiloxane is an easy and safe monomer to handle (particularly so when compared with silane compounds). In contrast to the extensive literature on the chemistry of hexamethyldisiloxane plasma deposits, relatively little has appeared on the electrical properties of these films.

In this paper, we report on our analysis of the chemical and electrical properties of plasma polymerized hexamethyldisiloxane thin films by from α-step, Fourier transform infrared spectroscopy (FT-IR), Auger electron spectroscopy (AES), and an impedance analyzer.

2. Experimental details

Fig. 1 shows a schematic diagram of the rf remote plasma polymerization apparatus. The plasma polymerization process includes three main steps: (1) the rf excitation of argon (Ar); (2) the decomposition of hexamethyldisiloxane by the excited argon; (3) film formation on a substrate.

The high-purity Ar (99.999 %) gas was supplied to the chamber from the top feed line as a carrier gas and hexamethyldisiloxane (99.5 %, Aldrich Chemical) from the side feed line as a monomer.

The chamber was evacuated to a base pressure of less than 2×10^{-2} Torr using a rotary pump. The pressure was measured using a pirani gauge (Okano Works, PG 1S).

Microscope slide glasses (Marienfeld, 75×25 mm), silicon wafers (MEMC, 100-oriented n-type), and potassium bromides (JASCO) were used as substrates. The microscope slide glass and silicon wafer substrates were ultrasonically cleaned with organic solvents. In addition to wet cleaning, the

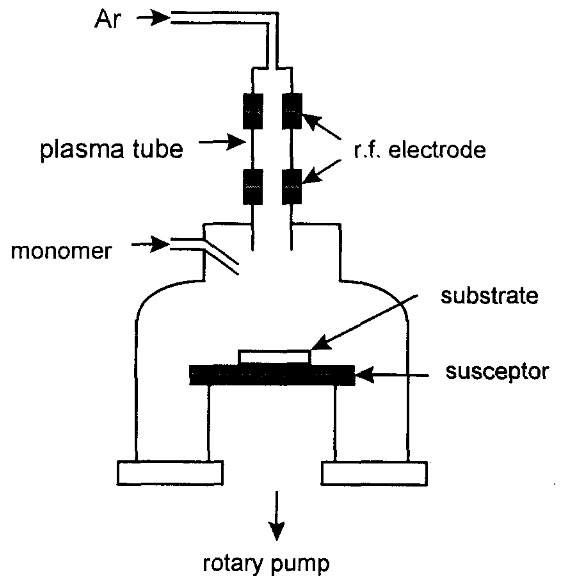

Fig. 1. Schematic diagram of remote plasma polymerization apparatus.

microscope slide glass and silicon wafer substrates were in-situ cleaned by Ar plasma for 10 min at the discharge power of 50 W.

Experimental conditions were carrier gas flow rate of 11 sccm(standard cubic centimeter per minute), total pressure of 1×10^{-1} Torr, discharge frequency of 13.56 MHz, and discharge power of 30-90 W. There was no additional substrate heating for a plasma polymerization. The films were polymerized with a thickness of 500 nm for all measurements.

The thickness of the films was measured by α-step (AJU Eximinc). The infrared spectra were measured in the range of 500 to 4000 cm1 by using Fourier transform infrared spectroscopy (FT-IR, Bruker IFS-48). Auger electron spectroscopy (AES, Perkin Elmer PHI-670) was operated at 10.00 kV of electric field and 0.0217 μ. A of current.

The relative dielectric constant was calculated by simple equation and the dielectric loss tangent was measured by Impedance Analyzer (Hewllet Packard, 4192A LF). For measurements of dielectric properties, an aluminum electrode of 3 mm width was evaporated in vacuum onto a

microscope slide glass.

3. Results and discussion

3.1. Deposition rate

Fig. 2 shows the relationship between the deposition rate and the discharge power. The deposition rate of the films was 8.25-32.5 nm/min in accordance with the discharge power.

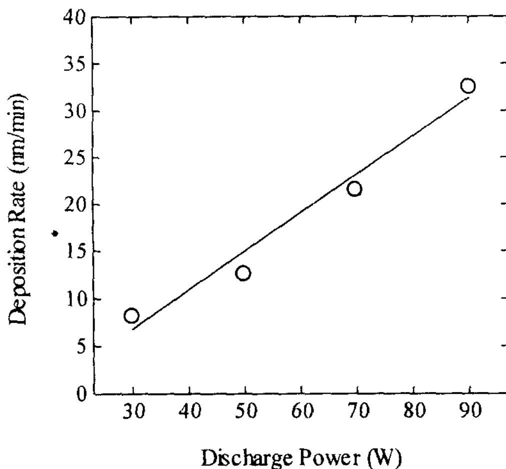

Fig. 2. Deposition rate on the discharge power.

This increase of the deposition rate is considered to originate from the concentration of the reactive fragments and radicals. Kokai et al. [11] have reported that the decomposition reaction of hydrocarbons takes place more easily with increasing the discharge power. Also, the concentration of reactive fragments and radicals is increased with the discharge power because the monomer molecules are decomposed into various fragments in plasma. The increase of deposition rate is considered as a result of phenomena as mentioned above.

3.2. Fourier transform infrared spectroscopy

Fig. 3 shows the infrared transmission spectrum of HMDSO monomer and PPHMDSO films. The only spectrum of the thin film prepared at the discharge power of 30 and 90 W is shown in Fig. 3 because the spectrum of the films as a function of the discharge power appeared all similar. The intensity of absorption bands was increased with the increasing discharge power as shown in Fig. 3. The variation of the intensity of absorption bands and the chemical structure of PPHMDSO film as a function of the discharge power suggest that the activation reaction possibly occurs by the fragmentation of Si—C and C—H bonds of HMDSO monomers, and also that the increase of the discharge power enhances the number of fragmented bonds per monomer in the activation step, leading to the enhanced character of cross-linked structure in the PPHMDSO film.

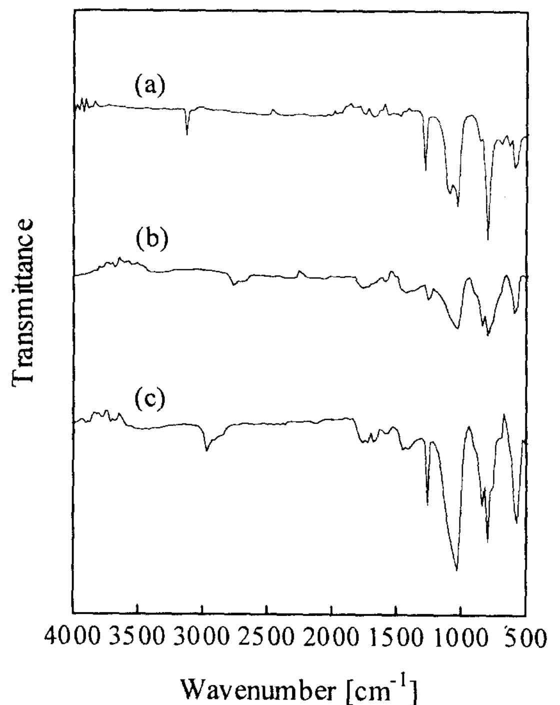

Figure 3. FT-IR spectra of HMDSO monomer and PPHMDSO films.
(a) HMDSO monomer, (b) PPHMDSO film at P = 30 W, (c) PPHMDSO film at P = 90 W.

The spectrum of HMDSO monomer exhibits the absorption bands as summarized in Table 1 [12,13].

Table 1. FT-IR band assignment of HMDSO monomer

Material	Peak Position (cm^{-1})	Band Assignment
HMDSO	3126.9	ν a (C–H) in CH_3
	1282.8	δ s (CH_3) in Si– CH_3
	1028.1	ν a (Si–O–Si)
	796.7 , 590.2	ν (Si–C)

Table 2. FT-IR band assignment of PPHMDSO film (discharge power : 90 W)

Plasma Polymer	Peak Position (cm^{-1})	Band Assignment
PPHMDSO	3466.4	ν (O–H)
	2968.7	ν a (C–H) in CH_3
	2449.8	ν (Si–H)
	1763.1	ν (C=O)
	1452.5	δ a (CH_2) in Si– CH_2– CH_2– Si
	1410.1	δ a (CH_2) in Si– CH_2– Si
	1261.6	δ s (CH_3) in Si– CH_3
	1028.1	ν a (Si–O–Si)
	839.1	ρ (CH_3) in Si–$(CH_3)_n$, n=2,3
	796.7	ρ (CH_3) in Si–$(CH_3)_n$, n=1,2
	900 ~ 500	ν (Si–C)

The plasma polymerized thin film spectrum shown in Fig. 3 is composed not only of the corresponding monomer bands but also of several new transmission bands which were absent in monomer spectrum, namely Si—H at 2449.8cm^{-1} Si—CH2—CH2—Si at 1410.1cm^{-1} and Si—CH2—Si at 1410.1 cml. The new transmission bands due to a probable oxidation were found in the spectrum of plasma polymerized film, such as O—H at 3466.4 cm^{-1} and C=O at 1763.1 cm^{-1}. These spectrum were summarized in Table 2.

3.3. Auger electron spectroscopy

AES was used to find the permeation depth of aluminum into the films when top electrode is deposited by evaporation aluminum. The thin film which was prepared with the discharge power of 90 W was used for this experiment. The aluminum was deposited by evaporation on the film. Fig. 4 shows the relationship between the atomic concentration and the sputter time.

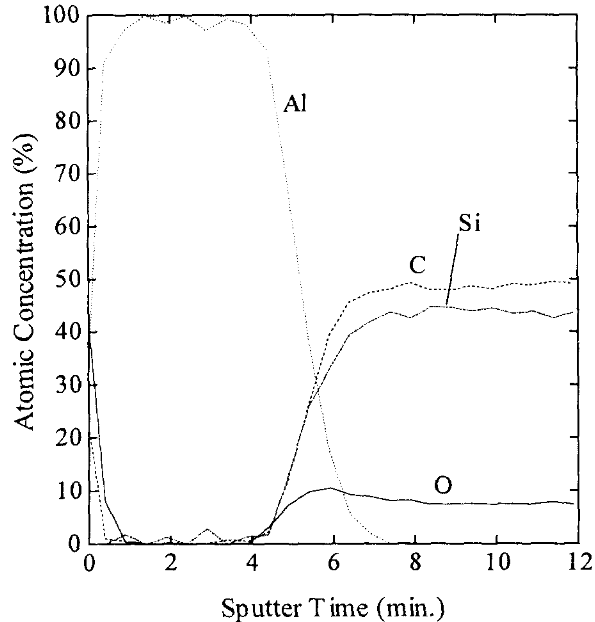

Figure 4. AES atomic concentration depth profile of PPHMDSO film. Discharge power: 90 W.

The surface of the top electrode is composed of only aluminum and oxygen. The oxygen content results from oxidation when the top electrode on the film is exposed to air. Aluminum contents gradually drops inside the film and then the composition of the film is revealed. The etching rate of the plasma polymerized hexa-methyldisiloxane thin film is ca. 15 nm/min. As shown in fig. 4, the permeation aluminum was appeared with the sputter time of ca. 2 min. Therefore, the permeation depth of aluminum into the film is ca. 30 nm.

3.4. Dielectric property

Fig. 5 shows the relationship between relative

dielectric constant, dielectric loss tangent and frequency at room temperature. The relative dielectric constant and dielectric loss tangent of PPHMDSO film at 90 W of the discharge power were increased 3.212 to 3.805 and 0.0026 to 0.0451 in the range of 10^3 to 10^6 Hz, respectively. As the discharge power was increased, the relative dielectric constant of the films was increased 2.273 to 3.212 and the dielectric loss tangent was decreased 0.0083 to 0.0026 at 1 kHz.

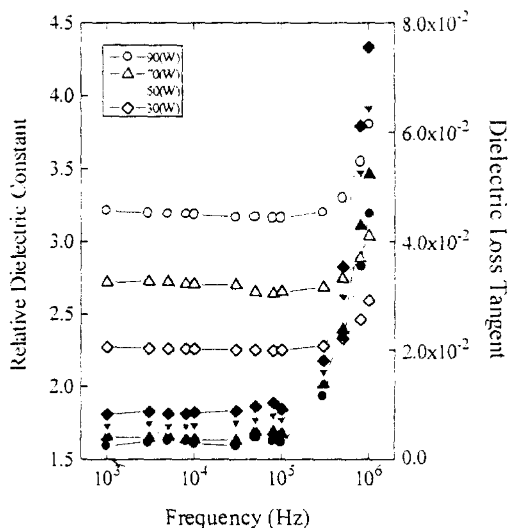

Figure 5. Relative dielectric constant and dielectric loss tangent vs. frequency for different discharge powers. Open, relative dielectric constant; solid, dielectric loss tangent.

This increase of the relative dielectric constant and decrease of the dielectric loss tangent are considered as a result of higher cross-link of the films with increasing the discharge power. If PPHMDSO film have smaller cross-link and higher voids, polarization will be revealed in the films. The dipole caused by polarization tries to rotate in alternative electric field, but the force of restitution is revealed because of the resisting power interfering with rotation. The dielectric loss tangent is caused by the force of restitution of the films.

In higher discharge power, the plasma polymerized films show higher cross-link because the concentration of reactive fragments increases with the discharge power. This phenomenon corresponds with the data of Fig. 3. The values of relative dielectric constant and dielectric loss tangent are almost uniform in the range of 10^3 to 10^5 Hz at the same discharge power, but these values increase abruptly in the range of around 10^6 Hz. The conventional polymers show the decrease of relative dielectric constant and increase of dielectric loss tangent around 10^6 Hz (This phenomenon is due to dipole polarization [14,15]). However, abrupt increases around 10^6 Hz of PPHMDSO films in this experiment are considered to be due to the presence of radicals rather than dipoles in the films and the parastic inductance [16] of capacitors.

4. Conclusions

The deposition rate of the films was 8.25-32.5 nm/min in accordance with the discharge power. FT-IR analysis indicated that the polymer thin film spectrum include several new bands which were absent in monomer spectrum. In AES analysis, the permeation depth of evaporation aluminum into the film was ca. 30 nm. As the discharge power was increased, the relative dielectric constant of the films was increased 2.273 to 3.212 and the dielectric loss tangent was decreased 0.0083 to 0.0026 at 1 kHz.

Acknowledgement

This study was made possible by support from the Ministry of Trade, Industry Energy under Industrial Technology Infrastructure Promotion Program.

References

[1] R. Szeto and D.W. Hess, *J.Appl.Phys.*, *52* (1981) 903.

[2] F.-O. Fong, H.C. Kuo, J.C. Wolfe and J.N. Randall, *J.Vac.Sci.Technol.*, *B6* (1988) 375.

[3] N. Inagaki, T. Nishio and K. Katsuura, *J.Polym.Sci., Polymer Letters Edition, 18* (1980) 765.

[4] M.W. Horn, S.W. Pang and M. Rothschild, *J.Vac.Sci.Technol., B8* (1990) 1493.

[5] A.M. Wrobel, J. Kowalski, J. Grebowicz and M. Kryszewski, *J.Macromol.Sci., Chem., A17(3)* (1982) 433.

[6] K. Kashiwagi, Y. Yoshida and Y. Murayama, *Jpn.J.Appl.Phys., 30(8)* (1991) 1803.

[7] T.S. Ramu, M.R. Wertheimer and J.-E. Klemberg-Sapieha, *IEEE Trans. on Electrical Insulation, EI-21* (1986) 549.

[8] M.R. Alexander, F.R. Jones and R.D. Short, *J.Phys.Chem. B, 101* (1997) 3614.

[9] M.R. Alexander, R.D. Short, F.R. Jones, M. Stollenwerk, J. Zabold and W. Michaeli, *J.Mater.Sci.,31* (1996) 1879.

[10] S. Cai, J. Fang and X. Yu, *J.Appl.Polym.Sci., 44* (1992) 135.

[11] F. Kokai, T. Kubota, M. Ichjyo and K. Wakai, *J.Appl.Polym.Sci., Applied Polymer Symposium, 42*, (1988) 197.

[12] R.J. Keller, *The Sigma Library of FT-IR Spectra,* Sigma Chemical Company, INC., Ed. 1, Vol.2, St. Louis, MO, 1986, p. 979.

[13] S.Y. Park, N. Kim, U.Y. Kim, S.I. Hong and H. Sasabe, *Polymer (Korea), 16(1)* (1992) 94.

[14] M. Ohuchi, A. Chiba, M. Date and T. Furukawa, *Jpn.J.Appl.Phys., 22(8)* (1983) 1267.

[15] R. Bartnikas and R.M. Eichhorn, *Engineering Dielectrics, Volume IIA,* ASTM Special Technical Publication, Philadelphia, PA, 1983.

[16] R. B. Standler, *Protection of Electronic Circuits from Overvoltages,* John Wiley Sons, New York, 1989 p. 202.

< This paper was also published on Proceedings of 5th ICPADM, May 25-30 >