

Structure-property relationships of hydrido organo siloxane polymer (HOSP)

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Summary

The structure and properties of Hydrido Organo Siloxane Polymer (HOSP) as a function of cure conditions have been analyzed. Fourier transform infrared spectroscopy, dielectric constant, and mechanical properties all indicated a dependence on the bake sequence of HOSP. FT-IR analysis indicated that the ratio of Si-O bonds in a caged (or ordered) configuration to Si-O bonds in a non-caged (or disordered) configuration changed as a function of both pre-cure hot plate bake conditions and cure temperature. The dielectric constant was lower for samples that received a high temperature hot plate bake (400°C) prior to the furnace cure independent of the furnace cure temperature, compared with samples that did not undergo the high temperature hot plate bake. In addition, adhesion was significantly improved with an increase in the cure temperature from 400°C to 430°C. These results indicate that both pre-cure hot plate bake conditions, and cure temperature affect the structure and therefore the properties of HOSP. Optimum properties are achieved when both the 400°C hot plate bake and a 430°C furnace cure are employed.

Introduction

The ever-increasing demand for faster, more efficient microelectronic devices has brought about a substantial drive to decrease the effective dielectric constant (k_{eff}) of microprocessor chips [1-9]. Hydrogen silsesquioxane (HSQ) and methyl silsesquioxane (MSQ) materials have been identified as candidates for inter-metal dielectrics (IMD) due to their low dielectric constants ($k < 3.0$), self-planarity, and gap-filling potential [2]. Therefore, the investigation of these materials' properties is ongoing in the semiconductor industry [1-9].

One of the useful techniques in discerning a change in a silicon containing material is Fourier Transform Infrared (FTIR) spectroscopy [6,10]. Silsesquioxanes are known to give strong, sharp peaks at 1119-1114 cm^{-1} and 1040-1030 cm^{-1} , which represent Si-O stretching in either a cage-like or non-caged configuration, respectively [1,9]. The cage-like Si-O configuration is often found in the structure of silsesquioxane (SSQ) oligomers [11,12]. During cure, oligomers crosslink in order to form the SSQ network, which has a higher percentage of the non-caged configuration [11].

In this work, the change in FTIR spectra, dielectric properties, and adhesion of HOSP, an MSQ/HSQ hybrid, with different cure cycles is explored. With greater knowledge of these properties, an optimal cure cycle can be identified and implemented.

Experimental

Materials

Hydrido Organo Siloxane Polymer (HOSP), with a target thickness of either 500 Angstroms or 2500 Angstroms in a cyclohexanone solvent, was provided by Honeywell Electronic Materials. Double polished silicon wafers were used as the substrate and were obtained from MEMC Southwest, Inc.

Fourier Transform Infrared (FT-IR) Spectroscopy

HOSP was hand applied and spun in a Brewer Science CEE-100 programmable spinner at 3000 RPM for 3 seconds then 500 RPM for 28 seconds. The substrates used for all samples were double polished silicon wafers. The samples were immediately removed from the spinner and baked on an S³ Flexifab stand-alone hot plate for two minutes at 150°C to remove solvent. In some cases, the samples were also baked at 400°C for 2 minutes in a Nitrogen atmosphere to avoid oxidation of the material. Samples were then cured in a Tempress furnace with a heating rate of ~5°C/min to the desired cure temperature (**Table 1**).

Table 1. Hot Plate Bake and Furnace Cure Conditions.

Sample	High Temp. Hot Plate Bake (°C) ¹	Furnace Cure Temp. (°C)	Furnace Cure Time (min.)
A	None	400	45
B	400	400	45
C	None	430	80
D	400	430	80
E	400,450 ²	None	N/A

¹All hot plate bakes done for 2 minutes unless otherwise noted.

²Sample was hot plate baked at 450°C for 5 minutes.

Samples were analyzed in a Nicolet 710 Spectrophotometer FT-IR. Prior to measuring each sample, a background was taken using a double-polished silicon wafer substrate. A small portion of the sample was inserted into the FT-IR chamber, which was purged with clean Nitrogen gas at a pressure of 15 psi. After closing the chamber, the chamber was allowed to purge for three minutes in order to remove any carbon dioxide or moisture from the system. Spectra were taken with 256 scans per sample using the Happ-Genzel apodization.

Electrical Measurements

Films were prepared on low resistivity p type wafers for dielectric constant measurements. In order to electrically characterize the films, Metal-Insulator-Silicon (MIS) capacitors were formed. Aluminum dots were evaporated on the top surface of the film and blanket Aluminum was deposited on the back of each wafer for ohmic contact. The capacitors consisted of the metal dots as one electrode and silicon as the other with the dielectric sandwiched in between. Since the substrates are P-type, all measurements were done at negative voltages in order to maintain accumulation and ensure that all voltage drops would be only across the dielectric.

Capacitance, capacitor area, and dielectric thickness were determined in order to calculate the dielectric constant. These properties were measured using an HP4275A LCR meter, a semi-automatic prober, and a Gaertner L114 B Ellipsometer, respectively. After measuring the thickness of each film ellipsometrically, the diameter of each dot to be measured was determined using the chuck stepper of the prober. The step size was adjusted so that the probe tip would line up with the diameter of the dot when the prober stepped. The capacitance was measured with a 50 mV AC signal and a -100 volt DC bias to ensure accumulation. The frequency was adjusted to minimize dielectric loss in order to maximize confidence in the capacitance measurements. The optimum measurement frequency was found to be 100 kHz giving loss numbers near 0.003. The dielectric constant, k , was found using the following formula:

$$k = (C * T)/(e^{\circ} * A) \quad (1)$$

C = capacitance

T = film thickness

e° = permittivity of free space

A = capacitor area

Adhesion Testing

Prior to testing samples **B** and **D**, a polyimide material was spun on the samples in a Solitec spinner. **B** and **D** were then hot plate baked on a Thermolyne 2600 at 100°C for approximately 30 minutes. The samples were then placed in a Blue M oven and furnace cured at 400°C for one hour. After cooling, the polyimide was divided into 4mm wide strips with a razor. These strips were utilized as peel strips for the Instron Model 4500, and samples were tested with a 90° peel angle from the substrate. The force recorded by the instron was divided by the diameter of the peel strip to get force per unit length.

Results and Discussion

Four samples (Table 1, Samples **A-D**) were analyzed with FTIR and special attention was paid to the 1119-1114 cm^{-1} and 1040-1030 cm^{-1} peaks. The ratio of these peaks, which represent the caged and non-caged Si-O stretching respectively, was used to determine the extent of reaction of the HOSP after cure. The IR spectrum of HOSP prior to curing shows a larger caged Si-O stretching band than non-caged (Figure 2a).

Since this film has only been hot plate baked at 150°C to remove the solvent, this should be representative of the uncured HOSP oligomer. After cure, the ratio of non-caged/caged Si-O stretching bands increased. The magnitude of this increase was dependent both on the pre-cure hot plate bake conditions and the furnace cure temperature and was used as an indication of the extent of reaction.

Samples that underwent a 400°C hot plate bake prior to cure (Samples **B** and **D**) showed a higher extent of reaction, indicated by the increase in the ratio of non-caged to caged Si-O stretching bands (**Figure 1**), compared with samples that did not receive the pre-cure hot plate bake (Samples **A** and **C**) (**Figure 2**). In addition, for samples with the same pre-cure bakes (with or without the 400°C bake), the higher cure temperature of 430°C resulted in a larger increase in the ratio of non-caged/caged Si-O stretching bands, compared with samples cured at 400°C (**Figure 1** and **Figure 2**). Therefore, the pre-cure 400°C hot plate bake was necessary to achieve the highest extent of reaction. Interestingly, even though the furnace cure temperature was equal to or greater than the pre-cure hot plate bake temperature, the presence of the hot plate bake affected the extent of reaction (the ratio of non-caged/caged Si-O stretching bands) after cure.

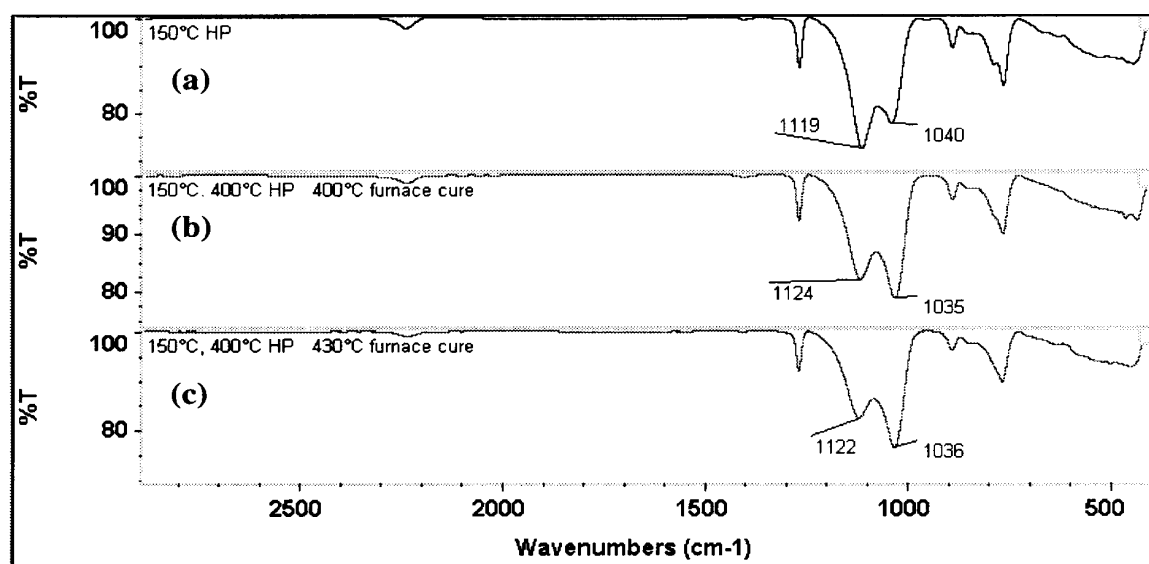


Figure 1. FT-IR Spectra of HOSP (a) Uncured (b) Sample B (Hot plate - 400°C - Furnace - 400°C) and (c) Sample D (Hot plate - 400°C - Furnace - 430°C).

Samples **A-E** were tested for their dielectric properties in order to determine the effect of the extent of reaction on the dielectric constant of HOSP. Samples **B** and **D**, which both received a 400°C pre-cure hot plate bake, had the lowest dielectric constants of the samples tested (**Table 2**). Samples with the lower extent of reaction, indicated by FT-IR analysis, had a significantly higher dielectric constant (**Table 2**). Therefore, the dielectric constant is significantly affected by the extent of reaction. In order to achieve the lowest possible dielectric constant for HOSP, both a pre-cure hot plate bake and a furnace cure are required.

Peel Strength data was collected for samples **B** and **D**. Both samples underwent a pre-cure hot plate bake at 400°C followed by a furnace cure. Sample **B**, which was cured

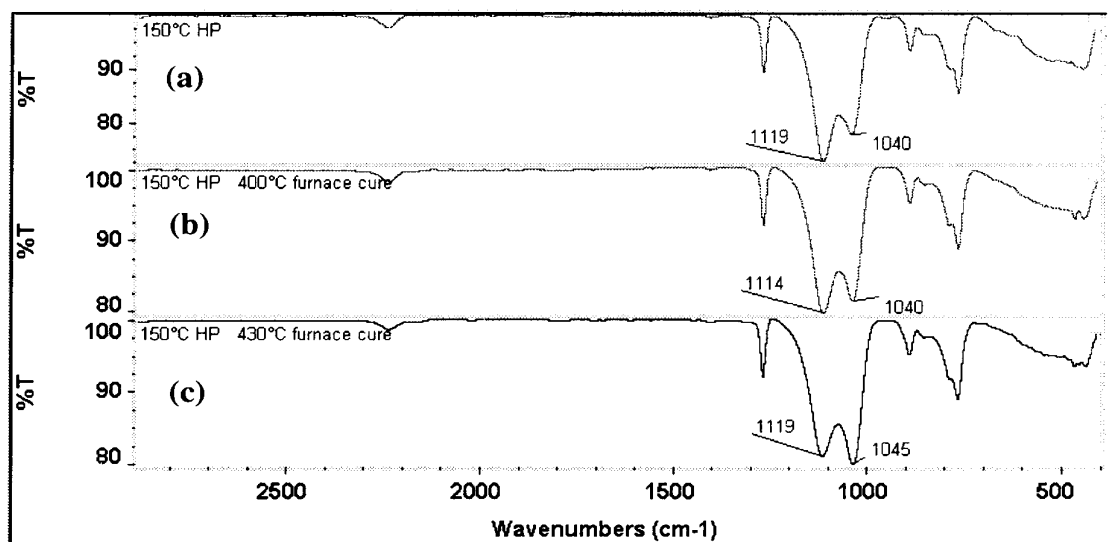


Figure 2. FT-IR Spectra of HOSP (a) uncured (b) Sample A (Furnace - 400°C) and (c) Sample C (Furnace - 430°C).

Table 2. Dielectric Constant of HOSP as a Function of Cure Conditions.

Sample	High Temp. Hot Plate Bake (°C) ¹	Furnace Temp. (°C)	Cure Time (min.)	Dielectric Constant (k) ³
A	None	400	45	2.89
B	400	400	45	2.57
C	None	430	80	2.89
D	400	430	80	2.55
E	400, 450 ²	None	N/A	2.87

¹Samples were hot plate baked for 2 minutes unless otherwise noted.

²Sample was hot plate baked at 450°C for 5 minutes.

³The measurement uncertainty is +/- 0.05

at 400°C, exhibited low peel strength of 1.5 +/- 0.2 gf/mm with cohesive failure within the HOSP layer. Sample **D** that was cured at 430°C (**Table 1**) had increased peel strength of 5.6 +/- 0.6 gf/mm with adhesive failure between HOSP and the substrate. Since failure of Sample **D** occurred at the substrate, the peel strength does not reveal the true strength of HOSP. It only indicates a significant increase in the mechanical strength of HOSP with the higher temperature furnace cure. Therefore, even though the FT-IR analysis does not show a large difference between these two cure conditions, this data indicates that the mechanical properties improve with higher cure temperatures and longer cure times.

Conclusion

The structure and properties of HOSP were analyzed as a function of cure conditions in order to optimize cure and therefore material properties. It was found that the addition of a 400°C hot plate bake prior to the furnace cure increased the final extent of reaction after cure. In addition, higher cure temperatures resulted in a higher extent of reaction, indicated by an increase in the ratio of non-caged to caged Si-O bonds. The samples with the high temperature hot plate bake and furnace cure either at 400°C or 430°C (samples with the highest extent of reaction) displayed lower dielectric constants than samples with the lower extent of reaction. In addition, the sample with the highest peel strength was the sample with the highest extent of reaction. The sample that had been through a high temperature hot plate bake with only a 400°C furnace cure showed significantly reduced peel strength giving cohesive failure within the HOSP. Therefore, in order to achieve optimum mechanical and dielectric properties of HOSP, it is necessary to implement both a high temperature hot plate bake, and a furnace cure of at least 430°C.

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