# *Wettability Studies of Plasma-Polymerized Hexamethyldisilazane*

## INTRODUCTION

A number of organosilanes have been plasma polymerized onto a wide range of substrates in the past. These films offer excellent thermal, dielectrical, and optical properties which make them very useful for diverse practical applications.[1–6] The plasma-polymerized films are, in general, crosslinked and possess superior adhesion quality to the substrate vis-a-vis films deposited by the nonplasma methods. Hexamethyldisilazane (HMDS) [$(CH_3)_3$—Si—NH—$Si(CH_3)_3$] is one of the commonly used organosilicon monomers and it has been deposited at audio (kHz), radio (MHz), and microwave (GHz) frequencies.[7] The properties of the HMDS layer depend on the frequency employed as monitored by infrared spectroscopy.

Also, some wettability, ESCA, and FT-IR results have been reported on HMDS deposited by radiofrequency discharges.[8] Hirotsu found that HMDS and diethylaminotrimethylsilane (DATMS) layers are as hydrophobic (monitored by water contact angle) as pure tetramethylsilane (TMS), indicating that the nitrogen in HMDS and DATMS is not at the surface. Interestingly enough, he reports that hydrophobicity increases with thicknesses up to 5 nm (50 Å) and subsequently stays constant. Also, the reported water-contact-angle values ($\theta_{H_2O}$) appear higher than one would have expected.

Here we report on the critical surface tension of wetting ($\gamma_c$) measurements on plasma deposited (13.56 MHz) HMDS layers as a function of thickness. We believe we are reporting for the first time $\gamma_c$ values on such films.

## EXPERIMENTAL

The hexamethyldisilazane monomer was obtained from PRC Inc., Gainesville, FL, and was used as received. The plasma deposition setup is shown in Figure 1. The deposition conditions employed were 10- to 15-W input power at 2 Pa (15 $\mu$m) pressure. This resulted in a deposition rate of 0.1 nm (1Å/sec).

The thickness of plasma-deposited samples was calculated gravimetrically and also by using a Sloan quartz crystal monitor installed in the plasma deposition chamber. The $\gamma_c$ was determined by the usual Zisman plot.[9] The following liquids were used for making contact angle measurements and were of spectrograde quality: hexadecane, polyglycol, 1-methylnaphthalene, methylene iodide, formamide, glycerol, and water.

Doubly distilled deionized water was used. All contact angle measurements were made using

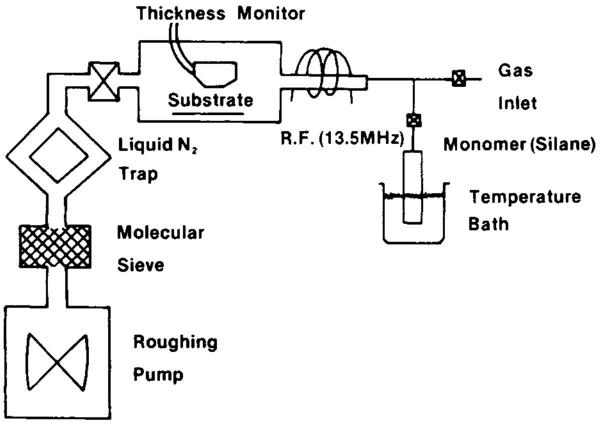

Fig. 1. Schematics of the plasma deposition system.

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a Rame Hart contact angle goniometer model A100. Contact angle values reported here are equilibrium values and these could be measured within ±1°.

## RESULTS AND DISCUSSION

A typical Zisman plot is shown in Figure 2. Figure 3 is a plot of $\gamma_c$ vs. HMDS thickness. The $\gamma_c$ of plasma cleaned-pure (uncovered with HMDS) $SiO_2$ should be high (~58 dyn/cm), as it could be wetted by almost all liquids except water, and, as one can see from this figure, it dramatically decreases even with a 1.5 nm (15Å) HMDS layer. It is interesting to note that the $\gamma_c$ reaches a minimum value after a certain thickness ~20 nm (200Å) and this corresponds to complete coverage of the substrate as found in our other studies.[10,11] Comparing with the literature, a $\gamma_c$ value of 22–24 dyn/cm corresponds to a surface with $-CH_3$ (methyl) groups sticking out.[9] Our ESCA analysis[10] shows the presence of nitrogen and oxygen in these films, but the $\gamma_c$ value indicates that the top surface is nothing but a "bed" of methyl groups, and nitrogen and oxygen are not present at the outermost surface but are buried underneath. The presence of oxygen is attributed to the residual oxygen present in the plasma deposition chamber. The formula for the HMDS monomer is $[(CH_3)_3—Si—NH—Si(CH_3)_3]$, so it is not surprising to find the surface replete with $—CH_3$ groups.

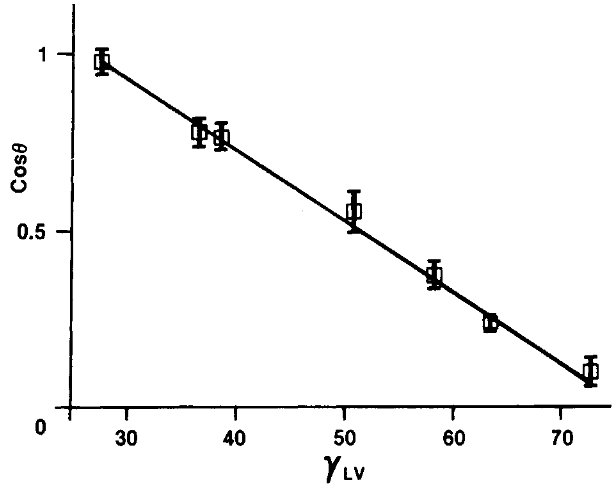


Fig. 2. Zisman plot for 15Å HMDS plasma deposited on thermally grown $SiO_2$.

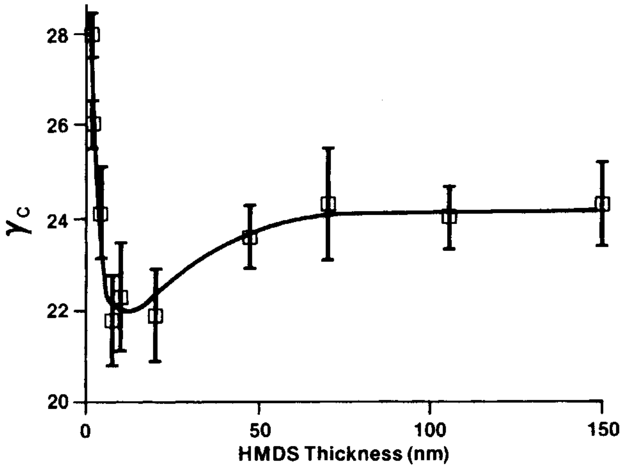
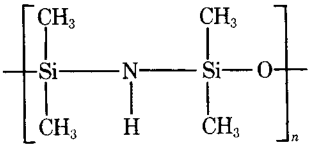


Fig. 3. Plot of critical surface tension of wetting ($\gamma_c$) vs. thickness of plasma deposited HMDS layer.

Also, we found by ESCA analysis N:O:Si:C elemental ratios of 1:1:2:5, and by IR analysis the presence of Si—O—Si and Si—N—Si linkages in the HMDS layers, possibly indicating the buildup of layers via



$$\left[ -\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\mathrm{Si}}}-\underset{\displaystyle H}{\mathrm{N}}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\mathrm{Si}}}-\mathrm{O}- \right]_n$$

The minimum in the $\gamma_c$ vs. HMDS thickness is quite interesting and it could possibly be due to different packing or morphology. Literature values for $\gamma_c$ for —$CH_3$ (crystalline) is 22, whereas, it is 24 dyn/cm for —$CH_3$ (monolayer).[9b] It should be noted that our values for $\gamma_c$ correspond exactly with those values in the literature. Initially, the HMDS grows in the form of islands and that is why we observe the combined effect of HMDS and $SiO_2$ on the contact angle ($\gamma_c$) values before the $SiO_2$ surface is completely covered with HMDS. As more and more HMDS is deposited, these islands coalesce and form a continuous film. Subsequent deposition takes place on the top of this film, so it should not be surprising that the packing or morphology of these subsequent layers is different from the first continuous film. Also, it should be added that our ESCA results[10] show that the elemental ratio in 10 nm (100Å) HMDS film (incomplete coverage of the substrate) is different from that in 20 nm (200Å) or thicker films.

We conclude from these studies that, in spite of the presence of nitrogen in the HMDS monomer, the plasma-deposited layers are as hydrophobic as monomers with pure methyl groups, as was observed by Hirotsu.[8] However, our $\theta_{H_2O}$ (see Table I) is lower than those of Hirotsu at every thickness of HMDS layer. This could be attributed to different deposition conditions. Also, we did not find any effect of aging on storage in clean containers in the laboratory environment for about a week, whereas such effect was reported by Hirotsu.

## CONCLUSIONS

The $\gamma_c$ of a plasma-cleaned, thermally grown $SiO_2$ surface is high (~58 dyn/cm), as it is wetted by almost all commonly used liquids except water. It drops dramatically with the plasma deposition of HMDS, reaching a minimum around 20 nm (200Å) and thereafter becomes constant at thicknesses greater than 60 nm (600Å).

The $\gamma_c$ of plasma-deposited films thicker than 60 nm (600Å) is 24 dyn/cm, indicating that the surface consists of only —$CH_3$ (methyl) groups. There is a dip of 2 dyn/cm at 20 nm (200Å), indicating a different packing.

In spite of the presence of nitrogen in the HMDS monomer and oxygen in the plasma-deposited HMDS film, the surface is bereft of both nitrogen and oxygen.

TABLE I

Thickness of Plasma Deposited HMDS on $SiO_2$, Zisman Critical Surface Tension ($\gamma_c$), and Water Contact Angle

| Thickness, nm | $\gamma_c$, dyn/cm | $\theta_{H_2O}$, deg |
|---|---|---|
| 0 | 58 ± 1.5 | 25.8 ± 4 |
| 1.4 | 28 ± 0.5 | 80.0 ± 3 |
| 1.5 | 26 ± 0.5 | 84.3 ± 2 |
| 4.0 | 24.1 ± 1.0 | 97.9 ± 2 |
| 7.5 | 21.8 ± 1.0 | 98.9 ± 1 |
| 10 | 22.3 ± 1.2 | 98.4 ± 1 |
| 20 | 21.9 ± 1.0 | 96.1 ± 2 |
| 47.5 | 23.6 ± 0.7 | 99.2 ± 2 |
| 70 | 24.3 ± 1.2 | 98.8 ± 2 |
| 105 | 24.0 ± 0.7 | 95.8 ± 2 |
| 150 | 24.3 ± 0.9 | 98.9 ± 1 |

## References

1. M. R. Havens, *J. Vac. Sci. Tech.*, **13,** 575 (1976).
2. J. C. Lee, *Appl. Opt.*, **17,** 2645 (1978).
3. J. S. Sandved and K. Kristiansen, *Vacuum,* **27** (4), 235 (1977).
4. G. Smolinsky, *J. Vac. Sci. Tech.*, **11,** 33 (1974).
5. A. M. Wrobel and M. Kryszewski in *Plasma Polymerization* M. Shen and A. T. Bell, eds., Am. Chem. Soc. Symp. Ser. No. 108, Am. Chem. Soc., Washington, DC, 1979, pp. 237–249.
6. P. K. Tien, G. Smolinsky and R. J. Martin, *Appl. Opt.*, **11,** 637 (1972).
7. A. M. Wrobel, M. R. Wertheimer, J. Dib, and H. P. Schreiber, *J. Macromol. Sci. Chem.*, to appear.
8. T. Hirotsu, *J. Appl. Polym. Sci.*, **24,** 195 (1979).
9. (a) W. A. Zisman in *Contact Angle, Wettability and Adhesion,* Adv. Chem. Ser. No. 43, Am. Chem. Soc., Washington, DC, 1964. (b) ibid., p. 21.
10. N. K. Eib, K. L. Mittal, and H. R. Anderson, Jr., presented at the Adhesion Society Meeting, Savannah, GA, Feb. 10–13, 1980.
11. N. K. Eib, K. L. Mittal and H. R. Anderson, Jr., presented at the Colloid and Surface Science Symposium, Lehigh University, Bethlehem, PA, June 15–18, 1980.

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