USE OF HEXAMETHYLDISILAZANE FOR OBTAINING MODIFIED SILICON OXIDE FILMS

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Abstract

The deposition of silicon oxide films by oxygen and organosilicate plasmas is a common practice in microelectronics and microstructure industries. Although it is not the most common organosilicate in use, HMDS presents interesting characteristics for plasma deposition systems due to the presence of Si-C in the molecule. To verify the possibility of obtaining thin films with high concentration of Si-C bonds, depositions were made using a 40 kHz capacitively coupled plasma reactor, and HMDS plus argon as reagents. Pressure (1 to 2 Torr), power (5 to 100W) and flow (Argon flows of 30 to 200 sccm and HMDS flows of 1 to 12 sccm) were varied. Films with good adhesion to silicon were obtained, with good uniformity and index of refraction around 1.6; indicating the existence of carbon in the film. Deposited films were analyzed with ellypsometry (for index of refraction), profilemeter (for thickness and deposition rate), FTIR (for determining the existing bonds) and Raman microscopy (to verify the uniformity and C-C bonds). Si-CH_3, Si-H, Si-N, N-H bonds were found, with low power (around 10W), high pressures and flows (around 2 Torr and 3 sccm) favoring the formation of Si-CH_3 and Si-N. Si-O bonds come from reactions of the molecule with the residual oxygen in the vessel. High power and/or flow favor the formation of Si-O bonds indicating oxidation of the forming film. Above 100W, Si-O or Si-OH bonds are found, typical of silicon oxynitride structures, but contaminated with organic compounds. The deposited films are hydrophobic and are being tested for their capacity of adsorbing nonpolar products.

1. Introduction

The interest in this work was to analyze the films that can be obtained by plasma enhanced chemical vapor deposition (PECVD), using an organic silicon compound of low cost - Hexamethyldisilazane (HMDS) - and a low frequency plasma source (40 kHZ).

The use of organic silicon compounds is common for depositing films in microelectronics as well as in optics and surface protection. One of the great advantages of its use is the ease of manipulation, since they are liquids of low toxicity. On the other hand, the use of plasmas in the deposition has the advantage of allowing the use of compounds that otherwise would not be polymerized. It is also possible to obtain films in a lower temperature compared with other methods, due to the active species formed by the plasma. Therefore, varying the process parameters it is possible to obtain polymer -like or ceramic-like films [1].

From the organic silicon compounds, HMDS had gained increasing attention, being used for the deposition of, among other films, SiC:H [2,3], and for the production of Si/C/N composites in powder form [4]. Its main characteristic however is to make surfaces hydrophobic, in chromatographic columns, as well as for preparing the surface of silicon for photolytography. In the first case, HMDS reacts rapidly with the OH groups of silica [5], as shown in reaction (1). This reaction occurs in the gaseous and solid phases, being even used to determine the quantity of OH in the surface. This new surface is stable up to 500 °C, when the OH groups begin the reappear.

Reaction (1) : $2\ SiOH + Me_3SiNHSiMe_3 \rightarrow 2Si\text{-}O\text{-}SiMe_3 + NH_3$

In the second case, besides the good adhesion to silicon, its use for the passivation of the porous silicon surface, presented $Si\text{-}CH_3$ bonds in the entire extension of the surface, with hydrophobic characteristics [6].

These peculiar characteristics of HMDS, in addition to its ease of manipulation, and considering that PECVD is processed in general in high power [3] and/or high frequency systems (13.56 MHz) [2, 7], lead us to study the films obtained in the polymerization of HMDS at low power (below 50W) and low frequency (40kHz), in order to verify the possibility of producing films with a high quantity of CH_3 radicals. These films should in principle be hydrophobic, and therefore have good adhesion to organic materials like polypropylene.

The carrying gas used was argon because Heyner [3] observed that N_2 plasmas favor the loss of carbon in the film, and as the intensity of the $Si\text{-}CH_3$ bond decreases with power and substrate temperature, we used low power without substrate heating [2]. Another interesting characteristic to verify is the formation of $Si\text{-}CH_2\text{-}Si$ or $SI\text{-}CH_2\text{-}CH_2\text{-}Si$ bonds as reported by Fracassi [7], which can indicate the formation of more than one polymeric structure in the same film, and also that there are two reaction sites_in the HMDS molecule: the silicon atom and the carbon atom respectively.

2. Experimental Arrangement

The equipment used is described in the article by I.H. Tan et. al., in this symposium, which was adapted for liquid reagents. The system can admit O_2, N_2 and Ar. The power can be varied from 10W to 300W, without electrode temperature control. For the deposition conditions used however, the temperature did not present significant variation, as measured before and after de deposition. The addition of HMDS without a carrier gas is also possible and was used in some cases.

Silicon wafers (3 inches, p-type, <100>, 10-20 Ωcm) were used, the deposition rate was calculated through the measurement of the film thickness, obtained by ellypsometry and/or profilemeter, so that the film thickness could be compared by two distinct methods. The index of refraction was also measured by ellypsometry. The wafers were also analyzed in its chemical composition by FTIR (Fourier Transform Infra-Red) and Raman microscopy, to verify the possible contamination by nonpolar organic compounds. This last analysis is necessary since it was verified that for organic silicon compounds, it is possible to form small graphite nodules on the deposited film [8]. The corrosion of the formed films was tested by immersion in HF (1:10 in volume) solution.

The deposition conditions were:

- 1 to 12 sccm of HMDS flows when a carrier gas is used. Argon was used at 20 to 200 sccm. When HMDS is used without argon, about 0.52g/min was consumed.

- The deposition time for most samples was 10 minutes when argon was used and 2 minutes when only HMDS is admitted.
- The deposition power was varied between 10 to 100W when argon was used, and 20 to 150W for pure HMDS.
- Deposition pressures were from 0.1 to 2 Torr.
- Substrate temperature is measured immediately before and after the deposition, being in most cases around 35 °C.

3. Results and Discussion

3.1. Deposition Rates and Index of Refraction

The index of refraction of the samples are in the range [1.5 to 2.4]. Reminding that the index of refraction of silicon nitride is 2.0, of silicon oxide is 1.4 and for organic films it is 1.6, the interest in obtaining indexes of refraction near 1.6 is therefore, in obtaining hydrophobic films, that can present interesting adsorption characteristics.

The variation of index of refraction as a function of power for various flows did not show any significant tendency. The deposition rate however, is strongly dependent of power as shown in figure 1, increasing with it. On the other hand, , an increase in electrode temperature decreases the deposition rate. The dependence of the deposition rate with the substrate temperature is a strong indicative deposition governed by neutrals. That is in accordance with Gerstenberg [9] in depositions using radio frequency (13.56 MHz). Moreover, for temperatures above 70 °C no film is formed, independently of deposition conditions. It can be concluded therefore, that the adsorption of HMDS and the active species formed in the plasma is crucial for the film formation.

We used a metallic structure in a "U" form over the silicon wafer, to verify the neutrals dependence of the reaction, by measuring the thickness of the film formed inside the structure channel. It is observed that for pure HMDS at 2 Torr, the whole area covered by the structure was deposited, but with a deposition rate four times slower.

3.2. FTIR and Raman Microscopy Analysis

Raman

The analysis with Raman Microscopy showed that for most deposition conditions the films is homogeneous. Graphite nodules are formed only for the following conditions:

- 1 Torr and 50W, in which a wafer was positioned under and another on the electrode. In this case, the wafer under the electrode showed graphite nodules contamination, which was not observed for the wafer on the electrode. This is a strong indication that high energies is necessary for the formation of the active species responsible for the deposition. A similar situation occurs for deposition with TEOS [10].
- 2 Torr, 20W, where a high concentration of graphite nodules is found. It is interesting to note that these nodules are not found near the edge of the wafer, suggesting that the high pressure favored the nucleation and the partial reaction of HMDS on the wafer. High nucleation can also be found when pure HMDS is deposited at 2 Torr, in which case nodules are formed, but not of graphite, since the Raman spectra indicates only the presence of CH_n (figure 2a).

More important than the heterogeneity is the probable stress in the film. Distinct structures were observed, or even the crack of the film in a large region (figure 2b). In these cases the Raman and FTIR spectra did not show any new band.

FTIR

Figure 3 shows the variation of relative intensities for the species of interest as a function of power. A typical spectrum is shown in figure 4. It can be seen that to maintain the $Si-CH_3$ bonds, low power, and high flow and pressure is needed. In other words, a higher the concentration of the reagent in the gas phase, increases the probability that the reaction occurs by attacking the nitrogen atom of the neutral molecule. Saturation occurs at 500 mTorr of pure HMDS, which corresponds to the best process condition. In this case, over 50W, no variation on the FTIR spectra or index of refraction is observed, with power increase leading only to a higher deposition rate.

3.3. HF Corrosion

To verify the organic polymer characteristics of the formed film, the deposited wafers were corroded by a diluted solution of HF, and showed that it is resistant to corrosion by this solution

3.4. O_2 Addition

Oxygen was added (from 0.5 to 3 sccm) to the following condition: 30W, 200 mTorr, 0.52g/min of HMDS. Even for these low flows, Si-O bonds were observed by FTIR. The addition of oxygen turned the surface less hydrophobic, as showed by water contact angle measurements.

3.5. Adsorption

We are interested in a hydrophobic film since it has a higher probability of adsorbing nonpolar compounds. Water contact angle was measured for all samples deposited with the addition of oxygen. The contact angles measured were all around 90 °, indicating that they were all hydrophobic.

4. Conclusions

A qualitative model for the polymerization of HMDS using low frequency plasma reactors is very similar to the deposition model in radio frequency reactors. The deposition depends primarily on neutrals, low power favors the maintenance of $Si-CH_3$ bonds, while higher power implies in polymers with more cross-link bonds ($Si-CH_2-Si$).

The active species formed presented two reaction sites: C and Si respectively. We did not find however, $Si-CH_2-CH_2-Si$ bonds as found by Dágostino in a RF powered reactor; so the formation of active species with carbon free radicals should be less pronounced in this system.

5. Acknowledgments

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6. References

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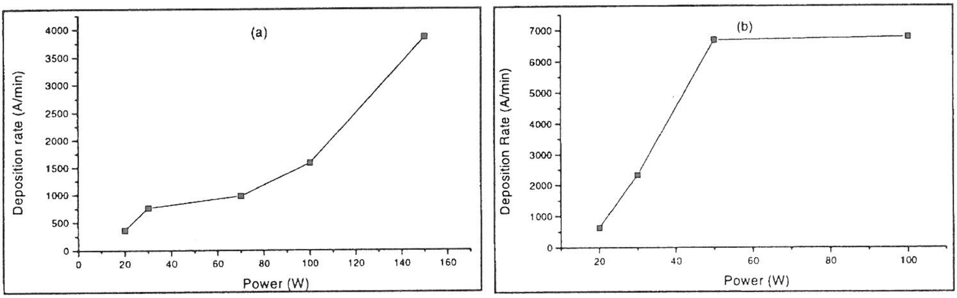
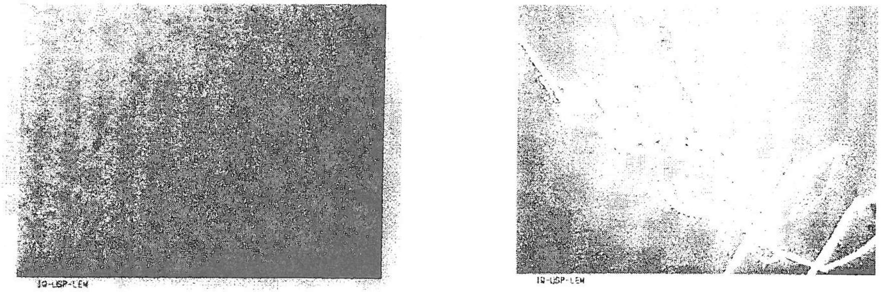


Figure1: Deposition rate as a function of power [HMDS, (**a**) 100 mtorr, 0,52 g/min, (**b**): 500 mtorr, 0,52 g/min].



(a) (b)

Figure 2: Raman photography (a) High nucleation found when pure HMDS is deposited at 2 Torr; (b) the crack of the film in a large region due to stress.

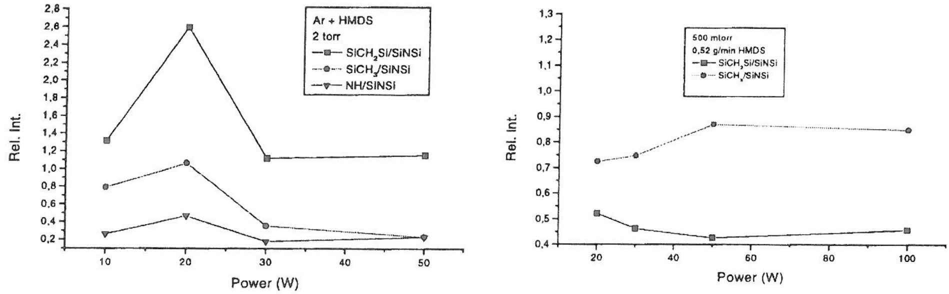


Figure 3: Variation of relative intensities for the species of interest as a function of power.

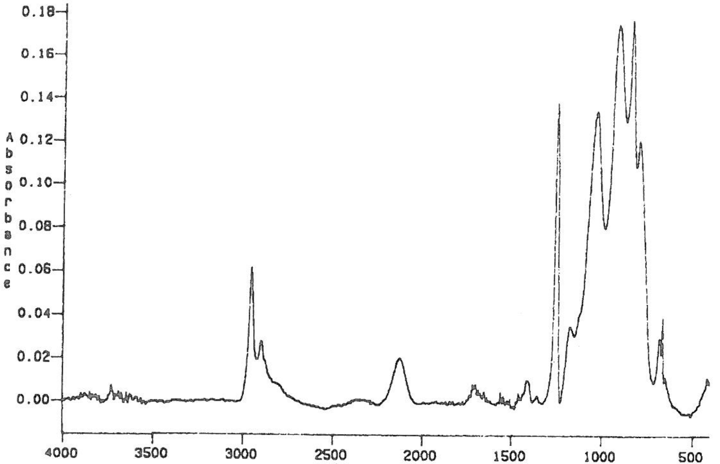


Figure 4: Typical FTIR.