PRODUCTION OF HIGHLY HYDROPHOBIC FILMS USING LOW FREQUENCY AND HIGH DENSITY PLASMA

S. Nogueira[a]; M.L.P. da Silva[b*]; I.H. Tan[c]; R. Furlan[d]

a) Depto. de Sistemas Eletrônicos, Escola Politécnica da Universidade de São Paulo, Brazil
b) Faculdade de Tecnologia de São Paulo, CEETEPS, UNESP, Coordenadoria do MPCE, São Paulo - SP, Brazil
c) Instituto Nacional de Pesquisas Espaciais – INPE, São José dos Campos, S.P. Brazil
d) Department of Physics and Electronics, University of Puerto Rico at Humacao, Puerto Rico

ABSTRACT

Hexamethyldisilazane was plasma polymerised on silicon wafers and on glass and quartz substrates, in order to obtain films with high concentration of CH_3 radicals. Two plasma reactors were used: a capacitive 40 kHz reactor and an inductive 13.56 MHz reactor. Very high deposition rates (up to 700nm/min), evaluated by profilometry, were obtained using the low frequency capacitive reactor, with much lower rates obtained at 13.56 MHz (capacitive and inductive coupling). The refractive indexes, measured by ellypsometry, were close to 1.6 (40 kHz capacitive reactor), and near 1.5 (13.56 MHz inductive reactor). Infrared analysis showed $Si-CH_3$ and mainly Si-N-Si -Si or $Si-CH_2$ bonds for the low frequency and inductively coupled reactors, respectively. Addition of nitrogen to the plasma did not lead to variations in the infrared spectra, but increased the chemical resistance of the film, probably due to cross-linking. Addition of oxygen resulted in the decrease of Si-N-Si bonds compared to $Si-CH_2$-Si and loss of $Si-CH_3$. in both reactors. The oxygen addition also did not improve chemical resistance and prevented the adhesion of photoresists to glass. Raman spectroscopy revealed the presence of CH_n bonds only. Contact angle measurements showed that these films are highly hydrophobic, and have high affinity to organic solvents, both polar and non-polar. They also have good chemical resistance to strong acid and basic solutions. The films were tested for the following applications: as an adhesion promoter of photoresists on glass substrates, as a defrosting protective layer, as an ultraviolet radiation protective layer, and as an adsorption coating in microstructures, using silicon or porous silicon as substrates. In all applications, the films obtained with hexamethyldisilazane in the low frequency reactor presented better results than the ones obtained with the inductive reactor.

1. INTRODUCTION

The search for environmentally friendlier equipment, the so called "green machines", is a general trend nowadays. Equipment with less pollution emission means cost savings in effluent treatment and thus productivity gain, i.e., this equipment achieves sustainability with a strategy of clean production [1-6]. Microelectronics technology offers an important contribution, with the production of much reduced size equipment, through what is commonly called micromechanics [7-9].

One of the contributions of micromechanics, is the manufacture of microchannels through photolithography of silicon wafers, and the deposition of very thin films, commonly achieved through plasma enhanced chemical vapour deposition (PECVD) [10-13]. The development of new thin films allied to the production of reduced size devices, or microstructures, offers thus new perspectives for clean production.

Silicon wafers, glass and plastics [8] are the substrates commonly used in micromechanics, so that adhesion of these new thin films is highly needed, especially in some applications, where light transparency is required once a glass layer is soldered to the photolithographed silicon wafer. New possibilities in microchannel technology would be possible if glass substrates could be easily photolithographed, and this would be possible if an adhesion promoter could be found for photoresists. Plasma enhanced chemical vapour deposition of silicon compounds is again a good candidate to be explored for this purpose, since the adhesion of the film to this substrate is chemically expected.

Organic silicon compounds are largely used in modern industry, being indispensable in the production of silicone polymers and for chromatographic columns, in which these polymers are responsible for the adsorption of compounds in the stationary phase. These compounds are also used in the production of defrosting layers. In gas phase, organic silicon compounds are commonly used for chemical vapour deposition (CVD) in microelectronics, optics and surface protection industries [14-16]. One of their great advantages is the easiness of manipulation, since they are liquids of low toxicity. On the other hand, plasma enhanced chemical vapour deposition (PECVD) has the advantage of allowing the use of compounds that would not be polymerised otherwise. It is also possible to obtain films in a lower temperature compared with other methods, due to the active species formed by the plasma [17,18].

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* malu@lsi.usp.br

From the organic silicon compounds in use, hexamethyldisilazane (HMDS) has gained increasing attention, being used for plasma deposition of silicon carbide (a-SiC:H), silicon carbonitride [18-20], Si/C/N composites in powder form [21], Si/C/N/H films [22-24], silicon oxide, silicon nitride, and silicon oxinitride films [25-27]. However, the main characteristic of HMDS, i.e, the production of hydrophobic surfaces as well as adhesion promotion, [28] is not commonly explored by plasma polymerisation [29]. Only recently HMDS thin films were evaluated as hydrophobic surfaces for compatibilization of alumina surface with organic compounds [30]. These films present high amount of $SiCH_3$ species and, due to their good adsorption characteristics [31], we also explored their use in the production of selective membranes [32] and grain protection [33].

Therefore, the aim of this work is a better understanding of HMDS thin films obtained at low power, i. e. with a high concentration of Si-CH$_3$ radicals, and compared it with films obtained in a high-density plasma deposition system.

Some new applications are also explored. Since in principle these films are hydrophobic and compatible with organic compounds like photoresists, they were tested for adhesion promotion. Deposited on glass, HMDS films would allow direct photolithography in these substrates by promoting the adhesion to photoresists. The current process involves many stages including the deposition of a gold layer [34].

These films are also resistant to corrosion by strong inorganic acids and bases, which is very important for the microstructure industry and for surface protection applications. These characteristics were not fully explored previously. Considering that HMDS films obtained at high power, present optical filter characteristics [16] and that the films with high amount of Si–CH$_3$ species can protect against ultraviolet exposure, it is interesting to verify the behaviour of the film in a wide range of wavelengths, especially in the ultraviolet range. A useful film could be produced for optical devices in microelectronics, transparent to certain wavelengths, or, again, for surface protection applications.

Moreover, besides a better understanding of HMDS deposition conditions with the above-mentioned characteristics (40 kHz capacitively coupled reactor), the objective of this work is to explore another rarely used plasma reactor system (high frequency 13.56 MHz inductively coupled reactor). Low frequency systems are characterized by high ion bombardment since the ions can be completely swept out of the plasma volume during one half cycle. The heavily bombarded film would be highly cross-linked, which could enhance chemical resistance. For comparison, some depositions at 13.56 MHz were carried out using the same reactor chamber. On the other hand, inductively coupled plasmas (ICP) are high frequency and high electron density systems (HD-plasma), which lead us to expect a high concentration of active species and high deposition rates. Furthermore, the typical low ion bombardment in these systems could result in less cross-linked, more adsorbent films. These chemically less resistant films could also be useful as sacrificial layers in microelectronics.

2. MATERIALS AND METHODS

The depositions were carried out using pure monomer plasmas as well as HMDS plasmas carried by argon, since N_2 plasmas favour carbon loss in the film, as observed by Heyner [29]. Addition of oxygen was also carried out in some depositions, in order to remove Si-N-Si bonds and increase Si-O-Si bonds. The presence of Si-O-Si bonds could result in a silicone type structure, with its known good electrical isolation, good temperature, chemical and ageing resistances. For comparison, N_2 was added to the plasma, at the same amount of oxygen.

The films deposited on silicon wafers were analysed by infrared spectroscopy (FTIR), profilometry, ellypsometry, Raman microscopy, and water contact angle. Compatibility and chemical resistance to various organic compounds, and inorganic acids and bases were tested. The use of the HMDS films as an adhesion promoter to photoresist and its resistance to HF corrosion were verified using glass as a substrate and photoresist photolithographed in 200 μm structures. Optical properties were verified using a spectrophotometer and adsorption of organic compounds was tested exposing a sample to a saturated benzene atmosphere.

2.1 Depositions in a Low Frequency Capacitive Reactor

The low frequency (40 kHz) capacitively coupled reactor used [35] had a stainless steel vacuum vessel with two 20 cm diameter electrodes 3 cm apart, one of them grounded and used as the substrate holder. Base pressures of less than 20 mTorr were reached within a few minutes. HMDS was injected either using argon as a carrier gas or by evaporation of the monomer at the reactor's low pressure, at ambient temperature. In the first case, pressure was directly proportional to the argon flow, and in the second case pressure was controlled by the pumping speed. The temperature of the substrate holder electrode was approximately constant and around 35 °C.

The deposition conditions are listed below:

- Power: from 20 W to 150 W for pure HMDS and from 10 W to 100 W for HMDS carried by argon
- Pressure: from 100 mTorr to 2 Torr
- Monomer flow: 0.5 g/min for pure HMDS and (3.4 to 6.9) mg/min for (30 to 80) sccm of argon flow.
- Deposition time: 3 minutes for pure HMDS 15-20 minutes for HMDS carried by argon

Higher power is required to obtain gas breakdown for pure HMDS compared to discharges with the presence of argon, so that the lowest power is higher in the first case.

P-type, <100>, 10-20 Ωcm silicon wafers, three inches in diameter were used as substrates.

In order to verify the importance of neutrals in the deposition process, a small stainless steel structure with an upside-down "U" form covered a small portion of the substrate. Ionic bombardment was thus prevented from reaching this covered area, so that film deposition occurs preferentially through the diffusion of neutrals into the channel formed.

The dimensions of the channel (1 mm in height, 5 mm wide and 15 mm long) were chosen by estimating the mean free path of argon at 100 mTorr, ambient temperature, and assuming that the mean free path of HMDS would be about twice this length.

Oxygen was added with flows varying from 0.5 sccm to 3 sccm, to a discharge condition with high deposition rate and high concentration of Si-CH_3 radicals (200 mTorr of pure HMDS at 30 W).

Deposition of pure HMDS on a glass substrate was done at 500 mTorr, 100 W, during 3 minutes, to verify the possibility of using the film as a defrosting layer. For comparison, Tetraethoxy-silane (TEOS) was also deposited in the same conditions. Another glass sample was deposited with the same conditions during 30 seconds for testing the photolithography process.

Deposition of pure HMDS on a quartz substrate was carried out at 500 mTorr, 50 W and 150 W during 3 minutes, in order to analyse, through spectrophotometry and Raman microscopy, the optical behaviour of the film and the adsorption properties of hydrocarbon compounds, respectively.

2.2 Depositions in a High Frequency Capacitive Reactor

Depositions at high frequency were carried out using the same reactor described previously but changing the power source to a 13.56 MHz one. The deposition conditions are shown in Table A:

HMDS was injected as a pure monomer, carried by argon (HMDS + Ar in the table) and with the addition of oxygen (HMDS + O_2 in the table).

Table A - Deposition Conditions for capacitive reactor at 13.56MHz.

	Power (W)	Pressure (Torr)	Dep.Time (min)	Monomer Flow (g/min)	Gas Flow (sccm)
HMDS	50	100	3	0.5	-
		300			
	70	500			
	100	100			
	150	300			
		500			
HMDS + Ar	70	2	20	0.0069	80
	150				
HMDS + O_2	100	300	3	0.5	3
	200				

2.3 Depositions in a Inductively Coupled Reactor

The inductively coupled plasma (ICP) [36] reactor used is powered by a 13.56 MHz source. A planar coil (5 turns, 30 cm outer diameter) is placed above the vacuum vessel, isolated through a borosilicate glass window. The stainless steel vacuum vessel has a 20 cm diameter sample holder, located 20 cm below the glass window. The plasma is confined to a region close to the glass window, so that deposition is carried out in a remote mode, with the sample distant about 5 cm from the plasma glow. Base pressures around 50 mTorr are reached with a mechanical pump.

Since the results in the capacitive reactor showed that pure monomer plasmas lead to higher deposition rates with high concentration of Si-CH_3 radicals, this was the process chosen for the ICP reactor. The deposition conditions are listed below:

- Power: from 25 W to 300 W
- Pressure: 100 mTorr to 500 mTorr
- Monomer flow: 1.38 g/min
- Deposition time: 5 to 30 min
- Substrate temperature: around 30 °C

Oxygen was added with flows of 5 sccm and 20 sccm for depositions at 300 mTorr with 100 W and 200 W. For these same deposition conditions, nitrogen flows of 5 sccm and 20 sccm were also added to investigate their influence in the chemical composition of the films formed.

In order to test HMDS films for adsorption applications, depositions in the inductively coupled reactor were chosen for covering the surface of porous silicon. Porous silicon is constituted of silicon monocrystals of dimensions varying from nanometer to micrometer range, with pore sizes of about the same dimensions. Porous silicon samples with pore sizes of about tens of nanometers were chosen for this test, and were covered with an HMDS film of approximately 100 Å in thickness, in order to avoid filling of the pores. The deposition was made in the inductively coupled reactor (25 W, 100 mTorr, 5 minutes) due to the low deposition rates enabling a more precise control of film thickness.

2.4 Analisys

Chemical characterisation was performed by FTIR (Bio-Rad model QS-300) to determine the main polar bonds, and by Raman microscopy (Renishaw model 2000, He-Ne laser) to detect non-polar bonds. The Raman equipment has an optical microscope visualising a 50 μm by 80 μm area and was used to verify the uniformity of the films.

A profilometer (model Dektak 3030) and an ellypsometer (Rudolph Research, Auto EL NIR-3) were used to determine the deposition rate and the refractive index respectively.

The hydrophobic character of the films was measured by the contact angle of a drop of distilled water, using a Rame-Hart goniometer.

Resistance and compatibility to various chemicals were tested using the following compounds: 1) solutions of NaOH (pH 14), NH_4OH (pH 10), H_2O (pH 6), H_2SO_4 (pH 3), and HCl (pH 1), were used to test resistance to inorganic acid and basic solutions; 2) Ethanol, Isopropanol, Acetone, and CCl_4, were used to verify the behaviour of the films with respect to organic solvents polarity. The tests were conducted in the following way: a drop of each compound was dripped over the surface of the films, and removed five minutes later. The affected area was then observed in an optical microscope (visualising a 50 μm diameter area). The dissolution of the film would be noticed by the formation of blisters or nodules, and chemical corrosion (film's removal) would appear as colour differences, steps or edges.

The films were also exposed to HF (1:10) for 10 to 20 minutes to test corrosion resistance.

Adhesion of the films deposited on silicon wafers to positive photoresist (OFPR 800 from Tokyo Ohka Kogyo Co.) was tested by dripping a small amount of the photoresist on the film and spreading it using a spinner (Dynapert PRS 14E, 3500 rpm). The samples chosen for this test were deposited in the low frequency reactor at 300 mTorr, 30 W and 100 W with pure HMDS; at 300 mTorr, 100 W for pure HMDS with 3 sccm of oxygen flux; and in the high frequency capacitive reactor at 300 mTorr, 100 W for pure HMDS with 3 sccm of oxygen flow.

Optical behaviour of films deposited on quartz was analysed by spectrophotometry (Hitachi UV 2001).

HMDS films deposited on glass were tested as a protective defrosting layer, by maintaining the films over a recipient with ice at 0 °C, and comparing the behaviour with untreated glass, glass deposited with PECVD-TEOS, and glass covered with silicone (E43, Semikron Co., wet process).

Photolithography on borosilicate glass was tested using an HMDS film as an adhesion promoter.

HMDS films were tested for benzene adsorption by exposure to benzene vapour for 24 hours in a closed reservoir, and analysed by Raman Microscopy immediately after opening.

3. RESULTS AND DISCUSSION

3.1 Deposition Process

3.1.1 Deposition Rate

In the low frequency capacitive reactor, the deposition rates increase with power (figures 1.a and 1.b) as commonly observed in organic silicon depositions, being significantly higher (up to 6800 Å/min) for pure HMDS than for HMDS carried by argon (up to 400 Å/min). An exception occurred at the higher pressure of 2 Torr for HMDS carried by argon (Figure 1.b) in which case there is a maximum deposition rate at 50 W. This effect was also observed by Heyner [29] in an experiment of HMDS carried by argon. He attributed it to cross linking favoured by the presence of argon and higher power levels, which would increase the density of the film (and consequently decrease its thickness), or to a competition between deposition and corrosion that also starts at higher power.

An upside-down "U" form structure was used to cover part of the substrate, at deposition conditions of 2 Torr, 50 W during 3 minutes, for pure HMDS. The whole covered area had a deposited film but with a deposition rate four times slower. This is an indication that at this condition neutrals govern the deposition process. The FTIR spectrum of this covered film is similar to the one obtained from the uncovered film, and is also similar to the spectrum of uncovered films obtained at lower pressures. At pressures below 2 Torr, no deposition occurred in the covered area.

Addition of oxygen at 200 mTorr and 30 W had a modest effect on deposition rates, which varied from 1000 to 1400 Å/min, for flows of 0.5 to 3 sccm, respectively. This increase in deposition rate is probably caused by an increase in the formation of active species.

For the 13.56 MHz capacitive reactor films were deposited at a much lower rate, about ten times slower, indicating that the much stronger ion fluxes of low frequency systems could be a determinant factor for this parameter. However, other factors, like the active species formed and the deposition mechanisms, are also affected by the frequency, and should not be ruled out.

In the inductively coupled reactor, the deposition rates are also lower, ranging from 14 to 500 Å/min, increasing with power and pressure (Figure 1c). With the addition of oxygen, deposition rates increase from 290 Å/min to 1100 Å/min, probably due to new active species formed by the reaction with oxygen atoms. Addition of nitrogen did not affect the deposition rates, which varied from 120 Å/min to 250 Å/min.

The much higher deposition rate in the low frequency capacitive reactor suggests that its much higher ion flux is an important factor in the film formation. Higher electron densities in high frequency systems apparently did not affect the deposition rate. Therefore, the deposition mechanism seems to be assisted by ions, with the ion flux supplying the energy necessary for the reactions to occur in solid phase. This could be the explanation for the lower deposition rate obtained under the "U" shaped structure.

3.1.2 Refractive Index

Figure 2 shows the refractive index as a function of power for some deposition conditions of pure HMDS and HMDS carried by argon, for the low frequency capacitive reactor. It can be seen that there is a tendency to reach the value of 1.6, which is typical for organic silicon films. No simple explanation could be found for the higher values obtained at low power and high pressure, since FTIR measurements did not show significant chemical differences at these conditions.

With the addition of oxygen, refractive indexes range from 1.4 to 1.8 with a trend towards 1.54, which is close to the refractive index of SiO_2 (1.462). In fact, Si-O bonds are detected in the FTIR spectra, corroborating these values.

At 13.56 MHz, no significant variations were found in the refractive index, which remained around 1.6.

In the inductively coupled reactor, refractive indexes varied from 1.45 to 1.55, tending towards 1.5 at higher powers, which is close to the refractive index of silicon oxide. Traces of Si-O bonds found in the FTIR spectra indicate the incorporation of the residual oxygen in the reactor. With the addition of oxygen, refractive indexes vary from 1.43 to 1.84 with an average of 1.63, decreasing to 1.48 at higher flows (20 sccm), which is closer to the refractive index of SiO_2. With the addition of nitrogen, refractive indexes varied from 1.44 to 1.48, with traces of Si-O bonds still present in the FTIR spectra.
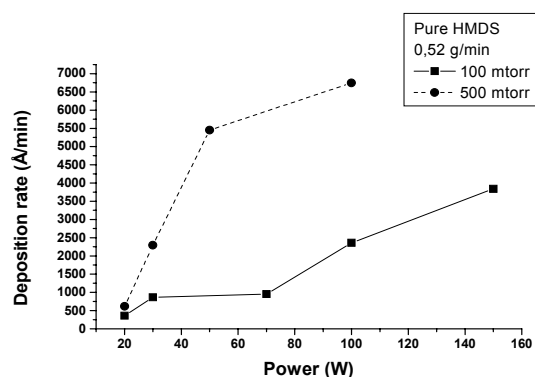
Figure 1.a – Deposition rate vs. Power for pure HMDS (0.52 g/min HMDS, 100 mTorr or 500 mTorr, low frequency reactor).
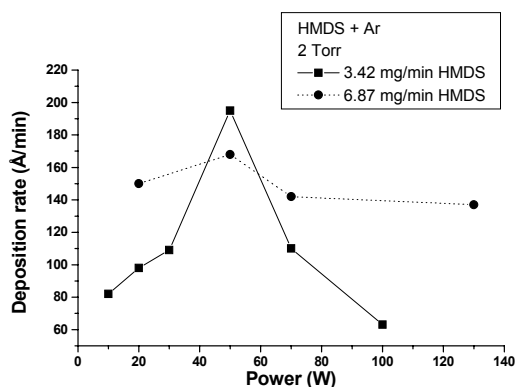
Figure 1.b – Deposition rate vs. Power for HMDS + Argon (3.42 mg/min and 6.87 mg/min HMDS, 2 Torr, low frequency reactor).
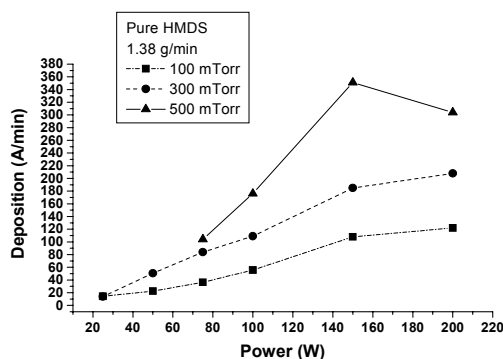
Figure 1.c – Deposition rate vs. Power (HD reactor).

All refractive indexes ranged from 1.4 to 1.6, except for low power cases in the capacitive low frequency reactor. In these cases, the values obtained were abnormally high, indicating that the reaction mechanisms were different. With the addition of oxygen, the refractive indexes tend to values closer to the refractive index of SiO_2. It is interesting to note that traces of Si-O bond are present in the FTIR spectra of films deposited at 13.56 MHz (in both capacitive and inductive cases) but are not detected in the spectra of films deposited at 40 kHz. The incorporation of oxygen is expected in

HMDS plasmas, and the absence of the Si-O peak in the low frequency cases could be associated to their higher deposition rates.
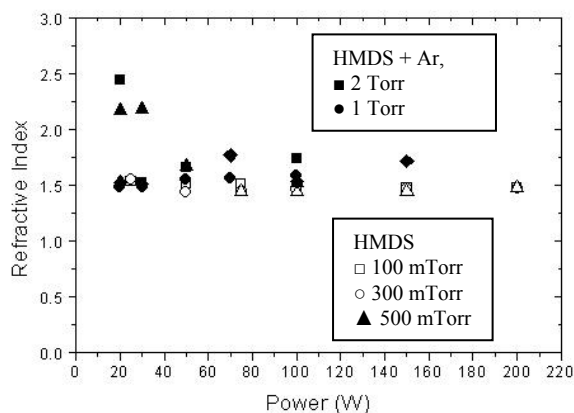
Figure 2 – Refractive index vs. Power for HMDS and HMDS + Argon (80 sccm Argon, 6.87 mg/min HMDS, low frequency reactor)

3.1.3 Infrared and Raman Spectra

Figure 3 shows a typical FTIR spectrum of the HMDS films formed. Figure 3.a shows the spectrum obtained in the low frequency capacitive reactor and Figure 3.b shows the spectrum obtained in the inductively coupled reactor. We are particularly interested in the Si-CH_3 (1250-1260 cm^{-1}), Si-CH_2-Si (1090-1020 cm^{-1}), and Si-N-Si (900-830 cm^{-1}) bonds. The macromolecular structure that would maximise CH_3 radicals would have high concentrations of Si-CH_3 and Si-N-Si bonds and low concentration of Si-CH_2-Si bonds (characteristic of a Si-CH_3 termination turning into a ramification). Since it was not possible to make a quantitative calibration of the spectral peak intensities, relative intensities of Si-CH_3 and Si-CH_2-Si peaks were measured with respect to Si-N-Si.

Figure 4 shows Si-CH_3/Si-N-Si and Si-CH_2-Si/ Si-N-Si relative intensities as a function of power for pure HMDS films deposited at 100 mTorr and 500 mTorr, in the low frequency capacitive reactor. Both relative intensities decrease with power, indicating that less carbon is being incorporated in the film as the power is raised. This effect is more pronounced for Si-CH_3 groups at lower pressure, probably because electron energies are higher, increasing the fragmentation of the methyl radicals.

For discharges with HMDS carried by argon (Figure 5), Si-CH_3/Si-N-Si relative intensities are much lower than in the pure HMDS case, and decrease with power independently of pressure or flow, while Si-CH_2-Si/Si-N-Si intensities remain fairly constant. This indicates that the diluted HMDS is fragmenting preferentially at methyl radicals. At higher pressures (2 Torr), flow of 6.9 mg/min and low power (20 W), the concentration of Si-CH_2-Si/Si-N-Si decrease, becoming comparable to Si-CH_3/Si-N-Si, indicating that a higher concentration of the reagent in the gas phase favours the fragmentation of the molecule at the nitrogen atom.
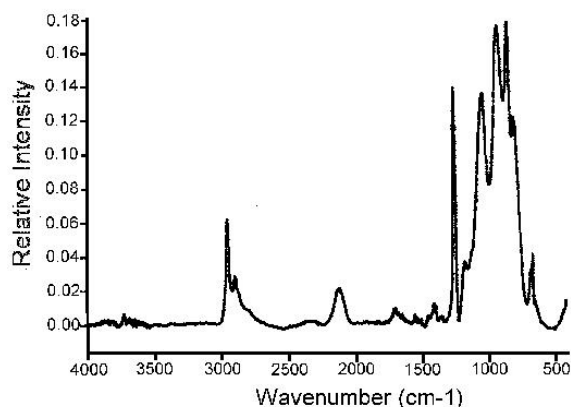
Figure 3.a – Typical results for pure HMDS (0.52 g/min HMDS, 100 mTorr, 150 W, low frequency reactor).
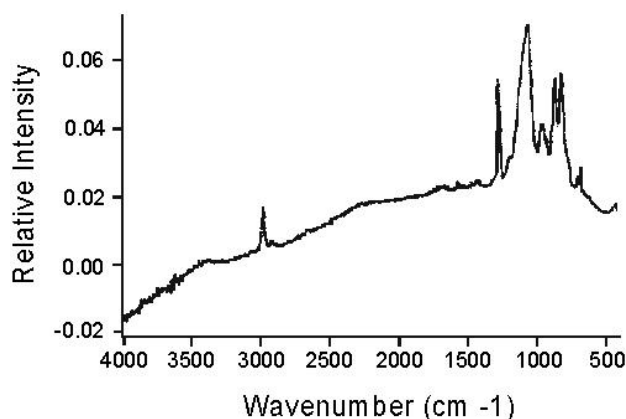

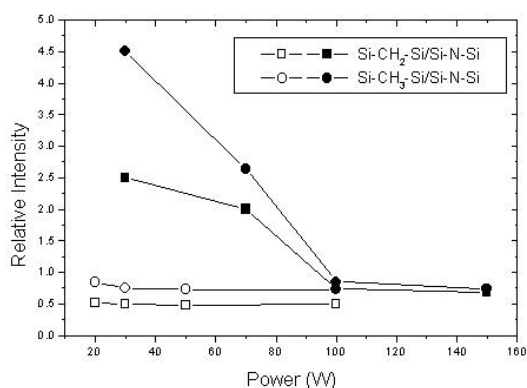**Figure 3.b – Typical results for pure HMDS (1.38 g/min HMDS, 500 mTorr, 150 W, HD reactor).**

Figure 4 – Relative intensity vs. Power (100 mTorr (■●) and 500 mTorr (□○), low frequency reactor).

With the addition of oxygen (Figure 6), traces of Si-O bonds begin to appear, and both Si-CH$_2$-Si/Si-N-Si and Si-CH$_3$/Si-N-Si relative intensities increase, showing that the oxygen atom removes preferentially Si-N bonds. At higher oxygen

flows Si-CH$_3$ and Si-CH$_2$-Si bonds are probably also removed, leading to the saturation observed at flows higher than 2 sccm.
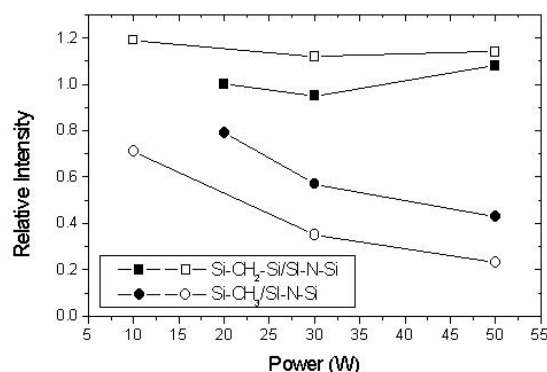

Figure 5 – Relative intensity vs. Power (1 Torr, 6.87 mg/min (□○) and 2 Torr, 3.42 mg/min (■●) HMDS, low frequency reactor).
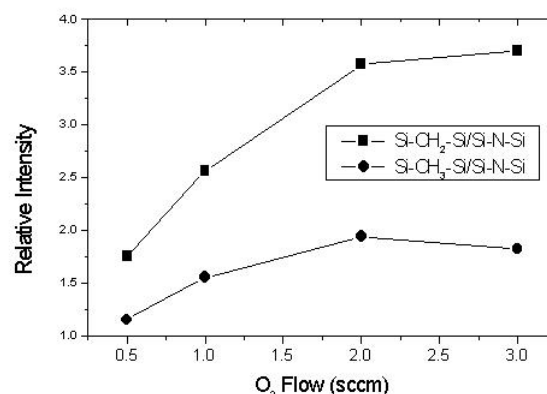

Figure 6 – Relative intensity vs. oxygen flow (200 mTorr, 0.52 g/min HMDS, 30 W, low frequency reactor).

FTIR spectra of films deposited in the inductively coupled reactor showed that Si-CH$_3$ and Si-CH$_2$-Si bonds tend to decrease with power, as also observed in the capacitive case, but with a more drastic variation. In all cases, Si-CH$_2$-Si is the strongest intensity found in the spectra, unlike the low frequency capacitive case. A small Si-O bond peak is also present in the spectra, probably due to residual oxygen in the reactor.

Addition of oxygen, resulted in the increase of Si-O peak and, like in the capacitive case, it leads to the decrease of Si-N-Si bonds, especially at higher powers (200 W). Addition of 5 sccm and 20 sccm of nitrogen flow at 100 W increases Si-N-Si peak intensities, but not at 200 W. The presence of nitrogen at lower power seems to favour the removal of carbon, the same not occurring at 200 W.

Films formed at 13.56 MHz in the capacitive reactor showed FTIR spectra similar to the inductive case, that is, high intensity Si-CH$_2$-Si bond peaks, and traces of Si-O bonds. Since the change in frequency was the only different factor relative to the spectra obtained at 40 kHz, it is seen

that the use of low frequency had the main advantage of low oxygen incorporation through Si-O bonds in the film.

Raman microscopy showed homogeneous films in all cases (capacitive and inductive), with CH_n bond being the only peak detected in the spectra. The only exception occurred at 2 Torr, 20 W where nucleation nodules (polymerisation starting at many points and coalescing after some time) were formed, probably by conventional polymerisation induced by the plasma. The refractive index in this case was also abnormally high as seen in Figure 2.

In order to verify the effect of ion bombardment, one sample was deposited in the low frequency capacitive reactor with pure HMDS at 1 Torr, 50 W with the substrate placed under the electrode, away from the plasma zone. Graphite nodules (C=C bonds) were found in this case indicating the decomposition of CH_3 groups. In the inductively coupled reactor, where the sample is also located away from the plasma, no graphite nodules were found, probably due to the higher energy of the electrons in this system.

3.1.4 Water Contact Angle Measurements

All films resulted hydrophobic. Water contact angles were between 91° and 105° for all pure HMDS depositions (both capacitive, inductive, low and high frequencies), even with the addition of oxygen and nitrogen, and between 80° to 90° in all depositions of HMDS carried by argon. The lower values in the case of HMDS carried by argon could be associated to cross linking induced by the presence of argon, replacing CH_3 radicals.

3.2 Applications

3.2.1 Chemical Resistance, Adhesion to Photoresit and Surface Protection

All films presented good resistance to all acid and basic solutions, with the exception of NaOH, which partially removed pure HMDS films. Also, all organic compounds, especially acetone, dissolved the films, but slowly.

All films, especially those deposited from HMDS carried by argon, showed good resistance to HF (1:10) corrosion, after 10 to 20 minutes of exposure.

Films produced in the inductively coupled reactor have less resistance to NaOH and HF corrosion. This lower chemical resistance could be caused by films formed with less cross-linking, since in this reactor ion bombardment is much lower that in the capacitive system.

The films obtained in typical deposition conditions in the capacitive reactor showed good adhesion to positive photoresist, except for the depositions made at 13.56 MHz with the addition of oxygen. This is expected since the incorporation of oxygen decreases the Si-CH$_3$ species and consequently the compatibility between the film and the photoresist.

In the inductive reactor case, the deposited films did not have a satisfactory adhesion to photoresist probably due to Si-O formation.

Thin HMDS films (less than 500 Å) deposited on glass showed good adhesion to both photoresist and the glass substrate. After ultraviolet (UV) exposure (wavelength=256 nm) using as mask a square of 200 μm, the sample was treated with HF, resulting in the corrosion of the unmasked glass surface. This result demonstrates the possibility of direct photolithography on glass.

The use of HMDS for defrosting applications was demonstrated, after verifying that untreated glass took 30 seconds to form the first visible water droplet, while in HMDS and TEOS treated samples this happens only after 3 minutes. Silicone treated glass presented intermediate behaviour, with the threshold of the first droplet appearance being difficult to quantify due to the lack of transparency after the silicone treatment. It is also interesting to note that the water droplet sizes in HMDS and TEOS treated samples were smaller than in the untreated glass.

3.2.2 Optical and Adsorption Properties

Films deposited on quartz using HMDS pure monomers and optimal deposition conditions (both reactors) were analysed in a spectrophotometer from 200 nm to 1100 nm. Typical results can be seen in Figure 7. The films presented good transparency in the infrared and visible region, but absorbs radiation with wavelengths below 400 nm. Although the FTIR spectra of both films are similar, the absorption onset is more abrupt for the film formed at 150 W (Figure 7c), which is an indication that the structure of the film is power dependent, probably due to cross-linking between chains. Ultraviolet absorption was expected, since in a previous experiment [37], no modification was observed in the infrared spectrum after a sample was exposed to UVA light (a 22 W lamp, with a wavelength of 350 nm, distant 5cm from the sample) for 20 hours and to UVC light (same parameters, but with a wavelength of 250 nm) for 5 hours.

Porous silicon samples were deposited with HMDS films in the inductively coupled reactor in order to test adsorption properties. The FTIR spectrum was not taken due to the thinness of the film. Raman spectrum and optical microscopy however, indicated that the porous structure was filled or bridged over by the deposition. The Raman spectrum showed only fluorescence, probably due to a malformation of the film induced by the porous structure. Figure 8 shows micrographs of the porous silicon, focused: a) below the surface of the film, on the porous silicon and b) on the surface of the film, on a small particle accidentally deposited above it. It can be seen in b) that the small particle lays on a smooth surface, indicating that planarization has occurred by a complete covering of the surface by the HMDS film. In Figure 8.a bigger clusters indicate high nucleation of HMDS in the surface. These results encourage the use of HMDS in vapour phase only [38], in order to cover the surface, preserving the porous structure of the substrate. Similar results were obtained for the low frequency reactor.
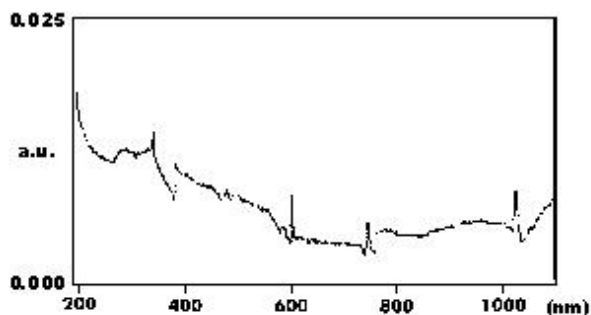
Figure 7.a - Spectrophotometer analysis of HMDS film (50 W, 500 mTorr, low frequency reactor).
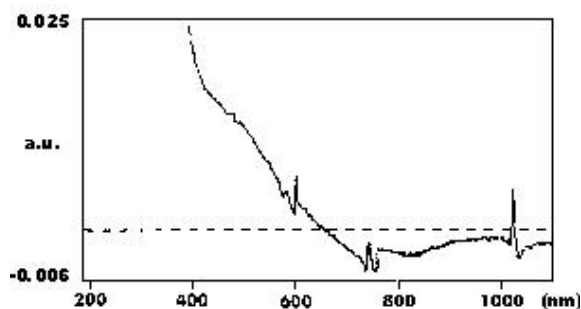

Figure 7.b - Spectrophotometer analysis of HMDS film (150 W, 500 mTorr, low frequency reactor).
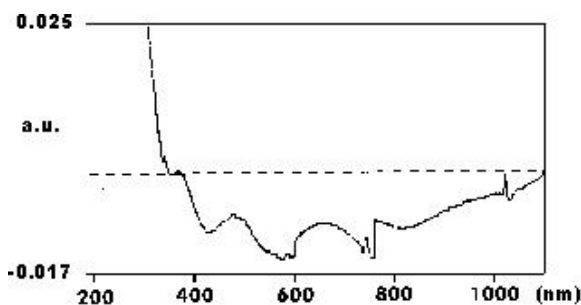

Figure 7.c - Spectrophotometer analysis of HMDS film (150 W, 500 mTorr, HD reactor).

Figure 8.a - Micrographs of the porous silicon, focused below the surface of the film (50X80 μm).

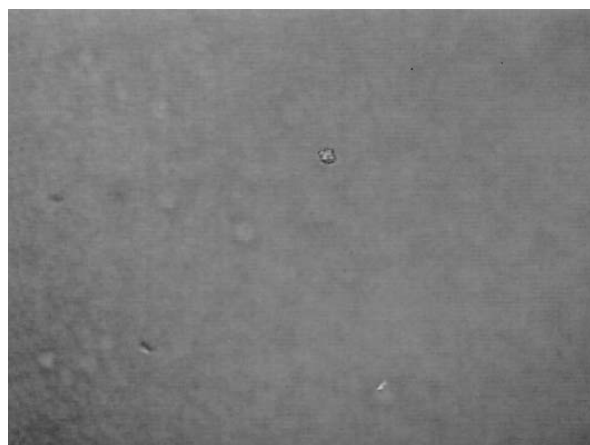**Figure 8.b - Micrographs of the porous silicon focused on the surface of the film (50X80 μm).**

HMDS films deposited on quartz samples were exposed to saturated atmosphere of benzene for 24 hours and then analysed in Raman Microscopy. The Raman spectra showed bands at 770, 1040, 1180 and 1625 cm^{-1} besides a wide band indicative of fluorescence at 3000 cm^{-1}. These bands can be assigned to the spectra of aromatic compounds, indicating the adsorption of benzene. Similar spectra were obtained for samples over which a droplet of benzene was deposited, and maintained in a benzene-saturated atmosphere for 4 hours. These samples were swollen at various points, showing the high affinity of the films to this compound and their good adsorption characteristics.

4. CONCLUSIONS

Plasma enhanced chemical vapour deposition of HMDS produces homogeneous hydrophobic films with high concentration of methyl radicals, and important properties for microstructure industry: good resistance to strong inorganic acids and bases (including HF corrosion), good affinity to organic compounds, and good adhesion to photoresists. Although all films are chemically similar, their properties differ according to deposition conditions and reactor characteristics, showing the versatility of HMDS as a reagent.

Films obtained in the inductively coupled reactor have low deposition rates, allowing a more precise control of film thickness. These films however are not appropriate as adhesion promoters of photoresists, and are not resistant to strong bases.

The use of a low frequency capacitive reactor resulted in much higher deposition rates (up to a factor of 12 higher in the case of pure monomer plasmas) if compared to the commonly used 13.56 MHz sources in both capacitive and inductive reactors. This suggests its use for passivation in micromechanics. Despite the lower deposition rates for films formed by HMDS carried by argon, these are the most resistant films to HF corrosion.

The films produced in the capacitively coupled reactor can be used in a wide range of activities. They can be used, for instance, for UV protection as shown in a previous work on paper [37], in which ultraviolet tests showed promising re-

sults for outdoor applications. Furthermore, its use for surface modification showed a series of advantages, such as the compatibilization of ceramic surfaces with organic compounds [30] or adsorption layer for sensor development [31].

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