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Plasma Polymerization of Silicon-Containing Monomers

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Plasma depositions of ultra thin films from seven silicon-containing liquid monomers were investigated using a continuos wave (CW) plasma source. The deposition rate of plasma polymerized films were determined using a quartz crystal microbalance (QCM) technique while the film composition were determined spectroscopiclly using primarily X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared method (FT-IR). The wettability of the plasma-polymerized films was also investigated by measuring the contact angles of water on the film surfaces. It was observed that the C=C absorption band was not present in these films. This observation is consistent with selective polymerization through the double bond. Oxygen was present in all samples investigated and this may be attributed to the quenching of radicals in the film by reactions with oxygen when exposed to atmosphere.
Keywords: plasma polymerization, silicon-containing monomers, deposition rate, quartz crystal microbalance (QCM), XPS

1. Introduction

Plasma polymerization has been widely used to fabricate thin and ultra-thin films from a variety of volatile compounds. The materials formed by plasma polymerization are significantly different from conventional polymer. Films formed in this manner are characteristically highly branched and highly cross-linked which make them extremely resistant to most chemicals and physically very stable. In addition, these ultra-thin films are homogenous with flat surface structure, pin-hole free and possess an excellent adhesion properties. The plasma polymerization technique has also been conventionally employed to fabricate thin functional films that could facilitate the surface modification of materials [1, 2]. Such films are expected to be useful as molecular recognition films rigidly fixed on the transducers of chemical sensors [3-5].

Plasma polymerized films (pp-films) derived from silicon-containing monomers have created a lot of interest by many investigators in a wide variety of areas. Plasma polymerized organosilanes have found application as a protective coating on metal [6], as a hydrophobic gas separation membrane [7], as corrosive protective coatings for microelectronic devices [8] and has also been considered for UV lithography applications since they provide a thin conformal and photosensitive layer at the wavelength [9]. Organosilane surface has also found application in trace metals detection since complexation to ethylenediamine ligands bound by siloxane bonds on the surface of a shear horizontal acoustic plate mode sensor were found to detect copper (II) [10]. Silicon-based plasma polymerized films have been established to provide hydrophobic layers on metals. These are to promote dropwise condensation of steam on the

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outer surfaces of utility turbine condensers tubes, instead of filmwise condensation, in order to increase the heat transfer coefficient [11]. A more recent interest is to use these materials as selective layers on the surface of quartz resonator in conjunction with biological components for use as glucose biosensors. Hexamethyldisiloxane plasma polymerized based thin film glucose biosensor was found to exhibit lower noise and reduce the effect of interference to a greater degree than sensors made using conventional immobilization method. Since the polymerization onto the substrate can be achieved in a clean environment without the use of any solvent (dry proses), chip fabrication for full wafer process can be designed to achieve mass production compatibility [12].

In this paper we report on work to characterize plasma-polymerized films derived from silicon-containing monomers obtained from a continuous wave (CW) plasma source. The deposition rates of plasma-polymerized films were obtained by employing quartz crystal microbalance (QCM) technique while the film compositon were studied spectroscopically using Fourier transform infrared methods (FT-IR), X-ray photoelectron spectroscopy (XPS) and contact angles.

2. Experimental

2.1. Materials

The monomers allyltrimethylsilane, vinyltrimethylsilane, vinyltriethoxysilane, 1,3-divinyltetramethyldisiloxane, 1,1,3,3-tetramethyl-1,3-divinyldisilazane, tetravinylsilane, diallyldimethylsilane used in this experiment were of analytical or guaranteed grade and were purchased from Shin-Etsu Co., Ltd. (Tokyo, Japan), or Wako Chemical Co., Inc. (Tokyo, Japan) and used without further purification. Monomers were however thoroughly degassed by repeated freeze-pump-thawing under vacuum to remove trapped atmospheric gases prior to use.

Table 1 indicates the chemical structure of monomer for plasma polymerization and its boiling point. Water was prepared by Milli-Q (Millipore Ltd.) with its specific resistance above 18 MΩ/cm.

2.2. Methods

Plasma polymerization equipment, model BP-1 Mark II, from Samco International Co., (Kyoto, Japan) was used to plasma-polymerize the monomers on to QCMs [13-15]. Figure 1(a) shows a schematic of the plasma polymerization equipment.

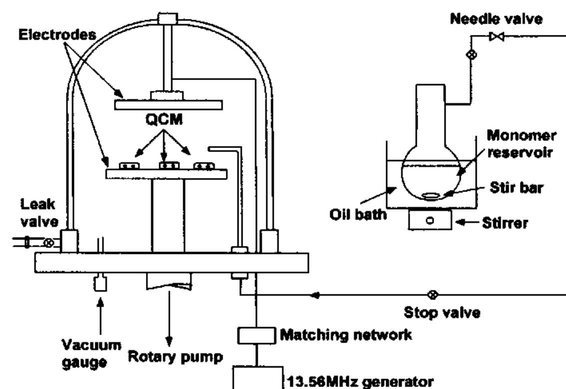

Fig. 1a. Schematic of the plasma polymerization equipment.

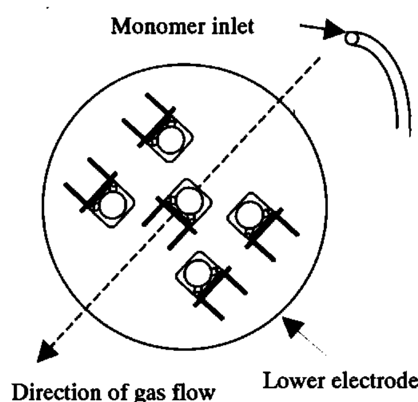

Fig. 1b. Position settings (a to e) of five QCMs on the lower electrode.

The deposition rates of the pp-films were measured with a QCM technique during the polymerization process. The QCM with gold electrodes on both of its surfaces (AT-cut of 9 MHz: 8 x 8 x 0.15 mm) was purchased from Seywa Crystal Co., Ltd. (Chiba, Japan). The pp-films were deposited on one side of the QCM. The deposition rates of the plasma-polymerized films are dependent on the positioning of the substrates. Therefore, five QCMs were placed on the lower electrode (diameter 100 mm) for the glow discharge. The position settings of the five QCMs on the lower electrode are denoted as shown in Fig. 1(b). Prior to plasma polymerization, the five QCMs were treated by plasma sputtering for 5 s under 100 W of RF power and 100 Pa of He pressure.

Vapor pressure of the monomers and the RF power of the glow discharge are two of the most important controllable parameters in plasma polymerization. In this study the polymerization conditions were always maintained at a vapor pressure of 100 Pa and RF power of 100 W. Our studies showed that under these conditions an optimum film-state of the polymer could be

Table 1. Chemical structures and their boiling point for the various monomers used in this study.

Monomer	chemical structure	b.p. (°C/mmHg)
Allyltrimethylsilane	$CH_3 Si (CH_3)_2 CH_2CH=CH_2$	84 / 760
Vinyltrimethylsilane	$CH_3 Si (CH_3)_2 CH=CH_2$	55 / 760
1,3-Divinyltetramethyldisiloxane	$(CH_2=CH Si (CH_3)_2)_2 O$	139 / 760
1,1,3,3-Tetramethyl-1,3-divinyldisilazane	$(CH_2=CH Si (CH_3)_2)_2 NH$	160 / 760
Vinyltriethoxysilane	$CH_3CH_2O Si (OCH_2CH_3)_2 CH=CH_2$	130 / 760
Tetravinylsilane	$(CH_2=CH)_4 Si$	63 / 760
Diallyldimethylsilane	$CH_2=CHCH_2 Si (CH_3)_2 CH_2CH=CH_2$	54 / 20

Table 2. Deposition rate of pp-1,3-divinyltetramethyldisiloxane films at various position on the lower electrode of the glow discharge.

Position	slope (Hz/sec)	intercept (Hz)	correlation coefficient
a	73.64	1310	0.996
b	78.50	2609	0.993
c	86.81	1356	0.993
d	60.41	-1507	0.993
e	75.89	518	0.968

Table 3. Average deposition rates for the various monomers used in this study.

Monomer	deposition rate (μg/min)	σ (μg/min)	C.V. $\times 10^2$ (%)
Allyltrimethylsilane	1.07	0.49	45.8
Vinyltrimethylsilane	1.41	0.33	23.4
1,3-Divinyltetramethyldisiloxane	4.50	0.57	12.7
1,1,3,3-Tetramethyl-1,3-divinyldisilazane	6.55	1.73	26.4
Vinyltriethoxysilane	11.1	2.39	21.5
Tetravinylsilane	29.7	10.4	35.0
Diallyldimethylsilane	1.34	0.46	34.2

The averages of deposition rates of the pp-films are calculated from the slope of the five positions (a to e) in the Figure 2. σ and C.V. represent the standard deviation and the coefficient of variation, respectively.

obtained. The monomers were vaporized at a constant temperature by an oil bath. The monomer vapor was then allowed to flow into the plasma reactor between two parallel electrodes that were 6 cm apart. A needle valve was used to control the pressure inside the reactor. The plasma polymerization was performed for 300 seconds with interruptions for measurements at 60, 120, 180 and 240 s. We obtained an optimum film-state of the polymers under these conditions. The apparatus and procedure for determination of the deposition rate have been described previously [15]. The oscillation frequency of the QCM was measured by incorporating the QCM in a transistor-transistor logic electronic circuit described in ref. 16 (circuit II). A universal counter was used to read the frequency with the data stored in a microcomputer. The relationship between the weight of the pp-films and the frequency shift is expressed in units of ng/Hz. When an AT-cut quartz crystal with its fundamental oscillation frequency of 9 MHz is used, adsorption of about 1 ng of material decreases the oscillation frequency by 1 Hz [17, 18]. All experiments for determination of the deposition rate of plasma polymer by QCM were carried out at 25 ± 2 °C.

Infrared spectra were obtained with a JASCO 610 FT-IR spectrometer in the transmission mode recorded at a resolution of 4 cm^{-1} while the instrument was purged with nitrogen gas. Each spectrum was recorded at an average of over 128 scans. For each deposition, a freshly pressed FT-IR-grade KBr pellets were used as substrates and placed always at the same position on the lower electrodes for all measurements. Structural analysis of the deposited films was carried out by XPS. The XPS spectra were obtained using a

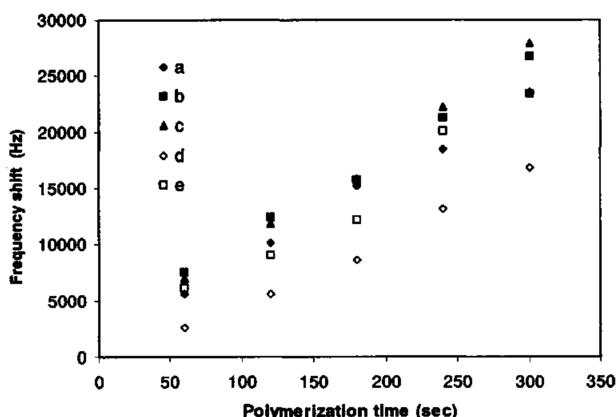

Figure 2. Frequency shift of QCMs in relationship to the polymerization time for the various positions on the lower electrode for 1,3-divinyltetramethyldisiloxane.

Perkin Elmer 5600 Multi Technique System. The X-ray source employed was an Al-K_{α} operating at 100 W (14 kV). The base pressure was 10^{-10} Torr. An electron gun was employed to neutralize charge buildup on the non-conducting film. The films were analyzed at an electron take-off angle of 75 ° measures with respect to the surface plane. To collect the pp-film, aluminum foil was placed over the electrodes. Following film deposition a small sample of the foil was cut out for XPS characterization. Measurements of the contact angles of water on deposited pp-films on glass slides were performed using a contact angle meter (model CA-D, Kyowa Interface Science Co., Ltd). The contact angle were measured by means of the advanced angle method and was carried out at 25± 0.1 °C. A 10 μl of Milli-Q water was applied by a micropipette. Five measurements at different places were carried out for each sample immediately after polymerization and the average value was calculated.

3. Results and Discussion

The deposition rates of the pp-films onto the QCM were measured directly by the shift in the oscillating frequency. Figure 2 shows the relationship between the deposition rates of pp-1,3-divinyltetramethyldisiloxane for the five positions (a to e) of the lower electrode and the polymerization time. A linear relationship was observed up to a polymerization time of 300 s. The regression of the polymerization time response for

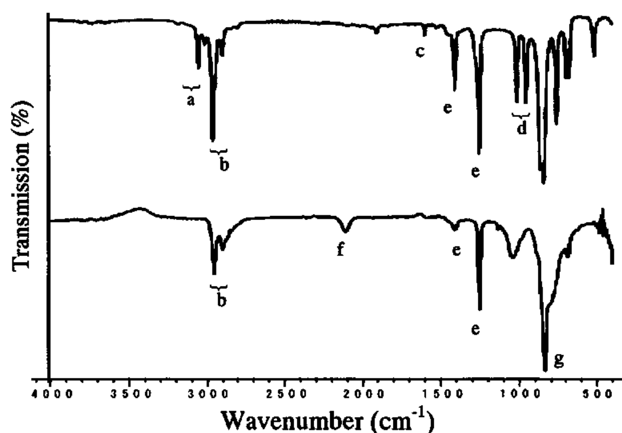

Figure 3. FT-IR transmission spectra of vinyltrimethylsilane monomer (top) and it's pp-film (bottom). Assignment of the IR absorption bands are as follows: a; =C-H stretch, b; C-H stretch, c; C=C stretch, d; C-H out of plane bend, e; Si-CH_3 vibration, f; Si-H stretching and g; Si-H bend.

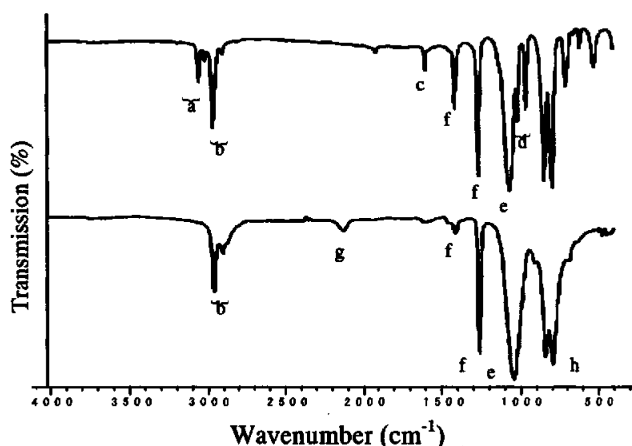

Figure 4. FT-IR transmission spectrum of 1,3-divinyltetramethyldisiloxane monomer (top) and it's pp-film (bottom). Assignment of the IR absorption band are as follows: a; =C-H stretch, b; C-H stretch, c; C=C stretch, d; C-H out of plane bend, e; Si-O stretch, f; Si-CH_3 vibration, g; Si-H stretching and h; Si-H bend.

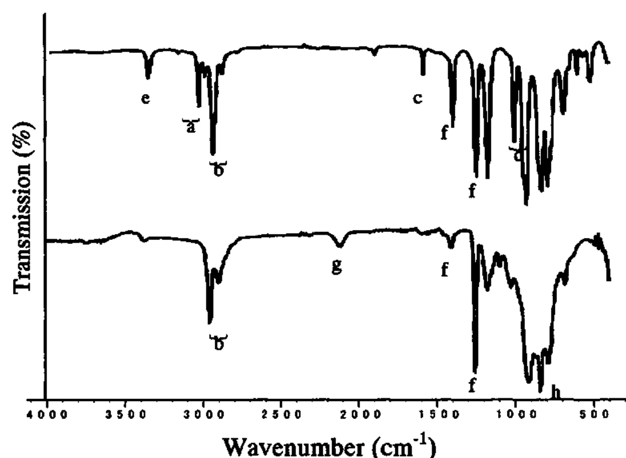

Figure 5. FT-IR transmission spectrum of 1,1,3,3-terамethyl-1,3-divinyldisilazane monomer (top) and it's pp-film (bottom). Assignment of the IR absorption band are as follows: a; =C-H stretch, b; C-H stretch, c; C=C stretch, d; C-H out of plane bend, e; N-H stretch, f; Si-CH_3 vibration, g; Si-H stretching and h; Si-H bend.

the positions a to e is summarized in Table 2. We define the individual deposition rates of the plasma-polymerized films using the slope of the line a to e for each sample. The averaged deposition rate for the pp-1,3-divinyltetramethyldisiloxane film was 75.05 Hz/s (4.50 μg/min). Table 3 summarizes the averaged deposition rates for the seven monomers. The values are in the order of tetravinylsilane > vinyltriethoxysilane > 1,1,3,3-teramethyl-1,3-divinyldisilazane >

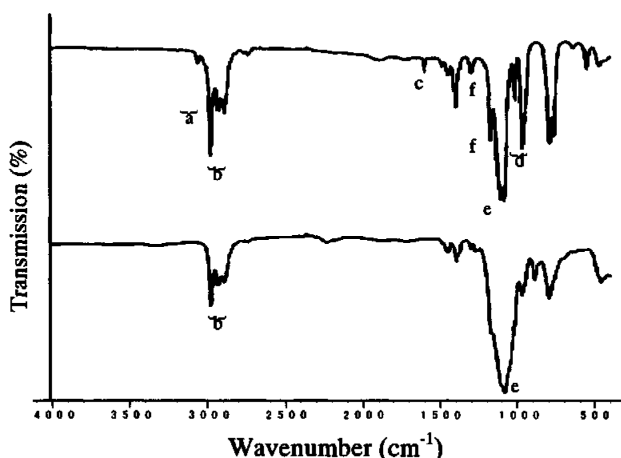

Figure 6. FT-IR transmission spectrum of vinyltriethoxysilane monomer (top) and it's pp-film (bottom). Assignment of the IR absorption band are as follows: a; =C-H stretch, b; C-H stretch, c; C=C stretch, d; C-H out of plane bend, e; Si-O stretch, and f; Si-OCH_2CH_3 vibration.

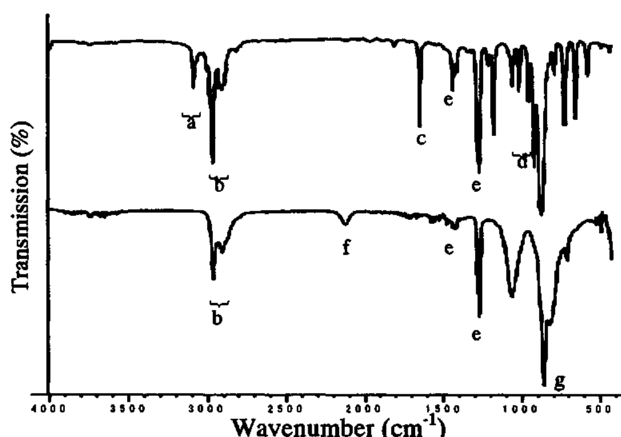

Figure 7. FT-IR transmission spectra of allyltrimethylsilane monomer (top) and it's pp-film (bottom). Assignment of the IR absorption bands are as follows: a; =C-H stretch, b; C-H stretch, c; C=C stretch, d; C-H out of plane bend, e; Si-CH_3 vibration, f; Si-H stretching and g; Si-H bend.

1,3-divinyltetramethyldisiloxane > vinyltrimethylsilane > diallyldimethylsilane > allyltrimethylsilane. Thus, the deposition rate of the pp-films is affected by the chemical structure of the monomer.

All the polymerizations were conducted under the identical conditions in terms of the settings on the equipment, which give higher gas phase concentration of the monomers with lower boiling points. This concentration effect is, however, often

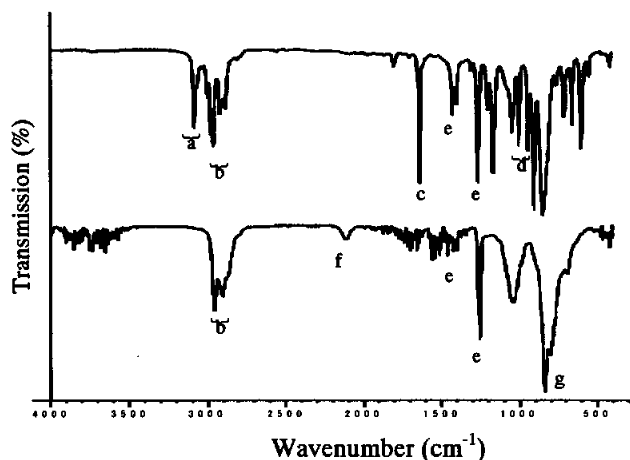

Figure 8. FT-IR transmission spectra of diallyldimethylsilane monomer (top) and it's pp-film (bottom). Assignment of the IR absorption bands are as follows: a; =C-H stretch, b; C-H stretch, c; C=C stretch, d; C-H out of plane bend, e; Si-CH_3 vibration, f; Si-H stretching and g; Si-H bend.

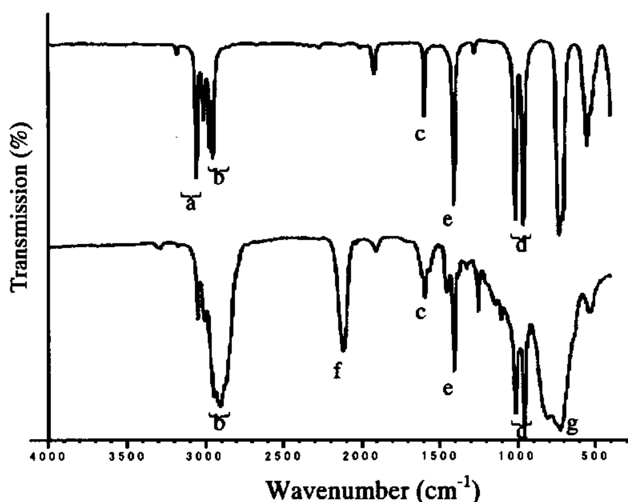

Figure 9. FT-IR transmission spectra of tetravinylsilane monomer (top) and it's pp-film (bottom). Assignment of the IR absorption bands are as follows: a; =C-H stretch, b; C-H stretch, c; C=C stretch, d; C-H out of plane bend, e; Si-CH_3 vibration, f; Si-H stretching and g; Si-H bend.

cancelled by the reaction pathway of the different monomers. Polymerization is assumed to proceed via a free-radical mechanism initiated through the collision of an electron with a monomer molecule. Dissociation of these molecule results in the formation of free radicals, which may add to intact monomers, denoted as the initiation. Polymerization then proceeds in the gas phase and on the surface. Finally, collision between two radicals leads to termination of the reaction by radical-radical coupling or disproportionation, as in the case of standard free radical polymerization.

FT-IR spectra for all the silicon-containing monomers and their respective pp-film are shown in Figures 3-9. As shown in the figures, the most of the absorption bands characteristics of compounds containing a carbon-carbon double bond, which were easily identified in the spectra of the monomers, disappeared in the spectra of the pp-films. Specifically, these absorption bands were the C-H stretch of the olefinic carbon-hydrogen bond which appeared in the region 3100 to 3000 cm^{-1}, the C=C stretching frequency in 1600 to 1675 cm^{-1}, and the out-of-plane bending of the olefinic C-H bonds at around 950 and 1000 cm^{-1}. A weak band near 1910 cm^{-1} in spectra of most of the monomers is identified to be the overtone of the fundamental band at 950 cm^{-1}. This band also disappeared in their respective pp-films. This observation is consistent with selective polymerization through the double bond. The presence of strong peaks at 3046 cm^{-1}, 1590 cm^{-1}, 1007 cm^{-1} and 952 cm^{-1} in the pp-film of tetravinylsilane is attributed to the stretching and bending of C-H from alkenes. This shows that the polymer stills have some double bonds remained incorporated in the film. Vibration bands around 2105-2117 cm^{-1} and 834 cm^{-1} in the pp-films indicate the presence of Si-H stretch and bend respectively. Zuri *et al.* [19] showed that Si-H stretch and C=O groups were present in the FT-IR spectrum of pp-film of hexamethyldisiloxane at high powers and disappeared at low powers. Thus we can infer that intensive fragmentation of the monomers occurred at our experimental conditions

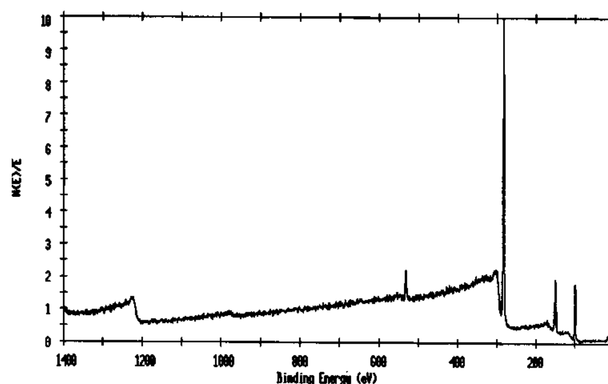

Figure 10. XPS broad scan spectrum of pp-diallyldimethylsilane at RF of 40 W and pressure of 100 Pa.

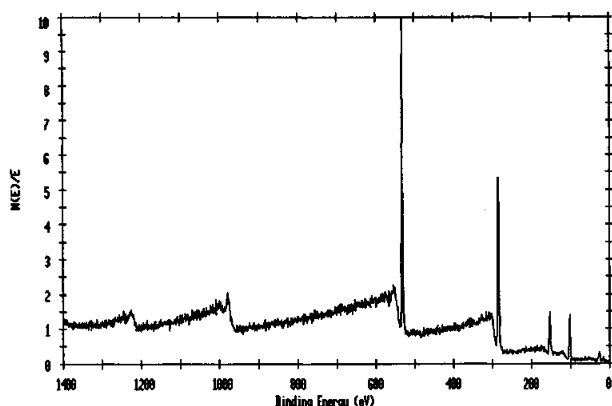

Figure 11. XPS broad scan spectrum of pp-vinyltriethoxysilane at RF of 40 W and pressure of 100 Pa.

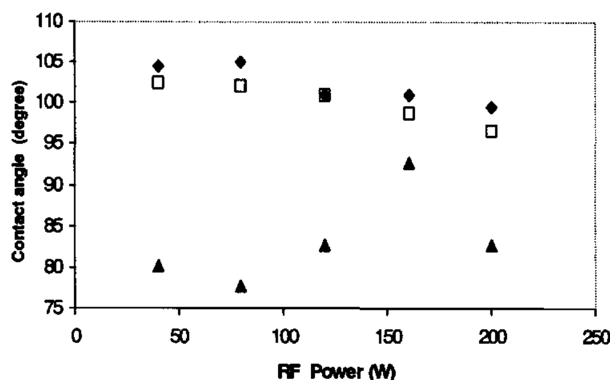

Figure 12. Contact angles of water for pp-films of allytrimethylsilane (◆), vinyltrimethylsilane (□) and vinyltriethoxysilane (▲) as a function of RF power.

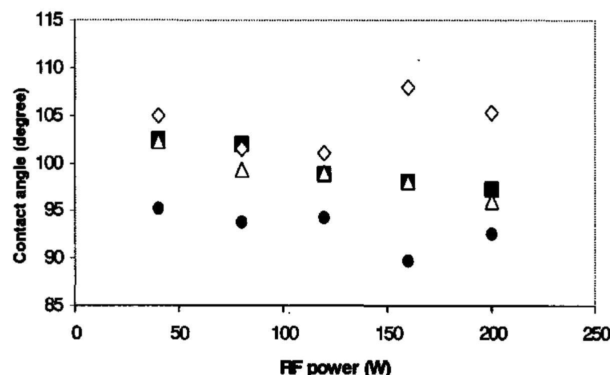

Figure 13. Contact angles of water for pp-films of 1,3-divinyltetramethyldisiloxane (■), 1,1,3,3-tetramethyl-1,3-divinyldisilazane (●), tetravinylsilane (◇) and diallyldimethylsilane, (△) as a function of RF power.

of 100W and 100 Pa. However, no peaks appeared strong enough to be visible around the region of 1700 cm^{-1} in the spectrum of the pp-films to indicate the presence of C=O group. We also noted that there was quite a strong absorption emanated around 1040 cm^{-1} in the pp-vinyltrimethylsilane, 1026 cm^{-1} in the pp-1,1,3,3-tetramethyl-1,3-divinyldisilane, 1041 cm^{-1} in the pp-allyltrimethylsilane and 1038 cm^{-1} in the diallydimethylsilane films. Since it is well known that plasma polymerized films contains long-lived radicals to react with atmosperic oxygen, we believed this peaks arises from the Si-O group in the pp-films. Another strong band, which originated around 788 cm^{-1} in all of the pp-film is assigned to the Si-C stretching.

Figures 10 shows the low resolution XPS spectrum of pp-diallydimethylsilane film which is typical of the XPS spectra of all pp-film of monomers without oxygen while Figure 11 shows the XPS spectrum of vinyltriethoxysilane representing spectra of pp-film of monomers with oxygen. Both XPS spectra exhibited peaks corresponding to C_{1s}, O_{1s}, Si_{2s}, and Si_{2p}. Thus, oxygen is present in all samples investigated and this may be attributed to the quenching of radicals in the reactions with oxygen when exposed to atmosphere. Table 4 shows the results of the elemental analyses of the pp-films obtained from high resolution scan of the pp-films at plasma powers of 40 to 200 W and monomers pressure of 100 Pa. The absence of nitrogen peak in the spectrum suggests that there was no appreciable atmospheric gas from leaks in the reactor during polymerization. From table 4, we can see that the different pp-films formed from the seven monomers used in this study all have lower carbon, higher silicon and higher oxygen content than their respective monomers. This result is consistent with previous work done on pp-film of tetramethyllsilane [20]. The higher oxygen content has been well known to be due to the reaction of radicals in the polymer with atmospheric oxygen. Except for plasma polymerized allytrimethylsilane and 1,3-divinyltetramethyldisiloxane films, all the pp-films showed a relatively lower carbon content while the percentage of silicon increased with increasing plasma power. The abundance of oxygen was always largest at highest power study. This seems to support the conclusion drawn by Zuri *et al.* [19] that as the plasma powers lowered, the pp-films forms began to resemble that of its monomers and with increase in plasma power, intensive fragmentation would occur and new chemical structures would result and the pp-films would become less organic.

Table 4. Surface atom concentration of the plasma polymerized polymer of the different monomers used in this study at different RF power as determined by XPS.

Substratum	RF Power (W)	C (%)	Si (%)	O (%)	N (%)
Allyltrimethylsilane	40	74.03	21.89	4.09	
$C_6H_{14}Si$	80	73.28	22.64	4.07	
	120	74.22	21.90	3.87	
	160	74.25	22.09	3.66	
	200	73.88	21.92	4.20	
	monomer	85.71	14.29		
Vinyltrimethylsilane	40	74.25	21.58	4.17	
$C_5H_{12}Si$	80	72.22	22.94	4.83	
	120	72.38	23.16	4.46	
	160	70.75	22.71	6.55	
	200	72.37	21.88	5.76	
	monomer	83.33	16.67		
1,3-Divinyltetramethyldisiloxane	40	67.51	20.87	11.61	
$C_8H_{18}OSi_2$	80	67.38	20.31	12.31	
	120	67.27	20.05	12.67	
	160	67.00	20.95	12.06	
	200	67.38	20.29	12.33	
	monomer	72.73	18.18	9.10	
1,1,3,3-Tetramethyl-1,3-divinyldisilazane	40	67.77	20.06	2.60	9.57
$C_8H_{19}NSi_2$	80	66.66	20.69	2.00	10.65
	120	68.08	19.11	3.39	9.42
	160	67.67	19.54	3.66	9.13
	200	69.50	19.43	3.09	7.98
	monomer	72.73	18.18		9.10
Vinyltriethoxysilane	40	58.04	12.06	29.90	
$C_8H_{18}O_3Si$	80	58.29	11.96	29.74	
	120	57.70	12.28	30.02	
	160	57.64	12.54	29.83	
	200	55.92	12.39	30.69	
	monomer	66.67	8.33	25.00	
Tetravinylsilane	40	82.19	13.92	3.90	
$C_8H_{12}Si$	80	82.64	12.11	5.25	
	120	82.24	11.74	6.02	
	160	80.60	11.70	7.71	
	200	80.97	11.57	7.46	
	monomer	88.89	11.11		
Diallyldimethylsilane	40	82.03	14.79	3.18	
$C_8H_{16}Si$	80	81.98	15.65	2.37	
	120	81.31	15.92	2.76	
	160	80.96	15.88	3.15	
	200	79.88	16.24	3.99	
	monomer	88.89	11.11		

Contact angle measurements are well-known technique to get the outermost surface property [21]. Figure 12 and 13 show the contact angles of water observed for pp-films deposited on glass slides for different plasma powers. All the monomers formed smooth transparent films on the glass surface. From the figures, the contact angles decreases as RF power increase for most of the films. A smaller contact angle means that the film surface has become more hydrophilic. Measured contact angles for plasma polymerized tetravinylsilane and vinyltriethoxysilane films increased drastically at RF power of 150 W and 200 W even though XPS data does not record any reduction in oxygen content for both films. Monomer that formed powders instead of films posses very high contact angles. Thus the higher contact angles could be due to fine powders form between the electrodes that dropped on to the surface of these films.

Plasma polymerized film formed by 1,3-divinyltetramethyldisiloxane monomer was observed to be higher than expected contact angles when compared to other silane containing pp-films that was investigated. XPS data from Table 4 showed clearly that the film has higher oxygen content than all the pp-films except pp-vinyltriethoxysilane film. The abundance of oxygen in the pp-film would suggest that the wettability of its surface would be lower than pp-vinyltriethoxysilane film but higher than the rest of the pp-films. Visual inspection of the film showed no noticeable dust or powder present on the surface of the film. Therefore for pp-1,3-divinyltetramethyldisiloxane, the wettability does not only dependent on the relative abundance of oxygen in the film but also dependent upon the spatial arrangement of the oxygen atoms within the polymer molecules [22].

3. Conclusion

Seven silicon-containing monomers were plasma polymerized using a continuos wave (CW) source. The deposition rates of the pp-films were determined to be between 1.07 and 29.7 μg/min. Tetravinylsilane were found to have the highest deposition rate while allyltrimethylsilane have the lowest among the seven monomers. FT-IR revealed that at the experimental conditions of RF power of 100 W and pressure of 100 Pa, all the pp-film has undergone degradation as evidence by the presence of Si-H stretching peak in their respective FT-IR spectra. Peaks emanating around 1040 cm^{-1} from the FT-IR spectra of pp-film from non-oxygenated silane monomers were identified to belong to the Si-O groups. The presence of oxygen in the pp-film was also confirmed by XPS and is attributed to the quenching of radical in the pp-film by reactions with atmospheric oxygen. Contact angle measurements of the pp-film showed that the existence of oxygen does not necessarily means an enhance wettability for that surface. Contact angle results from 1,3-divinyltetramethyldisiloxane showed that even though its oxygen content is much higher than most monomers used in the study, the surface wettability of the pp-film was only comparable to or even slightly higher. Silicon-containing monomers would be expected to produce pp-film with low dielectric property (low-*k* materials). New lower dielectric constants films are required for future generation integrated circuit. We are now progressing with experiments to fabricate semiconductor devices using pp-silicon-containing films and these results will be reported soon.

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