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# Plasma deposited thin films suitable as moisture sensors

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Plasma polymerized thin films from a mixture of hexamethyldisiloxane (HMDSO) and ammonia ($NH_3$) deposited directly onto a microdielectrometer chip have been evaluated as moisture sensors. Microdielectrometry was chosen as the measuring technique because of its fast response and real time detection capability. The sheet resistance of the plasma polymerized film was found to decrease by eight orders of magnitude with an increase in relative humidity from 0 to 92%. The moisture effect on the sheet resistance was also found to be reversible. The composition and structure of the films deposited from various mixtures of HMDSO/$NH_3$ have been elucidated by Electron Spectroscopy for Chemical Analysis (ESCA) and infrared spectroscopy.

## 1. Introduction

Sensors are the key component in a wide range of systems used in chemical process control, pollution monitoring, robotics and chemical warfare agent detection. In recent years, advances in computer technology have led to vast increases in computational power and speed, while size and cost have dropped sharply. Similar advances in sensor technology, namely higher sensitivity and response speed along with reduced size and cost are under way. In the past, ceramics composed of $TiO_2$–$SnO_2$, $MgCr_2O_4$–$TiO_2$, $V_2O_5$–$TiO_2$, ZnO–$Cr_2O_3$–$Li_2O_3$, $MgFe_2O_4$, etc. have been used commercially as moisture sensors. Determination of humidity by these sensors depends on changes in electrical resistivity resulting from adsorption of water on the surfaces of porous ceramics.

In the past plasma polymerization has been used to deposit unique thin films from a variety of monomers. These monomers may or may not have a formal polymerizable structure such as double bond, triple bond or a cyclic structure. The monomer primarily acts as a source of elements to build a macromolecular structure [1]. If two monomers having different functions and elements are polymerized by plasma polymerization, the resulting film will generally contain all the elements from both the monomers. Thus polymer films with a wide range of chemical and physical properties can be obtained easily by mixing two different monomers and plasma polymerizing. There have been several publications [2–5] on the preparation, characterization and applications of thin films deposited from a single monomer by plasma polymerization. Inagaki *et al.* [6] have used a mixture of monomers to deposit plasma polymerized films of varying surface energies. They have also evaluated these films for moisture sensors.

In this paper we report the preparation of thin film membranes by plasma polymerization of a mixture of hexamethyldisiloxane and ammonia, and evaluation of these films as moisture sensors using microdielectrometer.

## 2. Experimental procedure

### 2.1. Monomers

Monomers used for this study were hexamethyldisiloxane (Aldrich Chemical Co.) and ammonia, both used as-received.

### 2.2. Plasma deposition

A tubular plasma polymerization reactor was used for depositing thin films. Details of the tubular reactor have been discussed in earlier communications [7]. The substrates, glass slides and interdigitated electrodes (2 × 4 mm interdigitated circuit sensor), were placed at various positions inside the reactor. The reactor was then evacuated to a pressure of less than 10 μm. A mixture of hexamethyldisiloxane and ammonia was used as the starting material for depositing thin films. The plasma conditions used for depositing thin films are summarized in Table I.

### 2.3. Thickness measurements

The thickness of the films was determined by a Sloan Dektak thickness monitor. For determining thickness by this method the films were deposited on a smooth glass slide, a portion of which was masked to form a sharp step equivalent to the thickness of the film deposited. This method makes use of a fine stylus, which moves on a smooth surface and gives electrical signals to determine the roughness of the surface.

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TABLE I Conditions used for plasma polymerization

| Conditions | Experiment 24 | Experiment 45 | Experiment 47 |
|---|---|---|---|
| Initial pressure | 3 $\mu$m | 8 $\mu$m | 8 $\mu$m |
| Pressure with $NH_3$ | – | – | – |
| Flow rate of $NH_3$ (STP) | – | $5.52 \times 10^{-3}$ cm$^3$ sec$^{-1}$ | $6.64 \times 10^{-3}$ cm$^3$ sec$^{-1}$ |
| Pressure with HMDSO | 35 $\mu$m | 55 $\mu$m | 25 $\mu$m |
| Flow rate of HMDSO (STP) | $5.48 \times 10^{-3}$ cm$^3$ sec$^{-1}$ | $5.4 \times 10^{-3}$ cm sec$^{-1}$ | $4.19 \times 10^{-3}$ cm sec$^{-1}$ |
| Total HMDSO + $NH_3$ pressure | – | 69 $\mu$m | 68 $\mu$m |
| Total HMDSO + $NH_3$ flow rate | – | $9.8 \times 10^{-3}$ cm$^3$ sec$^{-1}$ | $1.15 \times 10^{-2}$ cm$^3$ sec$^{-1}$ |
| R.F. power | 10 W | 20 W | 20 W |
| Duration of polymerization | 240 min | 150 min | 180 min |
| Maximum rate of deposition | 5 nm min$^{-1}$ | 4.6 nm min$^{-1}$ | – |

### 2.4. Evaluation of films as sensors by microdielectrometry

The sensitivity of the films deposited on an integrated sensor towards moisture was evaluated by using a microdielectrometer [8–9], which determines the electrical properties over a range of frequencies from 0.01 to 10 000 Hz. The apparatus consists of an HP 85 computer/controller coupled with a signal generator and Fourier transform analyser developed by Micromet Instruments Inc. On-chip amplification by means of FETs and off-chip electronics (including an FT analyser) permits measurements of 0.1 PF at 1 Hz with good signal-to-noise ratio.

Using this microdielectrometer, sheet resistance of the film under different environment was measured. Humidity chambers ranging from 0 to 92% relative humidity were made by using saturated salt solutions.

### 2.5. Composition

Infrared spectra of plasma polymers in KBr pellets were recorded on a Perkin–Elmer 1310 infrared spectrometer. The polymer film for this purpose was deposited on sodium chloride crystal.

TABLE II Liquids used for determination of surface free energy of the films

| Liquid | Surface tension (dynes cm$^{-1}$ at 24 °C) |
|---|---|
| Water | 70.9 |
| Glycerol | 62.4 |
| 2-2′ Thiodiethanol | 53.1 |
| 1-Bromonaphthalene | 41.6 |
| Benzyl alcohol | 39.8 |

The compositions of the plasma polymerized films were determined by electron spectroscopy for chemical analysis (ESCA). An Mg$K_\alpha$ X-ray source with 1253.6 eV energy line was used and C1s, N1s, O1s and Si2p signals were analysed to determine the composition.

### 2.6. Surface free energy

Contact angles of liquids with various surface tensions were measured on films deposited on glass slides. These were measured using a Rame–Hart NRL contact angle goniometer. Three to four contact angle measurements were made on three or more drops, and the average values were recorded. Caution was exercised to avoid errors caused by evaporation of volatile liquids or non-equilibrium conditions. The series of liquids used for contact angle determinations are given in Table II and some critical surface tensions of the films are shown in Table III. Surface free energy of the films was determined by plotting $\cos\theta$ against $\gamma$ (surface tension) and extrapolating the line to $\cos\theta = 1$. The intercept on the $x$-axis at $\cos\theta = 1$ gave the critical surface tension or surface free energy of the films.

## 3. Results and discussion

### 3.1. Rate of film deposition

To determine the rate of deposition, the films were deposited on masked glass slides which were placed at various positions in the reactor. The mask was removed and the thickness was measured by Sloan Dektak thickness monitor. Fig. 1 shows the actual plot for the measurement of thickness. The difference in the two base lines seen in the curve gives the

TABLE III Critical surface tension of the films deposited at various positions in the reactor under different conditions

| Sample number | Position in the reactor (in) | Critical surface tension, $\gamma_c$ (dynes cm$^{-1}$) | Sample number | Critical surface tension $\gamma_c$ (dynes cm$^{-1}$) |
|---|---|---|---|---|
| 1/45 | 2.0 | 34.5 | 1/47 | 31.0 |
| 2/45 | 5.5 | 21.8 | 2/47 | 21.2 |
| 3/45 | 10.5 | 34.5 | 3/47 | 25.5 |
| 4/45 | 18.0 | 30.5 | 4/47 | 28.4 |
| 5/45 | 26.5 | 29.5 | 5/47 | 28.4 |

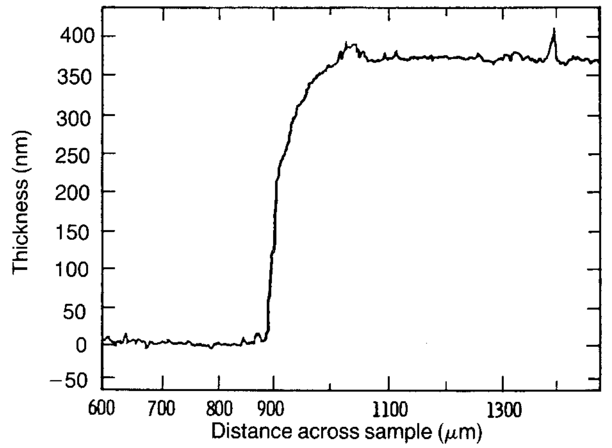

*Figure 1* A typical plot for thickness determination by the Sloan Dektak thickness monitor.

thickness of the film. Fig. 2 shows the rate of film deposition along the entire length of the reactor. The maximum rate of deposition (0.46 nm $\text{min}^{-1}$) is obtained at a distance 10 in from the monomer inlet.

### 3.2. Sensor evaluation

The rationale for using a mixture of hexamethyldisiloxane and ammonia as starting materials for depositing moisture-sensitive film is that they contain both hydrophilic (nitrogen, oxygen) and hydrophobic (silicon) elements, which are incorporated into the polymeric film. The composition, structure and other properties of the plasma polymerized films will be discussed below. Here, we will discuss the effect of humidity on the sheet resistance of the film. A magnified photograph of the sensors with the plasma deposited film used for this purpose is shown in Fig. 3. Using the microdielectrometer, sheet resistance of the film at various relative humidities (0, 48, 75 and 92%) was measured. The results of the effect of humidity on the sheet resistance are shown in Fig. 4. There was a decrease in sheet resistance from $10^{18}$ to $10^{10}\,\Omega$ $\text{square}^{-1}$ at 0.1 Hz frequency as the relative humidity increased from 0 to 92%. The moisture effect on the sheet resistance was found to be reversible, since by cycling the sensor through the relative humidity from 0% to 92% and then back to 0%, the original value of sheet resistance at 0% was obtained within the limits of experimental error (shown by notation △ in Fig. 4). The response time was also observed to be fast.

Infrared spectra of the film were taken to evaluate the effect of moisture on the structure of the film. Fig. 5a–c show three infrared spectra of the film which was exposed to three different relative humidities (0%, 48% and 92%). The IR spectra were taken immediately after the exposure. A broad peak between 3200 to 3800 $\text{cm}^{-1}$ observed after exposing the film to 92% relative humidity decreased gradually as the relative humidity was lowered. This peak is assigned to the absorbed moisture on the surface of the film. The film has the N- and O-containing hydrophilic groups which adsorb moisture at higher humidities.

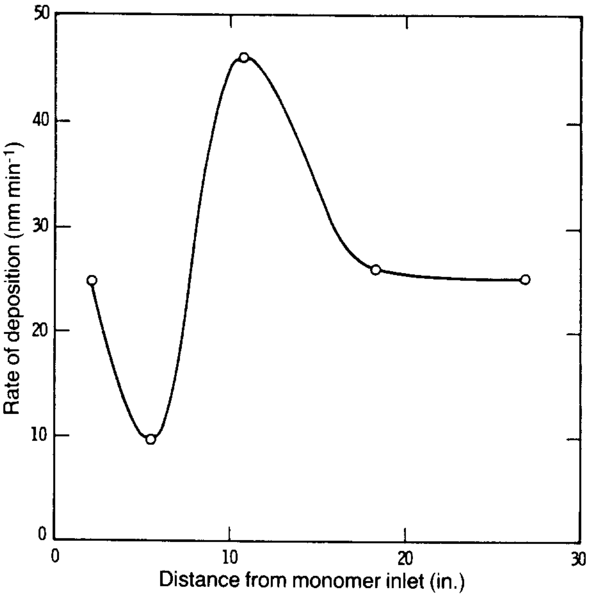

*Figure 2* Rate of deposition of HMDSO/$NH_3$ films at different positions in the reactor.

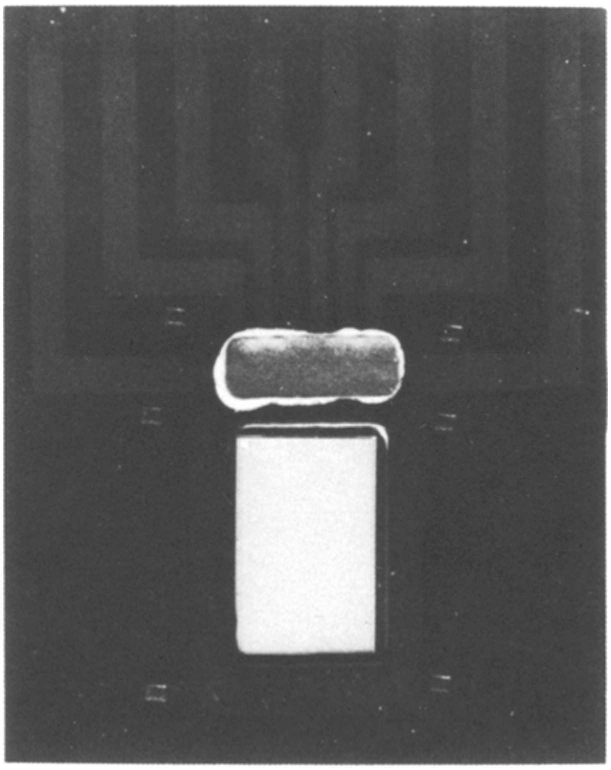

*Figure 3* Photograph of the plasma polymerized film deposited on the sensor used for microdielectrometry studies (actual width of sensor = 0.2 cm).

### 3.3. Structure and composition of the films

The infrared spectra of plasma polymerized films of hexamethyldisiloxane and its mixture with ammonia at various concentrations are shown in Fig. 6a–c. There are two ways by which the hydrophilic and hydrophobic characteristics of the films can be varied: (i) by adjusting the concentration of ammonia and hexamethyldisiloxane in the initial monomer mixture; and (ii) by depositing the film at various positions in the reactor.

The mixture ratios of HMDSO and ammonia are shown in Table IV. All these spectra were taken by

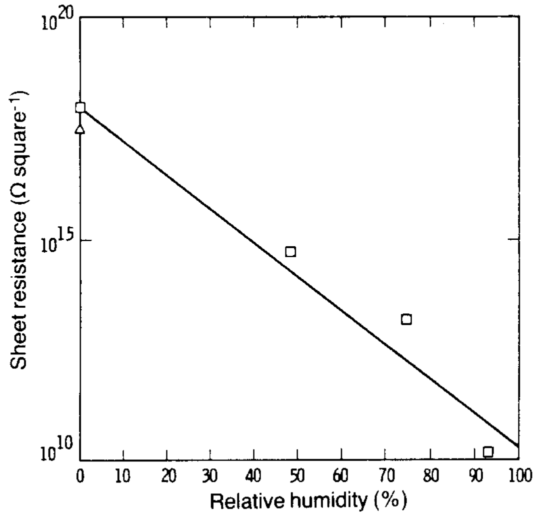

*Figure 4* Change in sheet resistance with humidity of a plasma polymerized film deposited on microdielectrometer chip. 0.1 Hz; 22 °C.

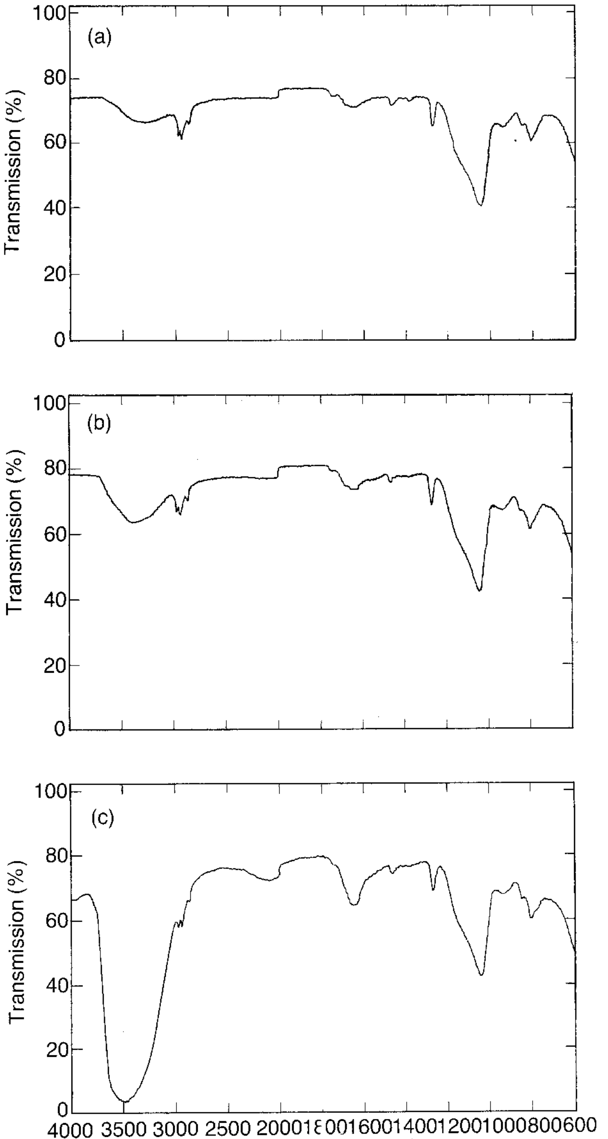

*Figure 5* Effect of humidity on the structure of the plasma polymerized (HMDSO + $NH_3$) films. (a) 0%; (b) 48%; (c) 92% relative humidity.

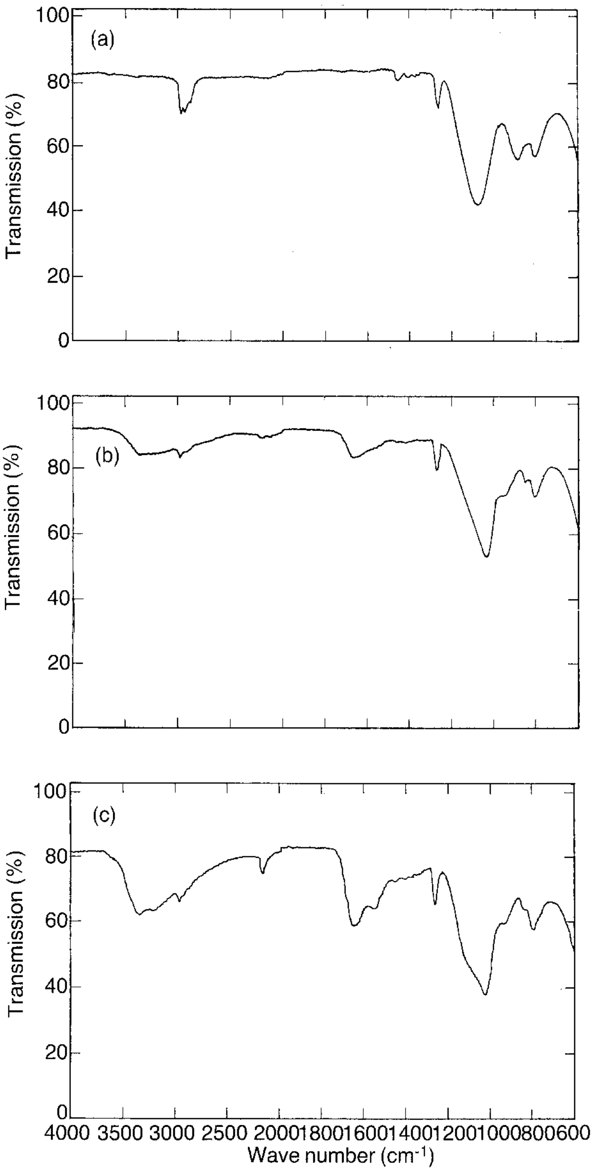

*Figure 6* Effect of ammonia concentration in the monomer feed on the structure of the plasma polymerized films. $NH_3$/HMDSO = (a) 0; (b) 1.02; (c) 1.58.

depositing thin plasma polymerized films directly on sodium chloride plates, with the position of the film deposition within the reactor kept constant at 10.5 in. The absorption peaks in the case of films deposited from pure HMDSO alone (Fig. 6a) may be assigned as follows:

2980 cm$^{-1}$ – CH, $CH_3$; 2930 cm$^{-1}$ – $CH_2$; 1455 cm$^{-1}$ – CH; 1265 cm$^{-1}$ – $Si(CH_3)$, $Si(CH_3)_2$; 1075 cm$^{-1}$ – Si–O–Si; 880 cm$^{-1}$ – Si–C; 800 cm$^{-1}$ – $Si(CH_3)_3$; $Si(CH_3)_2$; $Si(CH_3)$, Si–O–Si.

The polymeric thin films formed from a mixture of HMDSO and $NH_3$ show all the absorption peaks due to HMDSO and additional peaks due to incorporation of NH, N–C, N–O linkages in the polymer. The assignment of absorption peaks formed from a mixture of HMDSO and $NH_3$ (Fig. 6b and c) are as follows:

3360 cm$^{-1}$ – NH, 2960 cm$^{-1}$ – $CH_3$, 2160 cm$^{-1}$ – Si–H, 1660 cm$^{-1}$ – NH C(O), 1460 cm$^{-1}$ – $CH_3$, 1265 cm$^{-1}$ – $Si(CH_3)$, $Si(CH_3)_2$, $Si(CH_3)_3$, 1150 cm$^{-1}$

TABLE IV Peak height ratios of NH and methylene and NH and Si–$CH_3$ absorption bands in the IR spectra of plasma polymerized films under various conditions

| Experiment number | Figure number | Ratio of $NH_3$/HMDSO in the monomer | Peak ratios | |
|---|---|---|---|---|
| | | | 3360 $cm^{-1}$ NH<br>2960 $cm^{-1}$ $CH_2$ | 3360 $cm^{-1}$ NH<br>1265 $cm^{-1}$ Si–C |
| 24 | 6a | 0 | 0 | 0 |
| 45 | 6b | 1.02 | 0.9 | 0.818 |
| 47 | 6c | 1.58 | 1.32 | 1.75 |

– C–N, 1030–1130 $cm^{-1}$ – Si–O–Si, Si–O–C, 930 $cm^{-1}$ – N → O, 790 $cm^{-1}$ – Si–$CH_3$, Si–$CH_2$, 840 – CH.

The peak heights observed from NH, $CH_3$, Si–C, N–O and Si–O–C vary considerably with the variation in the concentration of the monomers in the feed. Table IV gives the ratios of the peak heights of NH absorption (3360 $cm^{-1}$) and methylene absorption (2960 $cm^{-1}$) and also NH absorption (3360 $cm^{-1}$) and Si–C absorption (1265 $cm^{-1}$) of the films obtained under three different concentrations of ammonia with HMDSO in the feed. The values clearly show that an increment in the nitrogen-containing linkages and a decrement in $CH_3$ and silicon-containing linkages occur with an increase in ammonia concentration in the monomer feed. Thus, by varying the concentration of the monomers in the initial feed, one can tailor the hydrophobicity and the hydrophilicity of the resulting film.

Another way of obtaining different compositions of silicon, nitrogen and oxygen in the film is by deposition at various positions in the reactor. The compositions of the films deposited at various positions in the reactor were determined by ESCA. A typical ESCA spectrum of a plasma-polymerized hexamethyldisiloxane/ammonia film is shown in Fig. 7. Peaks at 531, 400, 285 and 104 eV are assigned to O1s, N1s, C1s and Si2p, respectively. The C/Si, N/Si and C/N atomic ratios are calculated from the peak heights of C1s, N1s and Si2p for all the samples and are tabulated in Table V. As is clear from these atomic ratios, the films deposited near the monomer inlet (2 to 5.5 in) have a higher silicon content and lower nitrogen content than films deposited farther away from the inlet ( > 5.5 in).

Fig. 8a and b show ESCA (C1s, N1s, Si2p) spectra of the polymer films deposited at 2.0 in and 26.5 in, respectively, from the monomer inlet. These spectra clearly demonstrate the variation in silicon and nitrogen contents of the films deposited at two extremes of the reactor. The complex spectrum was subjected to curve-fitting procedures. Gaussian distribution was assumed; width and positions of the peaks were kept

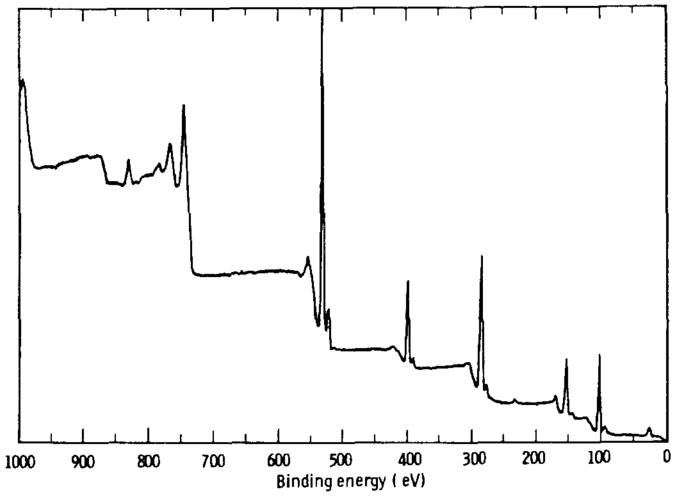

*Figure 7* A typical ESCA spectrum of plasma polymerized (HMDSO + $NH_3$) film.

TABLE V Composition of the plasma polymerized film determined by ESCA

| Sample number | Position in reactor from monomer inlet (in) | %C | %O | %N | %Si | L/Si | N/Si | C/N |
|---|---|---|---|---|---|---|---|---|
| 1/45 | 2.0 | 31.8 | 29.5 | 11.5 | 27.7 | 1.15 | 0.42 | 2.7 |
| 2/45 | 5.5 | 27.8 | 32.0 | 12.0 | 28.3 | 0.98 | 0.42 | 2.3 |
| 3/45 | 10.5 | 31.3 | 30.0 | 14.4 | 25.5 | 1.22 | 0.56 | 2.10 |
| 4/45 | 18.0 | 28.9 | 30.9 | 18.6 | 21.5 | 1.34 | 0.87 | 1.8 |
| 5/45 | 26.5 | 34.1 | 30.9 | 16.2 | 18.8 | 1.81 | 0.86 | 2.1 |

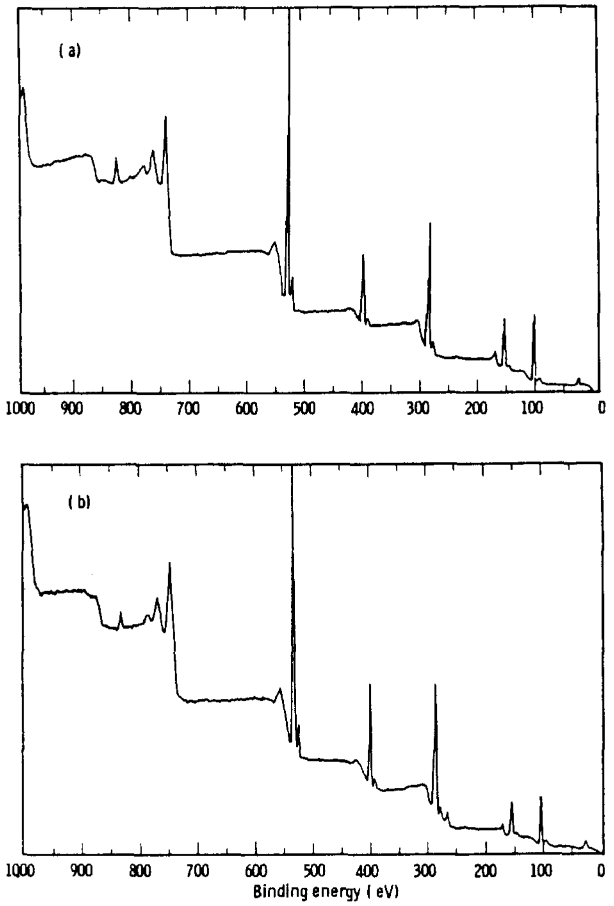

*Figure 8* ESCA spectra of polymer films deposited at various positions in the reactor. (a) 2.0 in; (b) 26.5 in from the monomer inlet.

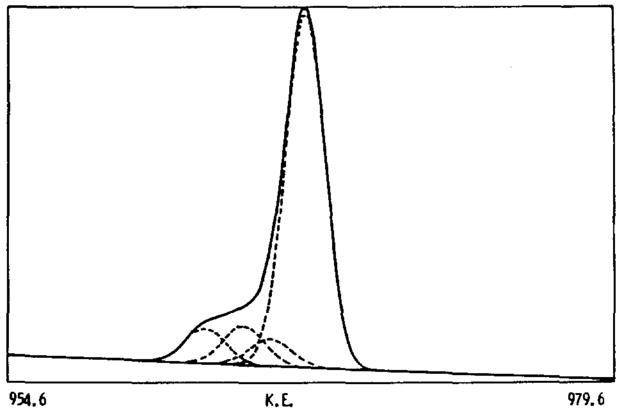

*Figure 9* C1s deconvoluted peak showing various linkages for the film deposited at 2.0 in from the monomer inlet.

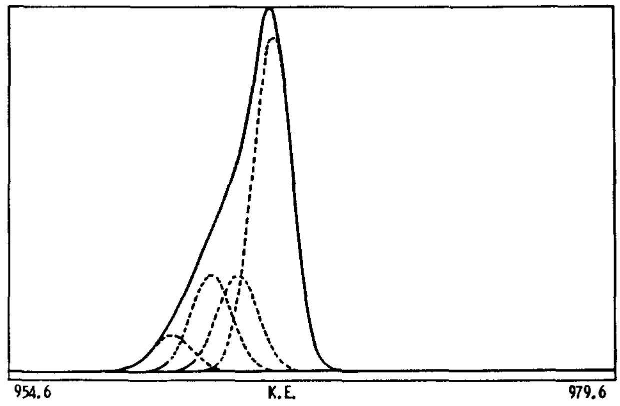

*Figure 10* C1s deconvoluted peak showing various linkages for the films deposited at 26.5 in from the monomer inlet.

the same while peak heights were varied to get the fit. These core level spectra, shown in Figs 9 and 10, are large with trailing tails and their full width at half maximum (FWHM) values were more than 2 eV. All the C1s peaks were deconvoluted and, according to this curve fitting procedure, each of the C1s spectra could be fitted by four Gaussian curves, indicating the presence of four components. The peak position and the relative peak area for each component are listed in Table VI. The C1s spectra for all the polymers involved four components centred at 284.6, 286.0, 287.1 and 288.7 eV. These components can be assigned as aliphatic carbon and C–Si, C–N, C–O and C=O features. Similarly, the N1s spectrum involves three components assigned as N–C (399.1 eV), N–C–(O) (400.2 eV) and N–O (402.6 eV) features. The Si2p spectra are composed of three components, assigned as Si–O (101.6 eV), $\mathrm{Si{-}(O{-}C)_{2\,or\,3}}$ and/or $\mathrm{Si{-}(O{-}Si)_{2\,or\,3}}$ (102.6 eV) and $SiO_2$ (104.3 eV). As is clear from Table VI, the C–Si and aliphatic carbon contributions are more and the C–N contributions are less in the polymers deposited closer to the monomer inlet, whereas the contribution of the C–N component increases and that of the C–Si component decreases significantly in the polymers deposited farther away from the monomer inlet.

## 3.4. Surface free energy of plasma polymerized films

To determine whether the polymer surfaces prepared from the HMDSO/$NH_3$ mixture are favourable to water adsorption, their surface energy was determined. Contact angle measurements were carried out on the samples using a series of test liquids having different surface tensions at room temperature (see Table II). A semi-empirical technique developed by

TABLE VI ESCA (C1s) spectra of polymers deposited at various positions in the reactor (HMDSO + $NH_3$)

| Sample number | Distance from monomer inlet | Core level | Peak position[a] (eV) and relative peak area (%) | | | |
|---|---|---|---|---|---|---|
| | | | Peak 1 | Peak 2 | Peak 3 | Peak 4 |
| 1/45 | 2.0 | C1s | 284.6<br>(70.7%) | 286.0<br>(8.4%) | 287.1<br>(10.7%) | 288.7<br>(10.2%) |
| 5/45 | 26.5 | C1s | 284.6<br>(57.5%) | 286.0<br>(17.5%) | 287.1<br>(17.5%) | 288.7<br>(7.5%) |

[a] Peaks 1, 2, 3 and 4 for C1s spectra are: 1 = C–Si and aliphatic carbon; 2 = C–N; 3 = C–O; 4 = C=O.

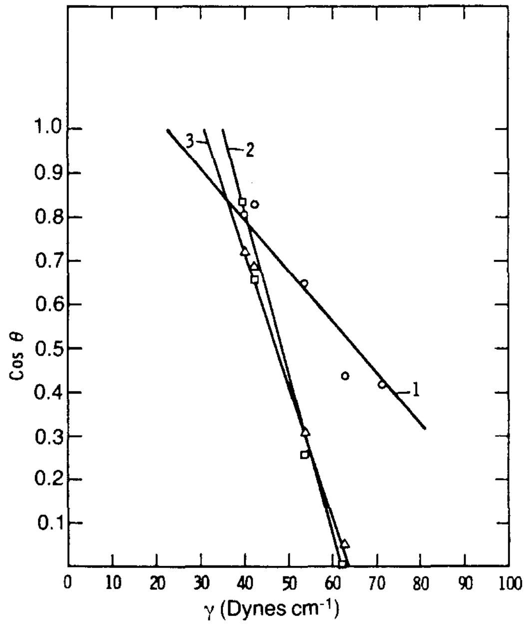

*Figure 11* Surface free energy of plasma polymerized (HMDSO + $NH_3$) films (Ex. 45, Table I) by Zisman plots. Distance from monomer inlet: 1, 5.5 in; 2, 10.5 in; 3, 18.0 in.

Zisman was used to determine $\gamma_c$, the critical surface tension of the solids. The Zisman-type plots of cosine $\theta$ as a function of surface tension of the liquid drop are presented in Figs 11 and 12. Critical surface tension values (the surface tension of a liquid that will just spread on the surface) are taken as the intercept of cosine $\theta = 1.0$ (Table III). There is no significant change in critical surface tension of the films prepared from different HMDSO/$NH_3$ mixtures, the reason being that both HMDSO and $NH_3$ have hydrophilic elements, namely oxygen and nitrogen, respectively. This hydrophilicity appeared to overcome the hydrophobic nature of silicon in HMDSO. However, the slope of the cosine $\theta$ against surface tension curves changes significantly for the films deposited at various places in the reactor.

## 4. Conclusions

This paper describes the plasma polymerization preparation of thin film sensor materials which are sensitive to moisture. Use is made of a microdielectrometer for fast response and real-time detection of the moisture in the environment. The monomers used to form such films are a mixture of hydrophobic (hexamethyldisiloxane) and hydrophilic ($NH_3$) type monomers. The film composition is easily tailored by altering the flow rate of the monomers. Infrared spectra and ESCA evaluation showed that silicon-rich films were deposited near the monomer inlet and nitrogen-rich films were obtained at the farthest end of the reactor. There was no significant difference observed in surface free energy of the films prepared from different HMDSO/$NH_3$ mixtures. However the slopes of the Zisman plots were significantly different for the films prepared at various places in the reactor, suggesting different wetting characteristics of the films of various compositions.

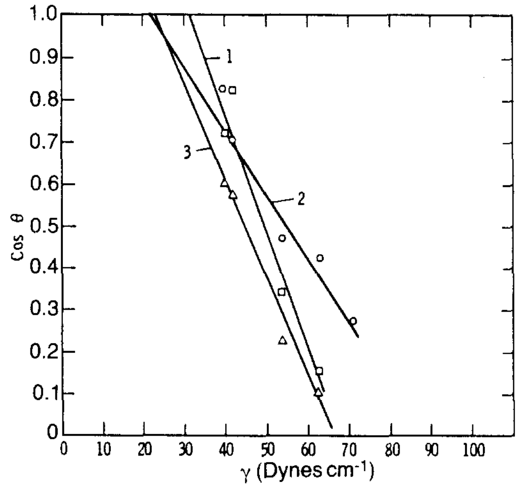

*Figure 12* Surface free energy of plasma polymerized (HMDSO + $NH_3$) films (Ex. 47, Table I) by Zisman plots. Distance from monomer inlet: 1, 2.0 in; 2, 5.5 in; 3, 18.0 in.

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