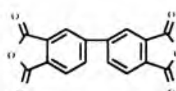
CHAPTER II

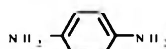
EXPERIMENTAL SECTION

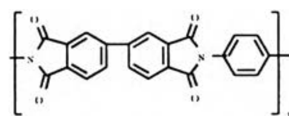
2. 1 Materials

The poly(amic acid)s, the precursor solutions are converted to fully aromatic polyimide coatings when exposed to heat. The cure properties, adhesion, solubility, and application conditions varied from one solution to another. In this experiment, Du Pont Pyralin® PI-2610 (BPDA-PDA), PI-2540 (PMDA-ODA) and PI-2579 (BTDA-ODA/MDA) poly(amic acid)s (PAA) in N-methyl-2-pyrolidone (NMP) solutions were used. Some properties of poly(amic acid)s solutions are listed in Figure 3.

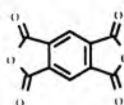
1. BPDA/PDA
   - Du Pont Pyralin® PI-2610
   - Viscosity 25 -30 poise
   - Solid content 10.5 %

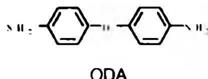


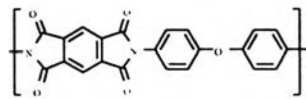




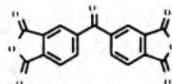
2. PMDA/ODA
   - Du Pont Pyralin® PI-2540
   - Viscosity 40 - 70 poise
   - Solid 15 %

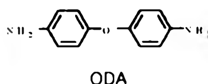


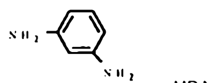




3. BTDA/ODA-MDA
   - Du Pont Pyralin® PI-2579
   - Viscosity 0.08 - 0.11 poise
   - Solid 9.5 %







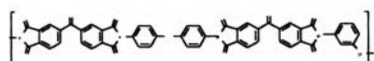


Figure 3 Chemical structures and some properties of poly(amic acid) precursors and the resulting polyimide films.

To adjust the rheological properties of the precursor solution, a thinner, TG9030 from Du Pont Electronics was used. This thinner is a solvent mixture of iso-propanol and NMP. All the products mentioned above are sensitive to heat. They should be refrigerated at 4°C maximum. Moisture contamination is detrimental to stability.

The adhesion promoter for those poly(amic acid)s enhances greatly the adhesion to SiO_2. The VM-651 from Du Pont Electronics, a solution of aminopropyltriethoxysilane, was used as the adhesion promoter in this experiment. It was diluted to a 0.1% and 0.05% solution in water/methanol (95/5) before applying to the water. We allowed the solution to equilibrate for 12 hours before using. Too weak or too strong solutions cause problems. After dilution, the adhesion promoter should be discharged after twenty days.

2. 2 Instrumentation

2.2.1 Fourier Transform Infrared Spectrometer (FTIR)

The BIO-RAD FTS45A Fourier Transform Infrared (FTIR) spectrometer was used to characterize the degree of imidization of the thin polyimide films. The FTIR experiment was done in a transmission mode with a resolution of 8 cm^{-1}, 16 numbers of scan per samples.

2.2.2 Wide Angle X-ray Diffraction (WAXD)

The X-ray spectra were obtained from the Philips Analytical X-ray diffractometer with PC-APD diffraction software. A copper tube anode with the generator tension of 40 kV and the current of 30 mA was used.

2.2.3 Thermogravimetric Analyzer (TGA)

Thermal stability of the thin films was observed from the weight loss, monitored by the NETZSCH TG 209 thermogravimetric analyzer using the NETZSCH TASC 414/3 thermal system controller. The chamber inside the analyzer was exposed to a continuous flow of N_2 as a protective gas at the rate of 10 ml/min. During monitoring the changing of the sample mass, the purging N_2 gas flow rate was 20 ml/minute.

2.2.4 Thermomechanical Analyzer (TMA)

A TMA7 extension analysis kit was equipped to the Perkin Elmer DMA-7e dynamic thermomechanical analyzer with the TAC 7/DX thermal analysis controller and a graphic plotter. It was used to measure the length of an extended sample as a function of the force and temperature applied to the sample. This allowed us to calculate the in-plane (x-y direction) coefficient of thermal expansion. For the out-of-plane CTE (z-direction) the compression probe was used instead. The extension probe was made up of quartz whereas the compression probe was the stainless steel.

2.2.5 Optical Microscope

The Leica Wild M-10 optical microscope equipped to the Sony camera adaptor to view the image in the Sony Trinitron Monitor was used to observe the film surface. The NIH image which is the optical density plot of the 2 dimensional image, in particular the film surface and the surface plot, was

captured and analyzed by the NIH image software running in Macintosh platform.

2.2.6 Atomic Force Microscope (AFM)

The atomic force microscope, model Nanoscope III from Digital Instruments, was used to study the surface topology of polymer films at a higher resolution compared to optical microscopy. The instrument was operated in the contact mode. At the probe stylus, the tip of a silicon nitride pyramid was used.

2.2.7 Electric Puncture Tester

The dielectric breakdown strength of the insulating polyimide films were measured by the electric puncture tester from Yasuda Seiki Seisakusho Ltd. The system is composed of the upper and lower electrodes as shown in figure 4 suitable for the narrow test specimen. The compressive force between the electrodes was approximate 500 g .

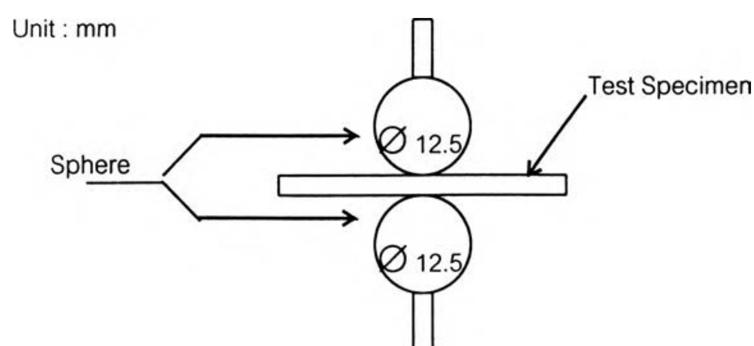


Figure 4 Electrode shape for electric puncture tester.

2.2.8 AC-Impedance/Gain Phase Analyzer

The out-of-plane dielectric properties were measured using AC Impedance/Gain-phase analyser (Hewlett-Packard HP 4194A controlled by an IBM PC/AT computer.

2.2.9 Oven with N_2 Gas Flow

The poly(amic acid), cast on the substrates, was cured in the oven with the N_2 gas flowing. For a good temperature control, a custom-built chamber of 10 cm width, 8.5 cm length and 21.5 cm depth with the conducting wire inside for heat supply was used. The smaller the chamber is, the better the temperature control even in the flowing of N_2 gas. The LFE temperature controller, model 3000 connected to the oven with a external solid state relay output was used to control the temperature and heating rate in the chamber.

2. 3 Sample Preparation and Characterizations

Du Pont Pyralin® PI-2610 (BPDA-PDA), PI-2540 (PMDA-ODA) and PI-2579 (BTDA-ODA/MPA) poly(amic acid)s in NMP solutions were used as precursors in this studies

2.3.1 FTIR

The PAA solutions were cast onto glass slides. Viscous solutions of BPDA-PDA (% solid = 10.5) and PMDA-ODA (% solid = 15) were diluted with a TG9039 thinner (PAA : TG9039 = 3 : 2) for smooth films surface. A thin solution of BTDA-ODA/MDA (% solid = 9.5) was cast on the substrate as received. The wet films were dried at 80°C for 30 minutes under N_2

atmosphere. The dried films were then cured by heating from 80°C to the final curing temperature which were varied from 100°C to 400°C with 50°C increment, followed by a 30 minutes soak period at the final curing temperature under N_2 atmosphere. The curing rate was 2°C/minute. To study the effect of curing rate, the films were cured at the final curing temperature of 400°C for 30 minutes while curing rate was varied from 1 to 8°C/minute.

The FTIR spectra were obtained from 16 scans ranging from 550-2000 cm^{-1}. The instrument resolution was 8 cm^{-1}. The degree of imidization as a function of temperature and curing rate was monitored by Fourier transform infrared spectroscopy, using the normalized change in peak height of the infrared band at 1780 cm^{-1}. This band arises from C=O stretching vibrations in the imide structure. For the calculation of the degree of imidization, we assumed that the films were completely imidized at the highest ratio of peak height at frequency of 1780 cm^{-1}over wave number of 1015 cm^{-1}.

$$\%\text{Imidization} = \frac{H(\nu 1778)_t \,/\, H(\nu 1015)_t}{H(\nu 1778)_T \,/\, H(\nu 1015)_T} \qquad (2)$$

where $H(\nu 1778)_t$ and $H(\nu 1015)_t$ are the peak heights at temperature t °C at frequency of 1780 cm^{-1} and 1015 cm^{-1}. The subscript T refers to the temperature which had the highest peak height ratio.

2.3.2 WAXD

The 20 - 30 μm spin coated BPDA-PDA and PMDA-ODA films and doctor blading of BTDA-ODA/MDA film on glass slides were dried at 80° C for 30 minutes. Then, the films were cured for 30 minutes at different curing temperatures. The curing rate was 2°C/minute. Wide angle x-ray diffraction

data were obtained from a Philips diffractormeter using Cu tube anode as source. The specimens were held horizontally in the apparatus. This geometry (with both source and detector moving during the scan) made it possible to examine all of the specimens.

2.3 3 TGA

To study the thermal stability, PAA solution of BPDA-PDA and PMDA-ODA were spin cast at 2600 rpm for 20 seconds on glass slides. The thinner solution of BTDA-ODA/MDA PAA solution was cast on glass slides by hand or doctor blading due to the rough film obtained from spin-coating. These films of BPDA-PDA, PMDA-ODA and BTDA-ODA/MPA were then dried at 80°C for 30 minutes. The effects of curing temperature, curing rate and curing time were studied. For the effect of curing temperature, the final curing temperatures were varied from 100°C to 400°C with 50°C increments. For the effect of curing rate the final curing temperature was 400°C, the heating rate was varied from 1, 2, 4, 6 and 8°C/minute and curing time was varied from 30, 60, 120. 180 and 240 minutes.

The polyimide films were scraped from the glass slides and put in the Al_2O_3 crucible. The thermogravimetric analyzer was used to monitor the changing mass of the samples with the empty crucible as a blank correction. The following temperature profile was used: starting temperature was 30°C; then, the chamber was heated to 950°C with a scanning rate of 10°K/minute and 60 K/min, respectively. Finally, the samples were held at isothermal conditions of 950°C for 30 minutes. The scanning rates of 10°K/minute and 60°K/minute were compared to study the instantaneous heating behavior in microelectronic gas sensors.

The effect of the silicon substrate was studied by casting the dilute solutions of (PAA : TG9039 = 3 : 2) of BPDA-PDA and PMDA-ODA

and the pure BTDA-ODA/MDA solution on silicon <100> orientation wafers. The films on silicon wafers were then dried and cured as done in the film-on-glass slide. The weight of the film attached to a silicon wafer was also monitored, using the same temperature profile as was used for the bare film. The adhesion promoter was applied on the precleaned silicon wafer for studying the effect of adhesion promoter on thermal stability.

2.3.4 TMA

The BPDA-PDA PAA and PMDA-ODA PAA precursors in NMP (Pyralin® PI-2610 and PI-2540) were spin coated at 2600 rpm for 30 seconds on precleaned silicon wafers (A precleaned silicon wafer was the wafer which was soaked with distilled water, followed by acetone and finally iso-propanol. Then it was dried on the hot plate) and the BTDA-ODA/MPA was cast by a glass slide onto a glass slide. All the PAA solutions were then dried in the oven at 80°C for 30 minutes under N_2 atmosphere. The films were thermally cured in the former oven by heating from 80°C to the final curing temperature of 400°C and soaked for a certain period at the final curing temperature. After curing, the samples were allowed to cool in air until a tempreature of 30°C was reached. The polyimide precursors were again applied on the top of the polyimide layer, dried and re-cured. The multi-layers of polyimide films were repeated 3 more times to make a 5 layer films with roughly 30 μm total thickness for an in-plane coefficient of linear thermal expansion (CTE) measurement. The film layering experiments were repeated 13 more times to create a 15-layer film with roughly 100 μm total thickness for an out-of-plane CTE measurement. The multi-layer films were removed from the glass slide by immersion in dilute aqueous hydrofluoric acid (HF : H_2O = 1 : 10) for 1 hour. The removed films were washed several times with distilled water and dried in a vacuum over at 50°C for 1 day.

The thin film for the in-plane CTE, using the TMA-7 extension analysis kit, was the multi-layer of polyimide films of roughly 25 μm in total thickness. Dimensions of the films were 2 mm wide and 15 mm long (between chucks). The films were heated from 35°C to 300°C and held for 10 minutes with 20°C/minute heating rate in order to remove absorbed water, to complete the imidization and to get rid of any residual stress. The films were cooled down at a heating rate of 5°C/minute to 35°C. The change in length of the polyimide film was measured, at a heating rate of 5°C/minute from room temperature air to 410°C. Since the thermal expansion coefficient was temperature-dependent, the average value between 50 and 300°C was used as the representative value.

The thermal cycling experiment was done by annealing the film at 300°C for 10 minutes, followed by cooling down to 35°C with a cooling rate of 5°C/minute. In the first cycle, the length of the film was monitored by heating the film with the rate of 5°C/minute to 300°C, holding for 10 minutes and cooling down to 35°C for 10 minutes. Similarly, the second cycle was done. These experiment were repeated for 8 cycles for each film.

The out-of-plane coefficients of thermal expansion (z-CTE) of polyimide films were measured on the compression probe. The multi-layer polyimide films of roughly 100 μm total thickness were cut to 1 cm in diameter. The specimen was placed on the sample holder equipped with an oven and annealed at 300°C for 10 minutes in air and subsequently cooled to 35°C before measurement. The z-CTE measurements of the annealed samples were performed during heating up to 300°C. The heating rate was 5°C/minute.

2.3 5 <u>Film Surface</u>

Dilute solutions of BPDA-PDA (PI-2610) and PMDA-ODA (PI-2540) (PAA : TG9039 = 3 : 2) and PI-2579 (BTDA-ODA/MDA) PAA

solutions were hanged on the precleaned 1 cm^2 silicon wafer which was heated at 50°C on the hot plate by micro-pipette. After dropping the 20 μl on the silicon wafer, the tip of micro-pipette was used to spread the solution to cover all pieces. The films on the substrate were then dried on the hot plate for 5 minutes and put in the oven for drying at 80°C for 30 minutes in N_2 atmosphere. The films were cured at 400°C for 30 minutes with a heating rate of 2°C/minute in N_2 atmosphere. The surface of the curing polyimide films could be observed by optical microscopy in bright field mode. To achieve a higher resolution of the surface topology, the films coated on the Si<100> wafer were analyzed by AFM where they were brougth into contact with the micorscope's Si_3N_4 tip at a trial and error load. When the tip had a good contact to the film, scanning of the film surface was started.

2.3 6 Dielectric Breakdown Strength Measurement

The polyimides films cured at 400°C for 30 minutes at 2° C/minute curing rate with a thickness roughly about 30 μm were used to determine the dielectric strength by applying the 50 Hz of power frequency to the test specimens. The voltage was increased from zero to a level well below the breakdown voltage. For test method, we followed the Japanese industrial standard JIS C 2110 using the short-time breakdown test. In general, all insulating materials are influenced by temperature and relative humidity in a manner that materially affects test results. In order to obtain reliable comparisons, it was necessary to standardize the humidity conditions, as well as the temperature, to which specimens of these materials were subjected prior to and during testing. The pretreatment of test specimens was done by keeping the specimens in the desicator at a temperature of 23 ± 2°C, relative humidity 24 % for 96 hours. The test temperature was set at 23 ± 2°C, with a relative humidity of 70 %. The specimens were mounted coaxially correctly facing

each other. The dial was adjusted to 0.5 on the current relay. The voltage was raised from zero with uniform rate such that breakdown occurred, on an average, between 10 to 20 seconds.

2.3.7 Dielectric Constant and Dissipation Factor

The procedure for measuring the dielectric constant and dissipation factor of the polyimide film was followed based on the standard ASTM Method-D150. The polyimides films cured at 400°C for 30 minutes at 2°C/minute curing rate were cleaned with acetone. The thickness of the thin film was measured by a micrometer and then aluminum foil was attached to the two sides of the circular polyimide film having a diameter of 0.6 mm. The samples were conditioned according to ASTM Method-D-618 by keeping them in air over night in a desicator at 21 ± 2 °C, relative humidity of 24% for 48 hours. After the pretreatment condition was reached, the capacitance and dissipation factor of five single sheet samples were measured by a Hewlett Packard HP 4194A capacitance measurement system at a frequency of 1 MHz. All of the dielectric measurements were performed in air at 21 ± 2°C and 40% relative humidity. The sample was inserted between the two plates of the micrometer electrode, adjusted to tune the network for the measurement circuit. Then the sample was removed and the electrodes were reset to restore the total capacitance in the circuit or bridge arm to its original value by moving the micrometer electrodes closer together.

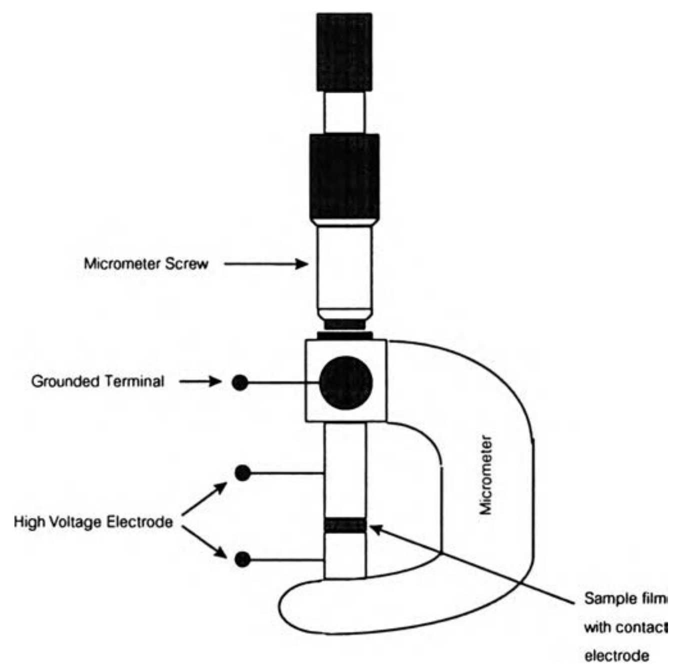


Figure 5 Micrometer-electrode system.