

## CHAPTER IV

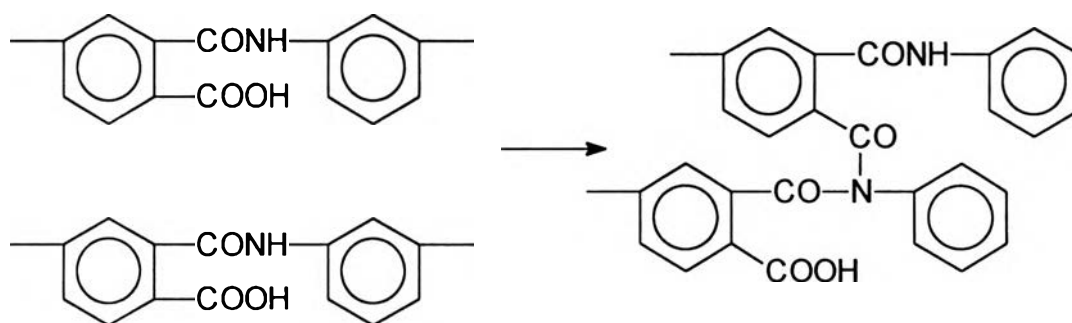
### DISCUSSION

#### 4.1 Degree of Imidization

Studying of thermal imidization is to look at the completeness of cyclization. Normally, an incomplete cyclization arises during curing, possibly causing defects in the polyimide films. FTIR is one of various methods in determining the degree of imidization. The imidization reaction of various PAAs having different structures have been followed by the intensities of IR spectra collected during dehydro-cyclization. Similar to the imidization studied by Numata et.al, (1982), when PAAs were heated, the rate of imidization was increased rapidly at curing temperatures of 100°C-200°C. Once the specific curing temperature was reached, the rate of imidization leveled off and was kept constant at temperature about 250°C for BPDA-PPD and PMDA-ODA and about 200°C for BTDA-ODA/MPD. So the appropriate curing temperature of each PAAs precursor is different because the difference in  $T_g$  of the resulting polyimide as Numata reported. Based on the observation of expansion temperature, the flexible chain BTDA-ODA/MPD had the lowest  $T_e$  due to the easy movability of the chain during the imidization reaction. A perfect imidization depends on the heat treatment conditions and chemical structures. The curing temperature above 250°C results in fully imidized films as seen in Figures 6 and 7. The selection of the appropriate curing temperature by considering only the degree of imidization for each PAAs is not enough. Physical properties of polyimide are also changed with varying the curing

temperature, for example, the degradation temperature, or the surface topology. These two factors will be discussed in a later section.

A comparison of the degree of imidization between the semirigid, BPDA-PPD, the semiflexible, PMDA-ODA and the flexible, BTDA-ODA/MPD is shown in Figure 9. The relative degrees of imidization of the films were evaluated by comparing the peak height ratios. The semirigid film, BPDA-PPD had the highest relative imidization. Because of the rigidity of the PAA precursors, it had more potential to undergo a cyclization, or intramolecular reaction than the less rigid PAAs which may undergo interatomic linking reactions as shown in Figure 35. For the lowest peak height ratio in semiflexible chains, we do not know the exact reason at the moment. However, the possible reason may be due to the high possibility to delocalize electrons along the semiflexible chain. So we can conclude that the degree of imidization is dependent of the chemical structure of polyimide films.



**Figure 35** The possible inter atomic links mechanism that occurred during the curing of poly(amic acid)s.

## 4.2 Thermal Properties of Polyimide Films

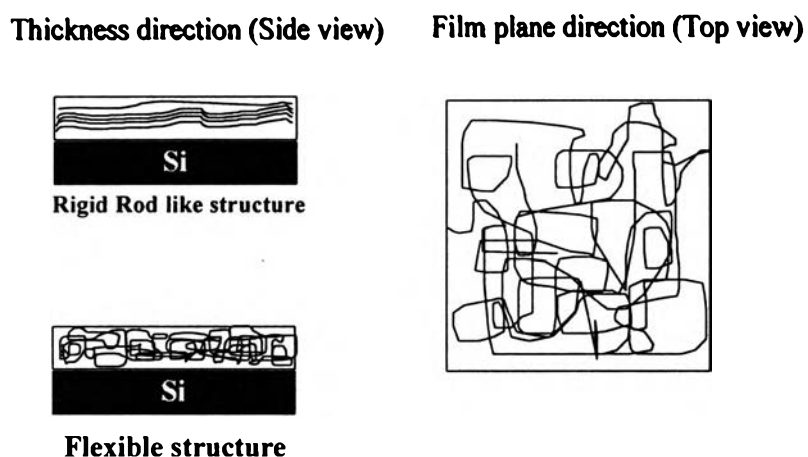
Thermogravimetric analysis (TGA) and Thermomechanical analysis are common techniques to determine thermal stability and the mechanical properties of films at high temperature. The TGA thermogram showed the weight of the film cured at different curing temperatures. Evaporation of water, solvent, and decomplexation occurred with incompletely imidized films. As seen in Figures 15-16, the weight loss was decreased at the curing temperature below 250°C and remained constant at curing temperature above 250°C. This confirmed that the polyimide film is more stable than the PAA film because some of PAA's precursor was still left in the film. On the other hand, the thermal stability depends on the degree of imidization. The fully imidized film of BPDA-PPD was stable up to 618°C. Other fully imidized polyimide films did also show an excellent thermal stability. The films coated on the silicon substrate exhibited a good thermal stability, higher than the specification for the microelectronic gas sensor application. To select the best film for gas sensors, every film in this experiment was considered as a potential candidate.

As long as the curing temperature was in a range above 250°C, the curing rate in a range of 1-8°C/minute did not affect both the degree of imidization and the degradation temperature.

The other thermal property of polyimide films was the expansion behavior of the film, which should be similar to that of the silicon ( $2.6 \times 10^{-6} / ^\circ\text{C}$ ). Although the X-ray diffraction spectra showed the amorphous phase on the fully imidized films cured at 400°C, anisotropic properties were observed from the difference of the in-plane CTE and out-of-plane CTE. In other words, we

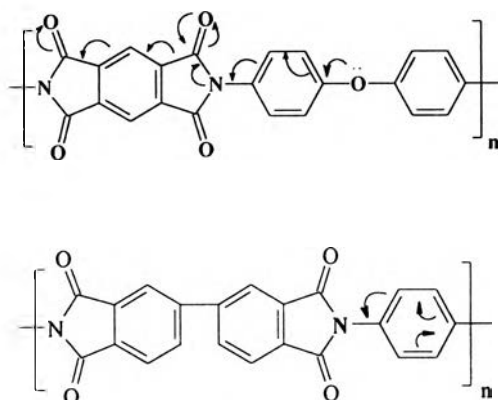
call them birefringence properties. Lin et.al. (1991) used the difference in the refractive index of the film in film plane and normal to the film plane to calculate the birefringence. The lowest value of in-plane CTE belonged to the semirigid BPDA-PPD but it had the highest out-of-plane CTE. This means that this rigid rod-like film preferably aligns in the thickness direction. For the flexible, BTDA-ODA/MPD which had the lowest in-plane CTE but the highest out-of-plane CTE, one can say that this polyimide film had oriented in the film plane direction more than in the thickness direction. But the X-ray diffraction spectrum of this flexible film showed no pattern of the alignment of the in-plane direction. So a possible model of orientation of this film should be the amorphous or the 3-dimensional random coil as seen in Figure 36, while the films containing semirigid rod like structure were more likely 2-dimensional random coils. Therefore, delaminating and bending of the film should occur in the semirigid BPDA-PPD film. Unfortunately, of all of those polyimide films, no one had an CTE close to that of silicon ( $2.6 \times 10^{-6} / ^\circ\text{C}$ ). The application of the adhesion promoter enhanced the delamination problem. Although the thermomechanical method can monitor the expansion behavior of the insulating films, the behavior of the film on the substrate was not studied by this method. Ree (1994) studied the chain rigidity and in-plane orientation, and thickness on residual stress of polyimide films using the stress analyzer with He-Ne laser beam. The molecular in-plane orientation, which is a critical factor to the interfacial film stress, becomes higher as the polymer chain rigidity is greater and the film is thinner. The resulting stress, if it is too high, may cause serious bending, delaminating, or cracking on the surface of the film. The orientation of the film will decrease with increasing thickness of the film as Jou-Huei Jou, et.al. (1992) reported. The high stress might be seen by the high out-of-plane CTE of the film, for example, the high out-of-plane CTE of BPDA-PPD rigid rod like polymer. That would cause easy

delamination and cracking in this film on the substrate. Furthermore, the ramping rate during cure of the polyimide film also affected the stress of the film [Jwo-Huei Jou , 1995]. Rapid rates of curing will induce stress in the film.



**Figure 36** Possible model for the polyimide film with the rigid and flexible chains.

Surprisingly, the expansion temperature of the semiflexible film, PMDA-ODA was higher than that of semirigid film which needs more thermal energy for the moving chain. If we look at the stability of the chemical structure of PMDA-ODA, it has a more stable structure due to the lone electron pair on the oxygen in the ether linkage which can delocalize along the polymer chain. But the electron in the BPDA-PPD polyimide film cannot delocalize at all around the chain, owing to the non-conjugate structure at the C-C linkage of the two phenyl rings in the dianhydride segment. Therefore, the more stable structure of PMDA-ODA needs more thermal energy to accompany the chain movement. Normally, the flexible chain structure moves easier than the rigid one, so  $T_e$  and  $T_y$  of the more flexible chain (BTDA-ODA/MPD) are higher than that of the less flexible one.



**Figure 37** Delocalization of lone pair electron on the PMDA-ODA chain compare with that of the BPDA-PPD.

The decrease in the in-plane CTE of the flexible chain might be the result from cross-linking occurring in the long term curing as well as the flexibility of the chain. Therefore, the possibility of cross-linking of the flexible chain polyimide was more likely than the rigid chains.

The thermal cycling experiment was performed as a test of the durability of polymer films on the gas sensor. The flexible chain structure BTDA-ODA/MPD shows an increase in the in-plane CTE as seen in Figure 24. This result is contradictory to the effect of curing time. Normally, the longer period of curing of the film should produce the lower in-plane CTE due to the cross-linking. For the semirigid and semiflexible films, the in-plane CTE were not changed after ten cycles of annealing.

### 4.3 Surface Topology of The Polyimide Films

The surface profile of the film was a crucial factor for a good protective polymer for the sensors application. If there are bubbles on the film, certainly, a heater contact in the gas sensor could be shorted out. From Figures 25-26, the smoothest surface was obtained from the film with the lowest viscosity, BTDA-ODA/MPD PAA. There was a little problem with the surface tension between the PAA solution and silicon wafer. This could be solved by warming the surface to 50°C and applying the solution on the substrate. However, on a micromachined device, it is questionable whether or not one can create a uniform surface by placing droplets of solution by hand onto the device. The method may not be precise enough and could lead to a wavy surface. From the surface profile obtained from the AFM (Figures 32-34) we found that smooth, uniform surfaces were quite good in all polyimide films with areas about  $5 \times 5 \mu\text{m}^2$ . It was suggested that a micro-dispensing technique may be appropriate for the small area of the gas sensor which has a dimension of only  $1.3 \times 1.3 \text{ mm}^2$ . The other technique of fabrication that we would suggest to do in the future is the vapor deposition technique which should be made compatible with the CVD of the Pt electrode on the gas sensor.

The application of adhesion promoter caused a rough surface as shown in Figure 31. This was due to the high surface tension of the solution of adhesion promoter on the surface of the silicon wafer. Improvement of smooth coating of the adhesion promoter was successfully accomplished by warming a solution of the adhesion promoter to reduce the viscosity of the solution, however, this approach has not yet been proven quantitatively. A sudden drying of the solution film on the hot plate can be helpful for the coating the

silane compound which was in the solution onto the silicon surface when the solvent was evaporated.

#### **4.4 Electrical Properties of Polyimide Films**

The reason for choosing the polyimide film as a protective polymer is its property to act as an excellent insulator. The dielectric break down voltage is one of many electrical parameters for investigating the degree of an insulating layer. The dielectric strength of polyimide film was compared with the well-known insulating layer polyethylene. It was found that the dielectric strength of polyimides were close to that of polyethylene. However, the dielectric strength is strongly dependent on the temperature, humidity and thickness [ASTM-D149-92, 1996]. In particular, the gas sensor needs a thin insulating layer, as far as the dielectric strength is concerned the thickness should be lower than the 1 mil thick film as reported in Table 4.

Measurements of electrical properties, especially capacitance values of these low dielectric constant polyimides are crucial to predict the integrated circuit performance [Flora and Chiu Ting, 1995]. Film orientation or anisotropic properties also affect the dielectric properties of the films. Fortunately, the fabrication of this protective polymer with the hand dropping technique showed low orientation, and gave essentially amorphous polymeric materials. So the anisotropy did not significantly influence the dielectric properties. But from Table 6, we can observe that the more rigid the films, the lower the dielectric strength of the films. This means that the film of the rigid chain BPDA-PPD can dissipate the energy better than the flexible film.