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Characterization of the imidization process of Low K-fluorinated polymide film during thermal curing

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The thermal curing (imidization) of the polyimide film was investigated using a differential scanning calorimeter and Fourier transform infrared (FTIR) spectroscopy. The rate and the degree of imidization of the film were found to be dependent on curing temperature, time, and thickness. The degree of imidization of the film rapidly increased between 200 and 350 °C and then remained constant for curing above 350 °C, indicating that the imidization reaction is complete at 350 °C. Also, it was found that imidization proceeds in two stages under an isothermal condition, which was characterized by an initial fast imidization step that changed into a second, slower imidization process. The slower imidization rate at the second stage is discussed and explained. A higher degree of imidization was obtained with thicker films because of the higher retention of the solvent in the thicker film. The depolymerization process during thermal curing was studied with FTIR. The highest degree of the depolymerization was reached with thermal curing between 225 and 275 °C. © *1998 Kluwer Academic Publishers*

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1. Introduction

Polyimides [1] are increasingly used in integrated circuits as interlayer dielectric (ILD) materials due to their excellent properties such as low dielectric constant, ease of application, easy patterning, and ability to planarize on the substrate. These properties have made them an attractive material as ILD materials in microelectronic applications [2]. These properties of the film can be obtained only when the polyimide film is completely imidized. A partially imidized polyimide film usually loses these properties. Therefore, before further characterization of the properties of the polyimide, the best curing condition for the fully imidized film should be determined.

In our studies various parameters affecting the imidization process of the polyimide film were first determined. The kinetics involving the imidization process were investigated with a differential scanning calorimeter (DSC) and Fourier transform infrared (FTIR) spectroscopy by examining the degree of the imidization as a function of the defined parameters (temperature, time, and film thickness). Also, other transformations occurring simultaneously during thermal curing such as depolymerization [3] and cross-link process [3] were studied with FTIR spectrometry. From these experimental results, the best curing condition of the thin polyimide film was determined.

2. Experimental procedure

2.1. Differential scanning calorimetry

Before actual measurements, the DSC instrument was carefully calibrated using an indium standard, confirming accuracy of temperature scale and heat capacity level. The polyamic acid precursor was pre-baked for 1 h at 120 °C, which was low enough to prevent any imidization from occurring in the film and long enough to remove all the solvent (NMP). Some of the pre-baked sample was additionally baked at the same temperature for 48 h to remove as much residual solvent as possible. The polyimide film was sampled by cutting out sections of the film with a standard paper punch. A punched polyimide film was placed in a sealed aluminum pan, using a sample pan crimper. A small amount of sample is preferred for obtaining maximum sensitivity and increasing the efficiency of heat transfer from the sample to its thermocouple. Less than 10 mg of the polyamic acid specimen was used for higher sensitivity. The sample and reference (empty pan) were heated at a predetermined temperature (10 °C/min) in N_2 ambient in such

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a manner that the temperatures of both the sample and reference stayed equal. The starting temperature was 100 °C, and the upper limit was 400 °C.

2.2. Fourier transform infrared spectrometry

The FTIR spectrometer used was a Perkin-Elmer 1800 double-beam system. The spectra were recorded in a transmission mode. All spectra were taken at 2 wave number resolution and represented the accumulation of 256 scans prior to the Fourier transform. The bare silicon substrate was measured first and stored for use as a base spectrum. The spectra of the polyimide film were obtained by subtracting the base spectrum stored in the memory. The polyamic acid films spun on silicon substrate were pre-baked at 100 °C for 24 hr, which was low enough to prevent any imidization from occurring in the film and long enough to remove all the solvent (NMP). The IR spectrum was recorded for the sample. The sample was then returned for the next stage of heating cycle at a temperature from 100 to 430 °C. The FTIR spectra of the sample were recorded. The cycle of sample heating and FTIR measurement was repeated to get FTIR spectra as a function of curing temperature, time, and film thickness.

The progress of imidization [4, 5] was characterized by plotting the changes in the characteristic imide peaks of 1778 and 1751 cm^{-1} carbonyl bands because they were fairly well isolated from the rest of the IR spectrum. As an internal reference standard, the band at 1012 cm^{-1}, attributed to the vibration modes of the aromatic moieties, was used. Spectra of polyamic acid/polyimide films were analyzed by a band ratio method. The area of the symmetric carbonyl stretch at 1751 cm^{-1} was divided with a reference aromatic vibration at 1012 cm^{-1}. A spectrum of uncured polyamic acid was subtracted to isolate the imide carbonyl band from the adjacent bands for more accurate measurements. To correct the reference band, a spectrum of the solvent, NMP, was also subtracted. There was an absorbance due to solvent at 980 cm^{-1}, which interfered with the quantification of the standard band at 1012 cm^{-1}.

The degree of imidization of the film was obtained by normalizing the sample band ratio with that of a fully cured polyimide film. The band ratio of the fully cured polyimide film was obtained by the IR spectrum of the sample cured above 350 °C because the magnitude of the band ratio of the polyimide did not increase for the sample cured above 350 °C and below 450 °C. The evolution of the imidization process of the partially cured polyimide was characterized by tracing the degree of imidization (normalized sample band ratio).

3. Results and discussion

3.1. Differential scanning calorimetry

The evolution of the imidization process was investigated using DSC at a 10 °C/min heating rate. Fig. 1a shows the DSC thermogram of the polyamic acid mixed with NMP solvent. Broad endothermic peaks are observed up to 310 °C, primarily due to the NMP evaporation. In the temperature range between 240 and 310 °C, the small and broad endothermic peaks associated with the imidization reaction are shown with maximum intensity at 276 °C on the top of the broad endothermic peak due to the NMP evaporation, indicating that two process (solvent evaporation and imidization) are occurring simultaneously in the temperature range up to 310 °C. To observe only the imidization process of the polyimide film clearly, without being disturbed by the solvent evaporation, the sample was baked at 120 °C for 48 h and measured by DSC; its thermogram is shown in Fig. 1b. The peaks corresponding to solvent evaporation have disappeared. The peaks for imidization are observed in the temperature range between 240 and 300 °C with a constant positive slope before and after the imidization process, corresponding well with the results obtained by using FTIR spectroscopy.

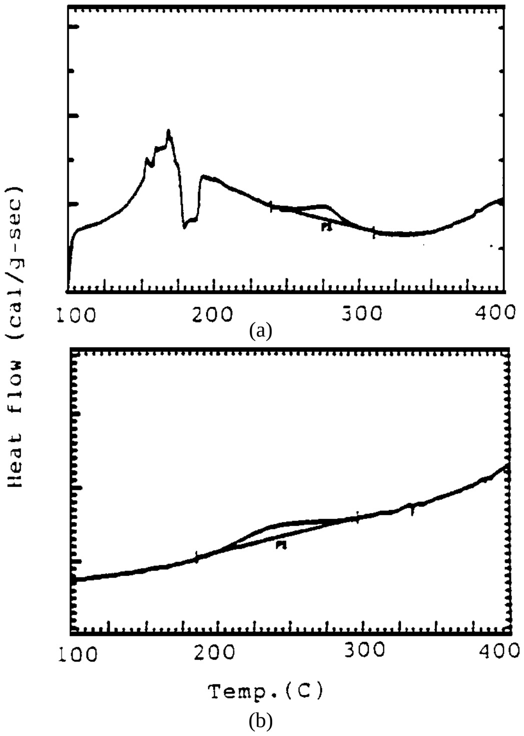

Figure 1 (a) DSC thermogram of the polyamic acid baked at 120 °C for 5 min and (b) of the polyamic acid baked at 120 °C for 48 hr.

3.2. Fourier transform infrared spectrometry

3.2.1. Identification of the characteristic peaks of the fully imidized film

In the IR spectra of polyimide in the range 650–4500 cm^{-1}, four kinds of bands at 1778, 1751, 1359, and 742 cm^{-1} [6, 7] are generally accepted as being characteristic of the imide rings. Fig. 2 shows the IR transmission spectra of the polyimide films cured above 350 °C that represent the fully imidized polyimide film. Most of the imide peaks generally appear sharp and symmetrical, making it easier to calculate their height and area. FTIR absorbance bands at 1778 and 1751 cm^{-1} are most commonly attributed, respectively, to the symmetric carbonyl group that is the characteristic peak of the polyimide. The bands at 1359 cm^{-1} have

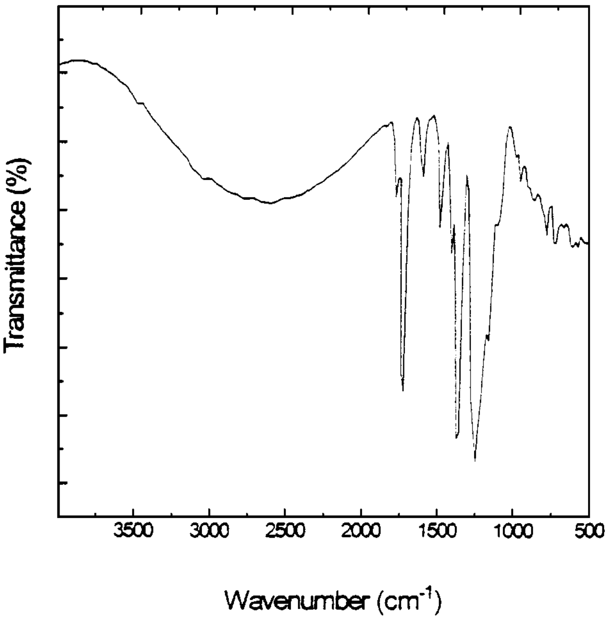

Figure 2 FTIR transmittance spectrum for the polyimide film soft-baked at 250 °C and subsequently hard-baked at 350 °C.

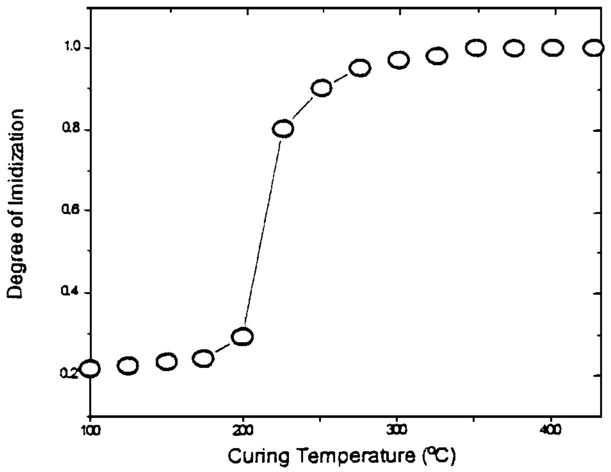

Figure 3a Degree of imidization obtained from the FTIR transmittance spectra.

been attributed to the C-N stretch in the polyimide. The band at the 742 cm^{-1} region has been attributed to deformation of the imide ring or to the imide carbonyl groups.

3.2.2. Kinetics of thermal imidization

As shown in Fig. 3a, the degree of imidization [8, 9] of the film is low for curing below 200 °C, rapidly increased for curing between 200 and 350 °C, and then constant for curing beyond 350 °C, indicating that the imidization process continues up to 350 °C with a slow rate at curing temperature below 200 °C, rapidly increases between 200 and 300 °C, and is then complete at 350 °C. The thermal curing beyond 350 °C does not contribute any more to the increase of the degree of the imidization of the polyimide film, clearly confirming that the imidization reaction is completed at 350 °C.

Fig. 3b shows the rate and degree of imidization of the polyimide film as a function of curing time at 150 °C, 200 °C, 250 °C, and 350 °C in N_2 ambient.

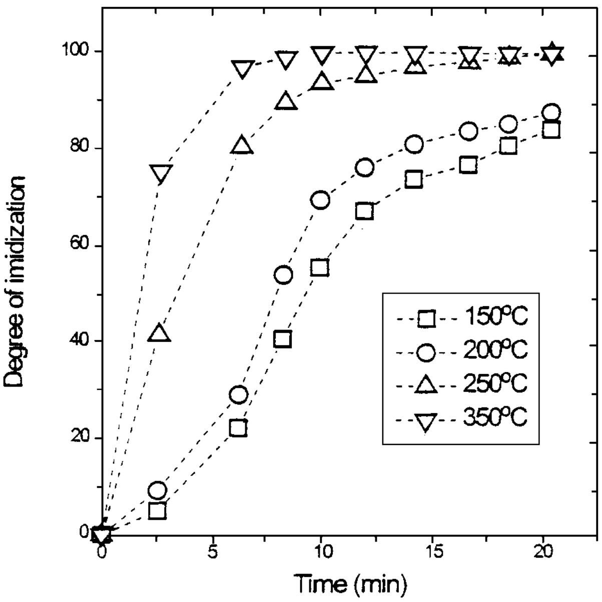

Figure 3b Degree of imidization obtained from the FTIR transmittance spectra as a function of the time at various curing temperatures. Imidization is complete in about 10 min at 350 °C in N_2.

The evolution of the imidization process of the partially cured polyimide was characterized as a function of curing time at different curing temperatures. It was found that imidization proceeds in two stages under isothermal conditions. The degree of imidization of the film was characterized by an initial fast step that changes into a second, slower process. As the curing temperature increases, the contribution due to the first stage increases. As a result, the degree of imidization at the starting point of the second stage is higher. In the second stage, the slope decreases continuously and can drop to almost zero, long before the reactive species are consumed. The slow rate of imidization at the second stage can be explained by the following [10]: (1) The *o*-carboxycarboxamide groups in the polyamic acid are in two non-equivalent kinetic states. One state is activated for imidiation, while the other is not. The active groups rapidly imidized during the first stage of imidization, while the remaining inactive groups imidized in the second stage. (2) The imidization process continues, and the glass transition temperature of the polyimide increases as its imide content increases. When the glass transition temperature reaches the temperature of the sample, the polyimide transforms from a rubbery to a glass state, and segmental motion ceases. As a result, it is very difficult for the amic acid groups to attain suitable conformation for imidization. The imidization proceeds in the glassy state but at a much slower rate. (3) The imidization process is enhanced by the presence of solvent. The decrease in the imidization rate is due to the loss of solvent that occurs upon extended heating. The initial rapid rate is attributed to the larger retention of a solvent NMP at the initial stage than the second stage, permitting increased molecular chain motions.

The degree of imidization was also characterized as a function of the film thickness in the range of 0.3 to 1.4 μm. Fig. 4 shows that the thicker films exhibit higher degrees of imidization than do thinner ones

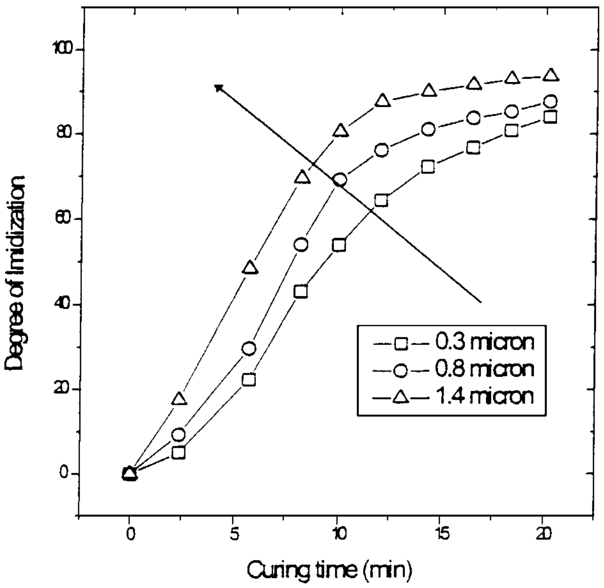

Figure 4 Degree of imidization from the FTIR spectra (as defined in the text) as a function of time and polyimide film thickness. Films were annealed at 250 °C in N_2.

because of their higher retention of the solvent in the thicker film, permitting increased molecular chain motions to attain suitable conformation for imidization. Solvent can escape from thinner films faster than from thicker ones. A higher degree of imidization can be obtained with a thicker film than a thinner one.

3.2.3. Depolymerization of polyamic acid during the curing process

An o-carboxycarboxamide in the polyamic acid can undergo three transformations upon heating: It can cyclize intramolecularly to regenerate the anhydride or it can cyclize to afford isoimide, or imide moieties. There is a small but significant amount of anhydride formed during the heating cycles. Its concentration can be monitored by following the anhydride carbonyl absorption band near 1860 cm^{-1} in the IR spectra of polyimide. As shown in Fig. 5, the intensity of the band increases as temperature increases. The maximum intensity is reached between 225 and 275 °C. The band then begins to decrease and eventually disappears between 350 and 430 °C.

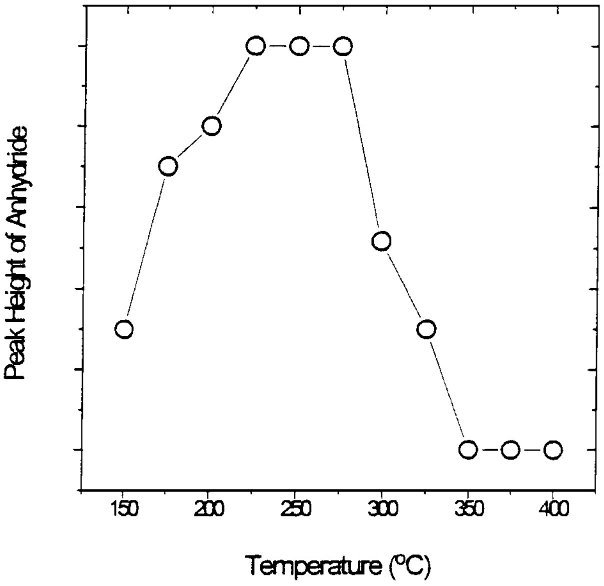

Figure 5 Anhydride carbonyl peak height in the polyimide film cured for 60 min in N_2 as a function of the curing temperature.

4. Conclusion

The kinetics of thermal imidization of the polyimide films has been investigated using DSC and FTIR spectroscopy to determine the best curing condition. The rate and the degree of imidization of the film were found to be dependent on the curing temperature, time, and thickness. The degree of imidization of the film is low for curing below 200 °C, rapidly increases for curing between 200 and 350 °C, and is then held constant for curing beyond 350 °C. The thermal curing beyond 350 °C does not contribute any more to the increase in the intensity of the characteristic imide band, indicating that the imidization reaction is complete at 350 °C.

It was found that imidization proceeds in two stages under an isothermal condition. The degree of imidization of the film was characterized by an initial fast imidization step that changes into a second, slower imidization process. The slower imidization rate at the second stage was discussed and explained. A higher degree of imidization was obtained with thicker films because of their higher retention of the solvent.

The depolymerization process during thermal curing was also studied with FTIR. The maximum intensity of monomers due to the depolymerization is reached during thermal curing between 225 and 275 °C. Its intensity decreases and eventually disappears between 350 and 430 °C.

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