Low Temperature Curing of Polyimide Precursors by Variable Frequency Microwave

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Polyimides are commonly used as a thermally stable insulator for semiconductors. To assure adequate chemical or physical properties, a layer of their precursors has to be cured in a convection oven at more than 300 °C. In this paper, we compare variable frequency microwave (VFM) heating with convection heating for curing various polyimide precursors and a photosensitive polyimide precursor. Then, we demonstrate that the use of VFM enables us to cure the precursor lower than the standard convection cure temperature while maintaining necessary film properties such as cyclization, T_g, T_d, and elongation.
Keywords: polyimide, curing process, microwave, buffer coating

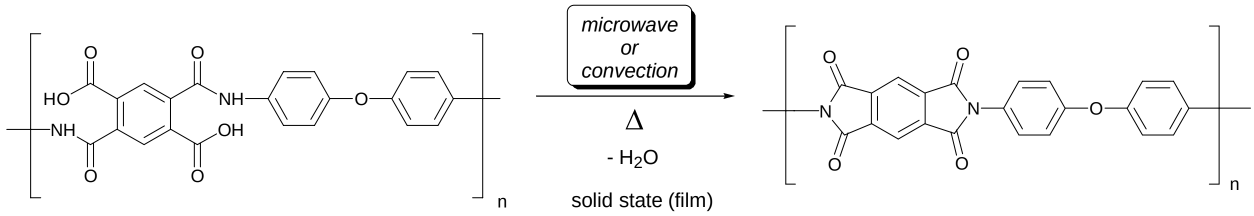
1. Introduction

Polyimides are widely used in silicon technology process integration such as insulating, buffer coating, and interlayer dielectrics, because of their excellent electrical, thermal, and mechanical properties [1]. For these purposes, soluble polyimide precursors, namely poly(amic acid)s, are applied initially, and then they are converted to insoluble polyimides in the solid state (*Scheme*). This curing process requires more than 300 °C curing temperature.

Recently, polyimides are applied to novel devices such as gate dielectric layers in organic field-effect transistors [2] or insulation layers in organic light emitting diodes [3]. However, fabrication of these devices requires much less than 300 °C curing temperature to obtain the satisfactory results. There are several approaches to reduce the curing temperature including the introduction of flexible structures or the addition of imidization promoters [4].

Microwave irradiation is currently a well-known method for heating materials and is utilized not only in many households but also in industry. It is employed to organic synthesis [5] and polymer science [6], since it offers a number of advantages over conventional, i.e. convection or diffusion, heating such as non-contact heating, instantaneous,

Scheme



rapid heating, and so on. Furthermore, the use of variable frequency microwave (VFM, vide infra) in the curing of polymers has been reported for polyimides [7] and others [8] for rapid heating.

Herein, we cured various polyimide precursors and a photosensitive polyimide precursor with a VFM oven and a convection oven. We then compare the resulting film properties, such as cyclization, T_g, T_d, and elongation, from the standpoint of low temperature cure [9].

2. Method

2.1. Materials

Non-photosensitive polyimide precursors, namely poly(amic acid)s, PIX-8103, PIX-3400, and PI-2611 were commercially available as solutions and obtained from HD Microsystems. Non-photosensitive polyimide precursors, SPL-6000 and SPL-1708 were also obtained from HD Microsystems. A photosensitive polyimide precursor HD-8800 was available from HD Microsystems as a commercial product.

2.2 Percentage of rigid chain length (PRCL)

Percentage of rigid chain length (PRCL) is one of parameters which express rigidity of a polymer chain [10]. The PRCL is applied herein to polyimides according to the previous literature for poly(ether sulfone), and is estimated by the following equation (1).

$$\mathrm{PRCL} = L_{\mathrm{rigid}}/L_{\mathrm{total}} \times 100 \qquad (1)$$

where, L_{rigid} is the length of a rigid part in a monomer unit, and L_{total} is the length of the whole of the unit. Generally, polymers having aromatic rings are high PRCL, and those having aliphatic or other flexible chains (eg. ether linkage) are low PRCL. In this study, the imide part as a common structural unit is omitted for calculating PRCL for simplification. The PRCL of fully aromatic polyimides are defined as 100%, and that of fully aliphatic polyimides are defined as 0%.

2.3. Variable frequency microwave (VFM) oven

Curing involving cyclization of a polyimide precursor was done with a MicroCure 2100, a Lambda Technologies Inc. product. Some of important features of this system include frequency sweeping from 5.85 to 7.00 GHz, and delivering power into a cavity. In as short as 100 milliseconds, over 4,000 frequencies are launched to ensure uniform energy distribution, and also to eliminate arcing to allow components and devices with metals or circuits to be processed. IR and Ga-As probes monitor the temperatures on a film and under a substrate, respectively. A feed back control is also introduced to the system to control the temperature of the sample to be cured. The control system adjusts the power level automatically to maintain the sample at the desired temperature.

2.4. Processing

A solution of a polyimide precursor was spin-coated on a silicon wafer, which was then soft-baked on a hot plate at around 100 °C for about 3 min to give a thin film whose thickness was adjusted to ca 15 μm. The resulting film was then cured by VFM irradiation in air. Irradiation power varied between 0 W to 500 W. And the cure was executed at 125 °C or 225 °C for 1 h or 4 h. On comparison to VFM cure, the soft-baked film was also cured in convection oven at 125 °C or 350 °C for 1 h under a nitrogen atmosphere by an INH-9CD-S, a Koyo Thermo Systems product. Then, the cured film was peeled off from the wafer with the aid of diluted hydrofluoric acid.

2.5. Evaluation of cured films

Degree of imidization was monitored by IR spectroscopy (Shimazu FTIR-8300). Glass transition temperature (T_g) was obtained by Thermo-mechanical analysis (TMA) using TM/SS6000 (Seiko Instruments Inc.). A T_g (TMA-based) is defined as an inflection point in a temperature-displacement curve. Thermo-gravimetric analysis (TGA) was conducted by using TG/DTA6300 (Seiko Instruments Inc.) to determine thermal degradation temperature (T_d). Tensile property was measured by Autograph AGS-100N (Shimazu) with 20 mm chuck distance.

3. Results and Discussion

3.1. Non-photosensitive polyimide precursors

3.1.1. T_g of convection cured films

As mentioned above, we choose polyimide precursors which are derived from various monomers (diamines and tetracarboxylic acid dianhydrides). Herein, we introduce PRCL (vide supra), since chemical structures of polyimides could be converted into numerical values. The calculated PRCLs of polyimides are listed in Table 1. This result indicates that rigidity of polymer chains increases in the following order: PIX-8103<SPL-6000<PIX-3400<SPL-1708<PI-2611.

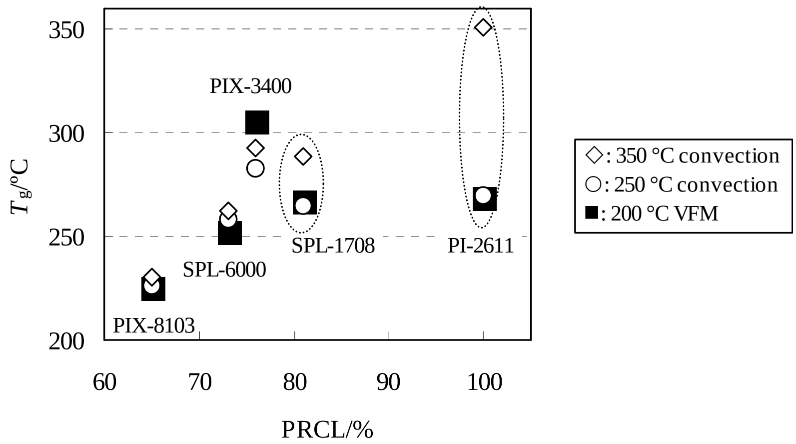


Fig. 1. PRCL of polyimide precursors versus T_g of cured films, ◇: 350 °C convection, ○: 250 °C convection, ■: 200 °C VFM.

Prior to VFM curing experiments, the polyimide precursor films on silicon wafers were cured with a convection oven at 250 °C or 350 °C for 1 h. Then we measured TMA-based T_g of the resulting films, since T_g is one of the important properties for thermally stable materials.

Table 1. PRCL of polyimide precursors used in this study

PI precursor	PRCL/%
PIX-8103	65
SPL-6000	73
PIX-3400	76
SPL-1708	81
PI-2611	100

The T_g is plotted as a function of PRCL as shown in Figure 1. We find that the T_g value for the 350 °C cured films increases linearly with increasing PRCL (◇ in Figure 1). A similar relationship is observed in the preceding result on poly(ether sulfone) [10]. We also find that the T_gs of the cured films of PIX-8103 and SPL-6000, whose PRCLs are relatively low, seem to be intact even if the cure temperature is reduced from 350 °C to 250 °C (○ in Figure 1). In contrast, the T_gs of 250 °C cured films drop down to ca 270 °C from their initial values for SPL-1708 and PI-2611, whose PRCLs are high. To our surprise, however, the T_g of PIX-3400 cured at 250 °C is found to remain high and close to the value for a 350 °C convection cure. We summarize as follows. The T_gs of polyimides are correlated with PRCL. For 350 °C cured films, T_g increases linearly with increasing PRCL. When the cure temperature is reduced, T_g decreases for high PRCL polyimides.

3.1.2. T_g of VFM cured films

We cured polyimide precursor films with a VFM oven at 200 °C. The T_gs of the resulting films are shown in the Figure 1 (■) in conjunction with convection cure data. It is noteworthy that T_g of films cured by VFM at 200 °C is found to be approximately identical to that of 250 °C convection cured films for PIX-8103, SPL-6000, SPL-1708, and PI-2611 (■ vs ○). This result suggests that cure temperature might be reduced with 50 °C by using VFM irradiation regardless of PRCL value. In other words, low temperature cure might be accessible for polyimide precursors independently of their structures [11, 12]. To our surprise, for PIX-3400, T_g of the film cured at 200 °C by VFM (T_g = 306 °C) significantly exceeds that of the 350 °C convection cured film (T_g = 293 °C).

3.1.3. Film properties of PIX-3400 with different curing method

As mentioned in the previous section, PIX-3400 exhibits a unique property for both VFM and convection. Thus, we measured several properties of the PIX-3400 films cured at various temperatures compared with the different curing methods (convection and VFM).

First, cyclization (degree of reaction or imidization) that is calculated from the IR spectrum is shown in Figure 2 (● for VFM cured films and ○ for convection cured films). We find that the cyclization of the 150 °C VFM cured film is equal to the case of 200 °C convection. This result implies the possibility of a 50 °C lower temperature cure. Moreover, the cyclization is improved significantly and almost completed at the low cure temperature region (more than 175 °C).

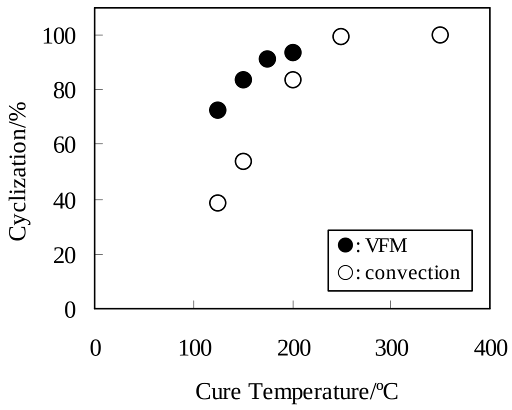


Fig. 2. Cyclization of PIX-3400 cured films, ●: VFM, ○: convection.

Next, as shown in Figure 3, we find that T_g of cured films by VFM at 175 °C and 200 °C is higher than that by convection at 350 °C (299 °C and 306 °C, respectively vs 293 °C). We emphasize again that VFM improves T_g (TMA-based) absolutely at the low temperature region. Surprisingly, using convection heating, T_gs of 150 °C and 125 °C cured films remain high (293 °C and 288 °C, respectively). Therefore, the abnormality of PRCL vs T_g may be attributed to the specific property of PIX-3400. Further investigation has to be done to explain this specificity.

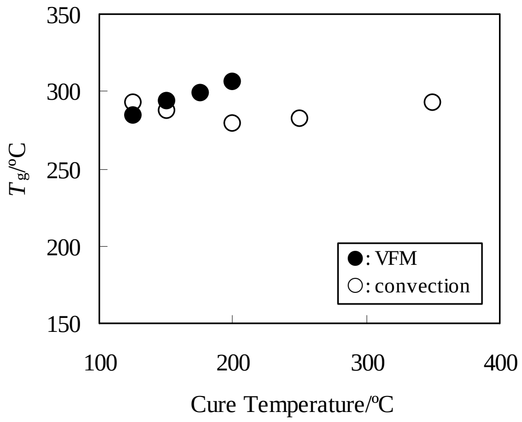


Fig. 3. T_g of PIX-3400 cured films, ●: VFM, ○: convection.

Next, we measured thermal degradation temperature (5% weight loss temperature T_{d5}) using TGA. The result is shown in Figure 4. We find that the VFM cured films at more than 150 °C exhibit excellent T_{d5} around 500 °C. Note that T_{d5} of the 200 °C VFM cured film (530 °C) is quite similar to that of the 250 °C and 350 °C convection cured film (526 °C and 533 °C, respectively). Therefore, the possibility of more than 50 °C low temperature cure is supported by the T_{d5} data.

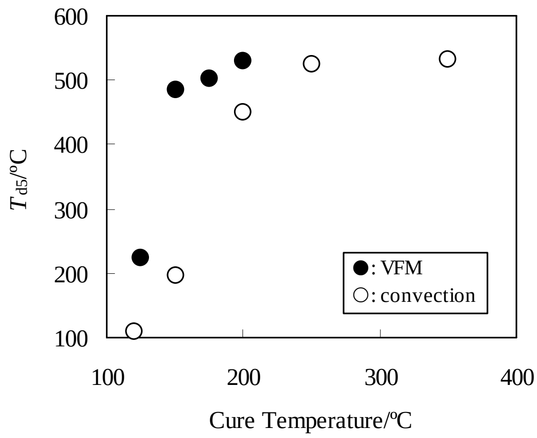


Fig. 4. Thermal degradation temperature (5%, T_{d5}) of PIX-3400 cured films, ●: VFM, ○: convection.

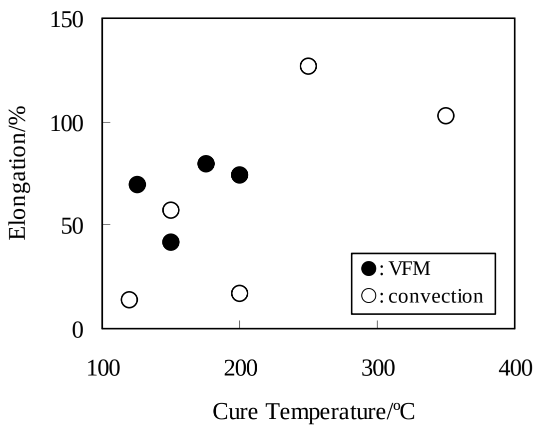


Fig. 5. Average elongation at break of PIX-3400 cured films, ●: VFM, ○: convection.

Finally, elongation at break of various cured films, which is the average value of more than five samples, is presented in Figure 5. We find that the value of 200 °C cured film is favorable by using VFM. Although the elongation of cured films by VFM at 175 °C and 200 °C is inferior to that by convection at 250 °C and 350 °C, this value is quite superior to that obtained by convection at 200 °C.

We have noted that owing to VFM, more than 50 °C lower temperature cure can be achieved while maintaining the necessary film properties, such as cyclization, T_g, T_d, and elongation, compared to the standard convection cure temperature for PIX-3400. According to our result, PIX-3400 can be processed with VFM at 175 °C and 200 °C. In addition, T_g of the VFM cured PIX-3400 film elevates significantly which is not realized by convection. We have also disclosed that 50 °C lower temperature cure can be accessible by considering the T_g data for all other non-photosensitive polyimide precursors we have examined.

3.2. Photosensitive polyimide precursor

A polyimide precursor, HD-8800, is positive-tone photosensitive, which can be developed by a common aqueous solution (2.38 wt% TMAH). The HD-8800 consists of not only a polyimide precursor but also photoactive compounds. We expect that VFM is able to accelerate a dehydrative cyclization (imidization) at a low temperature region in the presence of photoactive compounds. Thus, we measured the properties of a HD-8800 film cured by VFM or convection at various temperatures.

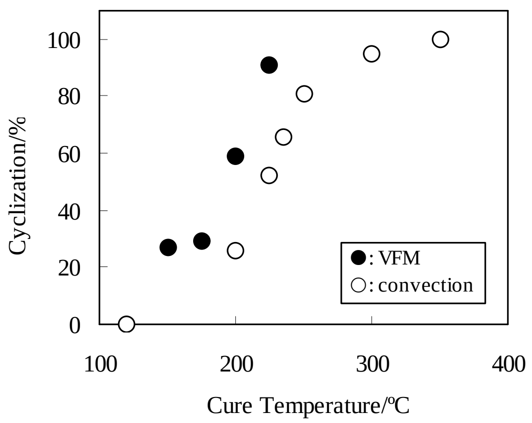


Fig. 6. Cyclization of HD-8800 cured films, ●: VFM, ○: convection.

First; degree of imidization is shown in Figure 6. The temperature-imidization curve of VFM cured film (●) shifts to ca 50 °C lower than that of cured film by convection (○). We also find that more than 90% imidization is achieved by VFM cure at 225 °C, which is comparable to convection cure at 300 °C. This result indicates the possibility of low temperature cure even for the photosensitive polyimide. Then, we measured T_g, and the result is summarized in Figure 7. The T_gs of both 175 °C and 200 °C VFM cured films are comparable to the value of 250 °C cured by convection. Moreover, at cure temperature of 225 °C, T_g is improved significantly by using VFM, and close to the value of the 350 °C convection cured film.

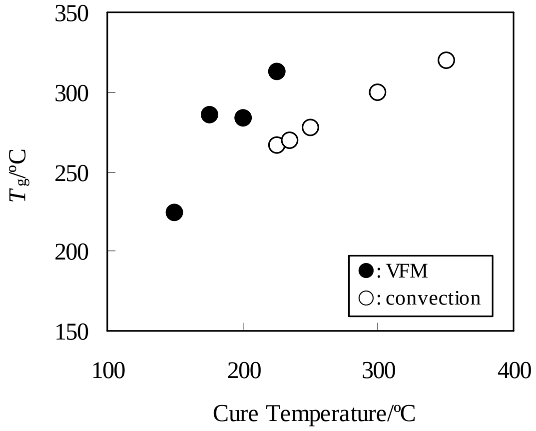


Fig. 7. T_g of HD-8800 cured films, ●: VFM, ○: convection.

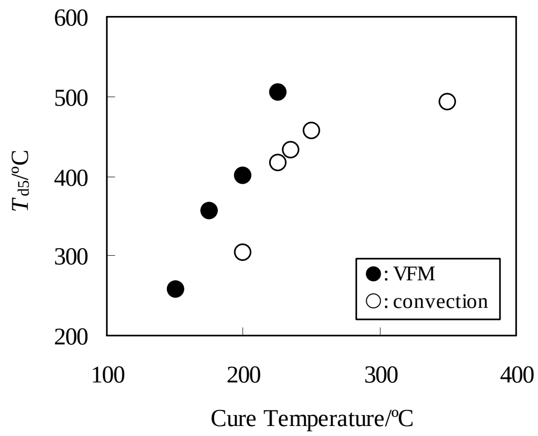


Fig. 8. Thermal degradation temperature (5%, T_{d5}) of HD-8800 cured films, ●: VFM, ○: convection

Next, we evaluated T_{d5} of the films to observe similar results for cyclization and T_g as expressed in Figure 8. The temperature-T_{d5} curve of VFM cured film shifts into a lower temperature region from that of cured film by convection. It is noteworthy to say that T_{d5} of the 225 °C VFM cured film is much higher compared with convection at the same cure temperature, and is also inaccessible with convection at 350 °C. These results suggest accessibility of reducing cure temperature by 50 °C and more. Finally, elongation at break of HD-8800 cured films was measured and plotted in Figure 9. We observe that elongation of VFM cured film somewhat drops at 225 °C from 200 °C. However, elongation of the film cured by VFM at 200 °C improves drastically compared with convection at the same curing temperature, and nearly equals that of a 300 °C convection cured film.

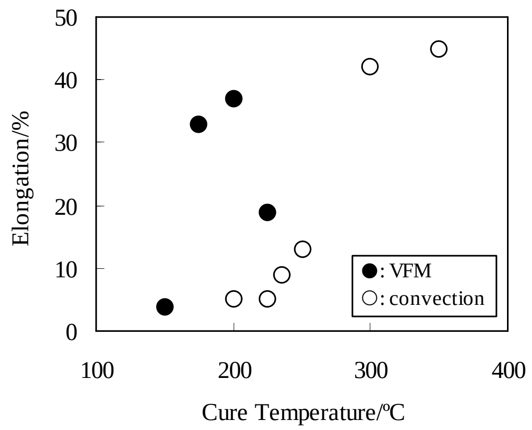


Fig. 9. Average elongation at break of HD-8800 cured films, ●: VFM, ○: convection.

We emphasize again that more than 50 °C low temperature cure is accessible by VFM while maintaining several properties compared with a standard convectional heating condition (300 °C to 350 °C) for HD-8800. More specifically, HD-8800 can be processed with VFM at 200 °C to 225 °C. This result suggests that VFM is a powerful and practical tool for low temperature cure of both non-photosensitive and photosensitive polyimide precursors.

The reason why polyimide precursors processed with VFM result in reducing curing temperature is yet to be elucidated. However, the difference in evaporation rate of remained solvent between VFM and convection has been reported [8]. There is an argument about a non-uniform temperature profile on a molecular scale [8, 11]. Further study is underway in our group.

4. Conclusion

Various polyimide precursor films have been cured by different heating methods which involve variable frequency microwave (VFM) heating and convection heating to study the possibility for reduction of cure temperature. We find that more than 50 °C lower temperature processing can be realized by VFM compared with convection methods to produce sufficient properties. VFM is found to be valid for polyimides independently of their PRCL values (the rigidity of the polymers). The low temperature cure is accessible regardless of photosensitivity of polyimides. In addition, some of polyimide films cured by VFM show significant properties that are not achieved by conventional methods.

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