Optimizing Polyimide Cure Using Infrared Spectroscopy and a Factorial Design

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Synopsis

The cure of a polyimide derived from pyromellitic dianhydride (PMDA) and oxydianiline (ODA) has been studied using infrared spectroscopy. A factorial experimental design, combined with regression analysis, was used to find the optimum curing conditions. It was shown that five micron films can be cured by heating at 230–250°C for times of five minutes or longer, while samples cured initially at 150°C did not cure completely when heated to higher temperatures.

INTRODUCTION

The increasing use of polyimides in microelectronic applications can be seen by the various review articles[1] and symposia proceedings[2] which have appeared recently. Most of these polyimides have required thermal imidization (curing) of a starting polyamic acid, and various cure cycles have been adopted. In several studies[3,4] the kinetics of imidization was followed using infrared spectroscopy, and this approach has been used in the present study. The polyimide investigated was that derived from pyromellitic dianhydride (PMDA) and oxydianiline (ODA). The conditions for each experiment were selected using a statistically designed matrix, namely that of a factorial design, to try to provide a firm statistical basis for the choice of optimized curing conditions. Details of these designs can be found in a number of sources, such as the volume by Box et al.[5]

EXPERIMENTAL

Sample Preparation

Solutions of the PMDA-ODA polyamic acid in an *N*-methylpyrrolidone/aromatic hydrocarbon solvent mixture[6] were obtained commercially from DuPont. Films were prepared by spin coating the solution onto silicon wafers which had been cleaned in an oxygen plasma. A spin speed of 2500 rpm gave films approximately 5 μm thick when fully cured. The wafers were heated first at 85°C on a hotplate in air, and then in ovens at temperatures up to 250°C. The ovens were flushed continuously with dry nitrogen and the wafer temperatures were monitored with thermocouples attached to the oven surfaces. Samples heated to 400°C were inserted into a tube furnace which was flushed with nitrogen.

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INFRARED SPECTROSCOPY

A sharp blade was used to cut a 2 cm square in the center of each film while it was still on the substrate. These pieces of film could then be easily peeled off the wafers except for samples cured to 400°C, in which case a drop of dilute HF (1:1 by volume) introduced under the films facilitated their removal. The films were held in a magnetic film holder and their infrared transmission spectra recorded using a Perkin-Elmer model 283 spectrometer.

The thickness of each film was measured (to 0.05 μm) at the center of each of the four sides of the square before the film was removed from the substrate. This was done using a surface profiler (Alpha-Step, Tencor Instruments) previously calibrated with a 2.345 μm standard supplied by the manufacturer. The polyimide films were observed to shrink considerably during the cure: typically, samples heated to 250°C would shrink to approximately 75–80% of their thickness after only a 150°C cure. The extent of cure (i.e., imide concentration) was estimated[3] by calculating $A(720)/d$, where $A(720)$ is the absorbance of the imide band at 720 cm^{-1} and d is the film thickness in microns. The absorbance was estimated from the peak height rather than from the peak area. The largest value observed for this ratio (0.121) was assigned a value of 100, and all other measurements were scaled accordingly.

EXPERIMENTAL DESIGN

The three variables examined for their effect on the extent of cure are shown in Table I. Thus, each sample was heated first at 85°C for between 2 and 20 min and then at a temperature in the range of 150–250°C for 5–45 min. The choice of these variables and ranges was based on previous experience with polyimide curing; if the important variables are not known, then a screening design (such as a fractional factorial[5]) would have to be carried out to determine which factors have a significant effect on the dependent variable.

If all combinations of the three variables at the extreme ends of their ranges are used, then one obtains a 2^3 factorial design; the experimental conditions of the resulting eight experiments are represented by the corners of the cube shown in Figure 1. In addition, experiments corresponding to conditions at the center of the cube were carried out; these therefore consisted of a cure cycle of 85°C for 11 min followed by 200°C for 25 min. Experiments corresponding to the corner points were run in duplicate, while the center point was replicated four times; these replicate runs are important

TABLE I
Variables Used and Their Ranges

Variable	Symbol	Range
Time at 85°C (mins)	X_1	2–20
Cure temperature (°C)	X_2	150–250
Cure time (mins)	X_3	5–45

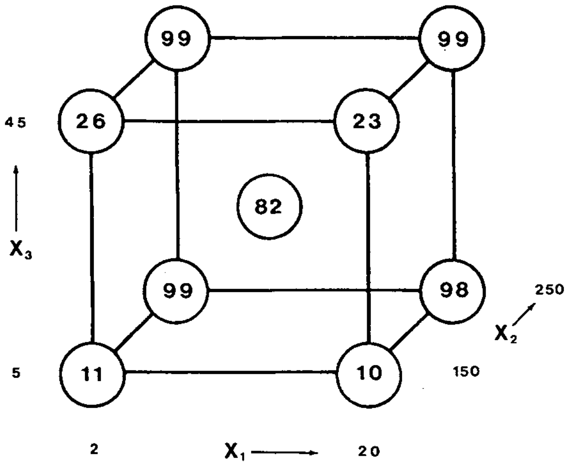

Fig. 1. Results obtained for the extent of cure using a 2^3 factorial design.

for the goodness-of-fit tests described below. Therefore, 20 experiments were run initially, and the order in which they were carried out was randomized using a table of random numbers; the center points, however, were assigned to the runs numbered 1, 7, 14, and 20.

The data obtained were evaluated using regression analysis[7] and the appropriate analysis of variance tables. All statistical calculations and the contour plot in Figure 2 were carried out using APL on an IBM 3081 computer. These APL programs are available as commercial IMB products.

RESULTS AND DISCUSSION

The first nine rows of Table II show the results obtained for the 20 experiments described above. Following standard practice the variables have

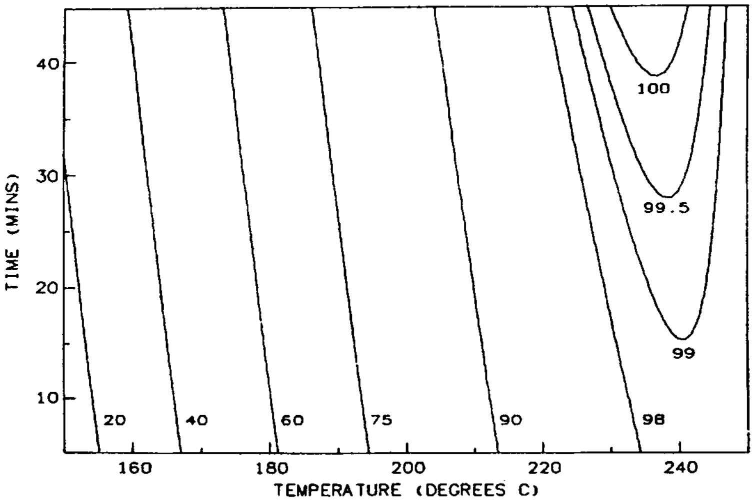

Fig. 2. Contour plot for the extent of cure using Eq. (3).

TABLE II
Results Obtained for Each of the Coded Experimental Conditions

X_1	X_2	X_3	Extent of cure
−1	−1	−1	11, 10
1	−1	−1	10, 10
−1	1	−1	100, 98
1	1	−1	99, 97
−1	−1	1	25, 26
1	−1	1	26, 20
−1	1	1	98, 99
1	1	1	100, 97
0	0	0	86, 82, 79, 79
−1	0	0	84
1	0	0	85
0	−1	0	20
0	1	0	95
0	0	−1	79
0	0	1	87
0	0	0	89, 87

been scaled so that their values range from −1 to 1, with the cube center point corresponding to the coordinates (0,0,0). The average results for each set of conditions are shown in Figure 1 at the appropriate positions on the design cube, and several qualitative inferences can be made by examining these values. Thus the effect of cure temperature (X_2) is pronounced, since experiments at 150°C gave cure values of 11, 10, 23, and 26, whereas the corresponding results at 250°C were 99, 98, 99, and 99. In contrast there appears to be little effect due to X_1 (time at 85°C). The effect of cure time (X_3) is clearly more complicated: at 150°C the change in cure with time is from 11 and 10 to 26 and 23, respectively, whereas at 250°C there is essentially no change. This indicates an interaction between the variables X_2 and X_3, an effect that would not be detected if a conventional one-variable-at-a-time approach had been used.

Regression analysis using these values and a first-order model (with interactions) leads to Eq. (1), where Y is the predicted degree of cure:

$$Y = 62.6 - 0.50X_1 + 40.6X_2 + 3.5X_3 + 0.25X_1X_2 - 0.13X_1X_3 - 3.5X_2X_3 \quad (1)$$

The replicate measurements can be used in a standard goodness-of-fit test, using the appropriate F statistic, to examine whether this model is acceptable or not. The result of this calculation is that the fit is not acceptable at the 95% confidence level, since the F statistic for the data is 161, whereas the critical F value for accepting the model is only 4.0. Geometrically this lack of fit is due to curvature of the response surface, for which the essentially first-order model (1) cannot account.

One approach to dealing with this problem is to use a full second-order model involving X^2 terms, but for this one needs to augment the design of

Figure 1 so that each variable is measured at three levels. In this study a face-centered design was chosen, i.e., additional experiments were run at points corresponding to the center of each face of the cube. These were not replicated, but two additional center points were measured and the order was randomized as before. These additional data points are given as the last seven rows of Table II. Regression analysis of these values leads to the equation

$$Y = 83.6 - 0.39X_1 + 40.3X_2 + 3.6X_3 + 0.91X_1^2 - 26.1X_2^2 - 0.59X_3^2 + 0.25X_1X_2 - 0.13X_1X_3 - 3.5X_2X_3 \quad (2)$$

In this case the model gives an acceptable fit at the 95% confidence level; the F statistic has a value of 0.5, and the maximum allowed value for accepting the model is 3.0.

One further refinement was carried out, viz. to eliminate those terms in (2) which do not contribute significantly to the fit. A backward elimination program was used,[7] in which variables are removed one at a time until only the essential terms remain. The final result is:

$$Y = 83.7 + 40.3X_2 + 3.6X_3 - 25.9X_2^2 - 3.5X_2X_3 \quad (3)$$

The variable X_1 does not appear in this final equation, i.e., the heating time at 85°C (for the range 2–20 min) has no effect on the subsequent cure. The interaction between temperature and time mentioned above is indicated by the presence of the X_2X_3 term.

The combined effect of temperature and time can best be seen in the contour plot of Figure 2, where the contours represent constant values of the extent of cure. The response surface rises quite rapidly to a flat plateau at temperatures higher than approximately 230°C. It is interesting that the cure is essentially complete even at short times (less than 10 min) at temperatures in the 230–250°C range.

Polyimide cure cycles generally involve a final treatment at 350–400°C. This helps remove any remaining solvent and has been reported to produce molecular ordering[8] or crystallization.[9] As Table III shows, however, this additional heating step does not change the extent of cure. These results were obtained from six separate randomized runs, with each sample receiving an "optimized" cure of 85°C for 10 min followed by 250°C for 10 minutes; three of the samples were given an additional treatment of 400°C for 30 min.

The effect of a stepwise cure involving lower temperatures was also ex-

TABLE III
Effect of Heating to 400°C on the Extent of Cure

Cured to 250°C	Cured to 400°C
97	95
95	98
99	99

TABLE IV
Effect of Stepwise Heating to 400°C on the Extent of Cure

Cured to 250°C	Stepwise cure to 400°C
95	79
97	82
99	75
95	73

amined: the sequence used was 85°/10 min, 150°/30, 200°/30, 300°/30, and 400°/30. Table IV shows the results for eight films run in randomized order; surprisingly, the stepwise cure produced films which were only 80% imidized or less. One explanation for this is that loss of solvent at 150° and 200°C, prior to full imidization, prevents complete cure at higher temperatures since the plasticizing effect of the solvent, required for facilitating the cyclization reaction, is no longer present. At 300°C or higher the uncyclized groups could be involved in side reactions such as decarboxylation or crosslinking, which might be reflected in altered properties such as thermal stability or mechanical strength. It has been observed[10] that samples heated to 400°C become insoluble in sulfuric acid, although this was attributed to molecular ordering rather than to chemical crosslinking.

In summary, it has been shown that short times (10 mins or less) are sufficient at high temperatures (230–250°C) to effect imidization of thin films of PMDA-ODA polyamic acid, and that heating at lower temperatures can lead to incomplete cure.

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