Low Temperature Curing of Polyimide Wafer Coatings

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Abstract

Polyimide films are commonly used on wafers as passivation layers, stress buffer layers, dry etch masks, structural layers, and re-distribution layers for chip scale packaging and wafer level packaging. These films are cured in convection or diffusion ovens at high enough temperatures (350-400°C) to assure adequate mechanical and electrical properties. These high temperatures can change the electrical properties of the devices. If the cure temperature of these films were lowered there could be a reduction in the film (and wafer) stress as well as a lower thermal budget for the devices. However, curing polyimide films at lower temperatures than 250°C has not been found to provide the mechanical, chemical, and dielectric properties required for the final device operation parameters or mechanical and dielectric protection.

This paper describes the use of variable frequency microwave (VFM) for the curing of existing polyimides at more than 50-150°C lower than the standard convection cure temperatures while maintaining the necessary final mechanical and chemical film properties. These films can be etched, patterned, metalized and further processed to make multi-layer structures. Further, we report on the continuing development of optimized polyimide materials suitable for curing at temperatures less than 200°C with VFM. Experiments to determine the relationship between molecular structure of the polyimides and the efficiency of microwave susceptibility are also described.

Microwaves and Polymer Films

The use of VFM in the curing of polymers has been reported for polyimides [1], BCBs, epoxies [2], and others. Microwave radiation acts on the molecular level by increasing the rotation of any dipoles in the backbone of the monomer, side chains, and all organic solvents and additives in the polymerization processes. Ring closures are enhanced and the activation energies of polymerization are decreased by 30-60%. Doped silicon wafers commonly used for electronic devices are also heated by the microwaves, which increases the thermal efficiency of the polymer film cure. Fortunately, there have been found no negative effects on the wafer devices at any level so the technique has been qualified for use with memories, microprocessors and other device structures.

There are other characteristics of microwave curing that are not at first intuitive. Since the mechanism of heating is not by conduction through the atmosphere, the cure chamber is not heated and neither are metallic, glass or ceramic fixtures. Cure profiles can be very rapid and the wafers can be removed soon after curing. The temperature of the film is directly monitored and is the basis for accurate closed-loop thermal control. Microwave curing of polymers is an especially opportune use of the technology but it is not a replacement for convection or diffusion heating in all cases.

Objectives and Approach

Because of the direct molecular action of microwaves on the polymer structure, there is an opportunity to "design the polymer" to be more efficiently coupled with the microwave energy. A simple example is the difference in the resultant dipoles of *cis*- (2.42 debye) and *trans*- (0 debye) diflouroethylene. The effective dipole moments of many polyimides are even higher (greater than 3).

This paper describes steps in a program designed to determine features and characteristics of polyimides that can be cured at substantially lower temperatures yet still provide the robust morphology and chemical resistance that make them highly desired in microelectronics applications. A similar program is underway for epoxy polymers as well.

The chemical and physical properties that will be evaluated include Tg, elongation, CTE (coefficient of thermal expansion), residual analysis (by TGA), % imidization (by FTIR), film thickness, and modulus. It is worth mentioning that the term "cure" usually implies the densification of the films beyond the imidization reaction and solvent removal. The most rigorous cure test of a polyimide film is the lack of out-gassing in subsequent processing steps.

The previously completed first steps of the program were to determine the feasibility of rapid curing and stress level reduction; low temperature cure; curing on different substrates, and the curing of thick (500um) coatings.

Results

HD Microsystems PI-2525 was chosen as a candidate for microwave curing. A designed experiment was run as a two-level, resolution IV experiment with six center points. The experiment was blocked with two fixtures. The power level is not continuous in the case of VFM but actually represents the duty cycle necessary to maintain the cure temperature profile selected. The variable settings are shown in Table 1:

Temperature	150C	160C	170C
Time	2 hrs	3 hrs	4 hrs
Power	140W	320W	500W
Vacuum	450 torr	600 torr	750 torr

Table 1

Temperature (0.0001>F) and time (0.0007>F) were found to be significant (Figs. 1,2) but power and vacuum had no effect (R^2adj = 0.921) with respect to % imidization.

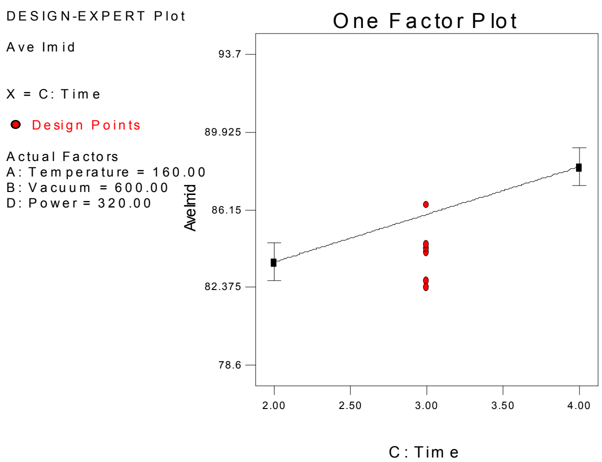

Figure 1

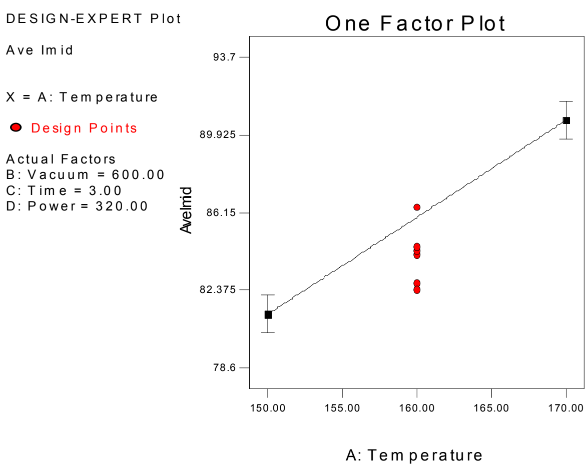

Figure 2

A level of 93% imidization, as measured with FTIR, was achieved with PI-2525 at 170°C and 4 hours with the VFM technique.

The next step was to determine structural features that directly affect the lowering of cure temperature. The selection of different lengths of the rigid chain monomer is the focus of this report. Since a shorter chain molecule would have more freedom of rotation and movement, it was proposed that it would be more receptive to microwave heating.

The HD Microsystems polyimide PI-2611 was chosen as the standard (100%) chain length example. The polyimides PIX-3400 and PIX-8103 have percent rigid chain lengths (PRCL) of 76% and 65% respectively. Other photosensitive polyimides, including HD-8800 (66% PRCL), are part of the study but not reported on here.

The designed experiment was a two-level factorial, resolution IV with three center points for curvature and estimate of experimental variance. The variables and levels are listed in the table below. In the case of the PRCL variable, a polyimide was selected as discussed above (Table 2).

PRCL	65%	76%	100%
Temperature	150C	175C	200C
Time	2 hrs	3 hrs	4 hrs
Power	180W	340W	500W

Table 2

The responses of Tg (Figure 3) and elongation (Figure 4) show a significant effect from PRCL despite a rather modest R^2(adj) value of 0.677.

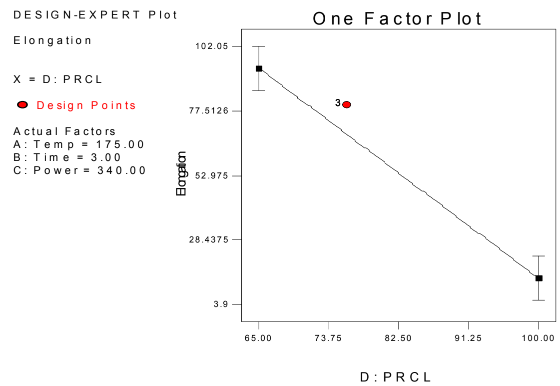

Figure 3

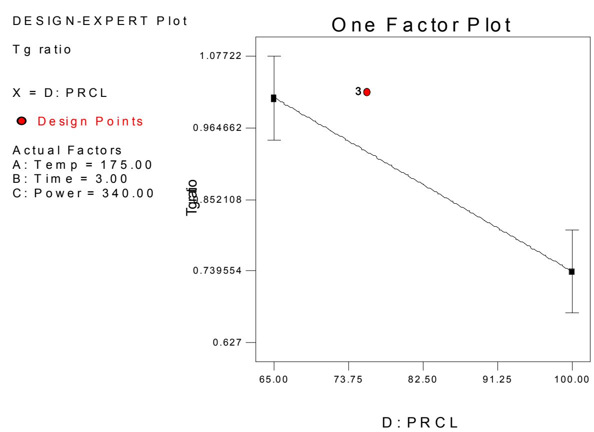

Figure 4

The 5% residual analysis temperature, as measured by TGA, was found to have strong interactions between temperature/time and temperature/power. The indications are that a profile of 150°C, 4 hours and 180 Watts provides the best cure.

The PIX-3400 material (used as the center point of PRCL) when cured at 175°C with VFM resulted in even better physical properties than 350°C curing (Table 3).

	Tg	Elong.	TGA5%	CTE	Mod.
Conv. 350°C	293°C	60%	-	50ppm	3.0GPa
VFM 175°C	299°C	120%	515°C	41ppm	2.8GPa

Table 3

In another experiment with an aqueous etch PBO polymer that is normally cured at 350°C for five hours in a diffusion oven at a semiconductor facility, the use of VFM reduced the cure to 225°C for four hours or 250°C for two hours. The measure of cure effectiveness was the lack of any out-gassing after the subsequent process steps of hot TMAH etch, dry, sputtered aluminum coating of the wafer, and a further 329°C heating test for twelve (12) hours.

Conclusions

Since this study is the beginning of a thorough evaluation of structural property relationships, there is still data being collected, results analyzed, and more experiments planned. At this point there are some clear indications however.

The use of shorter rigid chain lengths in the design of polyimides can be used to reduce cure temperatures well below 200°C with VFM. Tg, elongation, CTE, modulus, and residual analyses suggest that the low temperature VFM cured polyimides have similar morphologies to samples cured at much higher temperatures by conventional means.

References

1. Kohl, P.A. *et al*, *IEEE Transactions (CPMT)*, Vol 24, No.3 (2001), pp.474-481.
2. Garrard, R. *et al*, "Curing Low Yields & Reliability issues in Photonics Assembly", *Proc. Of the Pan Pacific Microelectronics Symposium*, Maui, Hawaii, February 2002.