

# Low Temperature Curing of Polymer Films for Wafer Level Packaging

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## Abstract

*The thermal cure of polyimides in excess of 300 °C for redistribution is a common process for wafer level packaging. Variable frequency microwave (VFM) curing at less than 200 °C has been shown to provide an equivalent cure method for some polyimides. The mechanism of microwave cure is discussed and compared with data taken from polyimides having varying backbone rigidity and dipole strengths. Use of these comparisons in designing more microwave-efficient polymers might provide even lower curing temperatures for the packaging of sensitive devices.*

Key words: wafer level packaging, polyimide, curing, microwave, low temperature

## Introduction

Wafer level packaging (WLP) often begins with the application and thermal cure of a dielectric material (usually a polymer). Subsequent steps may include additional layers of dielectric material alternating with patterned metal layers. The curing of thin polymer layers (5-20  $\mu$ m thick) is typically done at significantly higher temperatures than devices are normally exposed to during other processing steps in the packaging routine. Polyimides and polybenzoxazoles are commonly used for this process and are cured at 350°C or higher to obtain adequate physical and chemical properties.

Recent advances in polymer chemistries have provided somewhat lower temperature (250-300°C) curing materials or the end user has chosen to cure the polymers less fully and accepted reduced film quality. This allows the device manufacturer to reduce the thermal budget (time-temperature) seen by the devices or it allows a temperature-sensitive device to survive the packaging process.

The relatively new technique of Variable Frequency Microwave (VFM) curing has been shown<sup>1 2 3 4 5</sup> to reduce the curing temperatures of commercially available polymers to 150-200°C while providing film properties equivalent to the same polymers conventionally cured at 350°C. Curing times are also reduced with microwave curing as would be expected.

There is both a debate concerning the mechanism of this cure temperature reduction as well as interest in

optimizing the polymer structures to take advantage of this mechanism. This paper continues the discussion by comparing the efficiency of VFM cure on specific polymers with the mechanical and electronic features of those polymer structures.

## Theory

Microwave heating of insulating materials is the result of the electric field polarizing the dipoles in the material and the inability of this polarization to follow extremely rapid reversals of the electric field.<sup>6</sup>

The equation for reaction rate (k) depends on both the frequency of molecular collisions (f) and the orientation factor (p) besides the activation energy and temperature.

$$k = f p e^{(-E_a/RT)}$$

Clearly the imidization reaction of a polyimide (Figure 1), for example, would proceed at a faster rate if the excitation of the amic-acid dipoles and amine dipoles by microwave energy caused them to be in more frequent collisions and at more rapidly changing orientations.

It appears that molecular motions caused by electric fields are the root cause of the rapid and low temperature curing of these materials by microwaves. It is well known that the Gibbs free energy of a system is dependent on both the enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of that system.

$$\Delta E = \Delta H - T \Delta S$$

With conventional (convection or infra-red) heating, the whole of the material is progressively heated by

conduction so the entropy term is generally very small. With microwave heating the entropy of the system is much higher due to the specific localized heating of each of the dipoles throughout the bulk of the material simultaneously.

This mechanism is further enhanced by the rapidly varying frequency. The direction of polarization also keeps changing with the sweeping frequencies and its reflection from the walls of the cavity. The VFM sweeping is from 5.85 GHz to 7.0 GHz with a sweep time of only 0.1 second. With the bandwidth divided into 4096 frequencies, the resident time for each frequency is only 25 ns. In contrast to the standing wave pattern established with fixed frequency microwaves, there is not enough time to allow charge buildup even on metals, which makes it possible to process electronic components. This Variable Frequency Microwave environment has been determined to have no effect on semiconductor device properties by several semiconductor fabricators.

### Polymer Rigidity

It is well known that the T<sub>g</sub> of a polymer correlates with its percentage rigid chain length (PRCL).<sup>7</sup> Examples of rigidity includes aryl (-C<sub>6</sub>H<sub>4</sub>-) at 100%, ketone (-C-CO-C-) at 33% and ether (-C-O-C-) at 0%. Cosines of the bond angles are used relative to the main axis. As previously reported<sup>8</sup>, a linear relationship was found between the PRCL of some polyimides and the efficiency of VFM cure. This efficiency is calculated from the ratio of the T<sub>g</sub> of VFM cured films at 150-200°C to that of films cured by convection at 350°C. This relationship for five polyimides is demonstrated in the Figure 2. Polyimides with shorter rigid chain lengths (low PRCL) were cured to the same extent with VFM as convection but at much lower temperatures.

The multiple data points for each material represent a range of VFM curing temperatures and times as shown in Table 1. Note the significant difference between the apparently good fit of A, B, D, and E and the significantly more efficient cure of C. The glass transition temperature was used as the metric rather than percent conversion due to the inaccuracies of infra-red measurements at high conversions. The T<sub>g</sub> is also a more relevant property to microelectronics manufacturers.

Additional data on the properties of the VFM cured polyimides (Table 1) displays equivalent elongation, CTE, modulus, and volatile residuals as with higher temperature curing by convection.

The release of volatile solvents and water are assisted by the bulk heating property of VFM as well as the

efficiency of transport through a uniformly heated medium. This was further demonstrated by the lack of blistering of aluminum films sputtered onto a polymer film coated wafer which was baked at 330°C for twelve hours.

### Polarizability

It has been proposed<sup>9</sup> that the apparent low temperature curing of polymers with VFM is the result of "local" heating of the dipoles of the molecule to much higher temperatures than the bulk temperature as measured by surface probes (on either the film or wafer side). From this argument it might be expected that polymers with more and stronger dipoles would be better candidates for low temperature curing with microwaves.

Some calculations have been performed to determine the molecular induced dipole moments or polarizabilities of these same polyimides.<sup>10-11</sup> Each bond dipole has three vectors represented by b<sub>L</sub> (longitudinal), b<sub>T</sub> (transverse), and b<sub>V</sub> (vertical). Table 2 lists some of the vectors that were used in these calculations. One bond b<sub>L</sub> was chosen as the primary vector and the other dipole vectors were summed from the cosines of the bond angles in a matrix array.<sup>12</sup>

Ether and ketone linkages are commonly found in polyimide backbones in addition to the amic-acid reaction sites. These make up the majority of effective dipoles in these calculations since all of the polyimides here have amic-acid linkages. The amic-acid and amine structures were considered in the monomeric state for simplification. As the polymerization continues there is likely to be steric hindrance for further imidizations but this was not included in these calculations. Where the polyimides were mixtures the molecular polarizabilities were combined according to the percentages of each structure. A simple sum of the bond polarizabilities without respect to the bond angles was included since it could be argued that the VFM technique has a high amount of randomization of the electric field. The two sets of numbers were very similar as shown in Figure 3.

This result could either be interpreted as linear with some untreated factor(s) responsible for the lack of fit; or as a curve demonstrating a "saturation" of the polarizability effect. Note that the vector array sums are only somewhat higher than the simple sums.

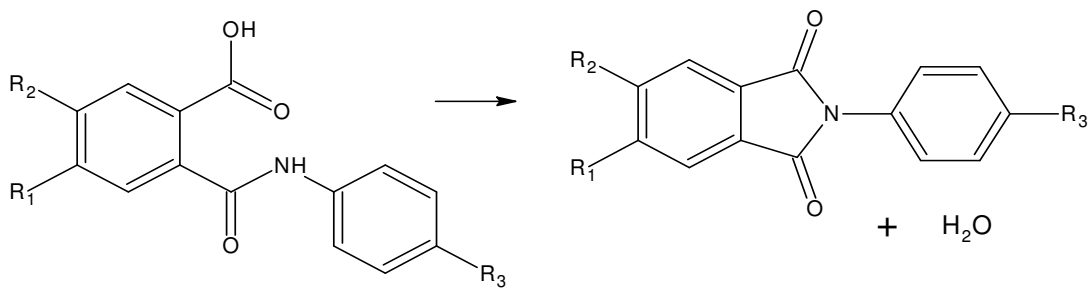
### Conclusions

From the data above, it is clear that lower microwave cure temperatures for polyimides can be used if the polymer backbone is less rigid. There is also a

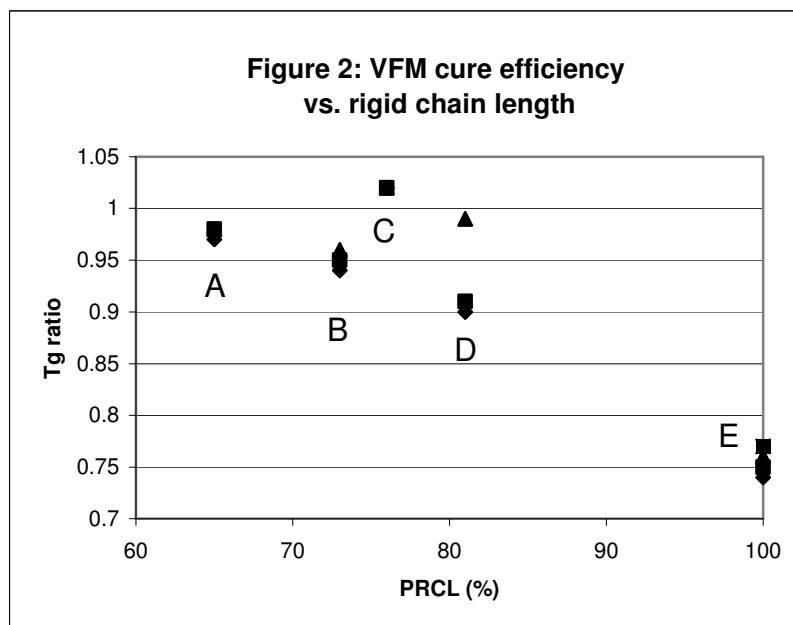
reduction in cure temperature when more dipoles are included in the structure in addition to the ones at the reaction site. In both respects, polyimide C deviated from linearity the most but the reason(s) are yet unclear and under investigation. The fact that polyimide E was the most rigid and contained the fewest dipoles makes conclusions less clear but the relationship between rigidity and low temperature cure with VFM is more convincing than the numbers of dipoles even though the movements of the dipoles

are the source of heating. With more studies it may be possible for polyimides and other polymers to be designed specifically for VFM curing at even lower temperatures.

In practical application for wafer level packaging it has been shown that much lower cure temperatures are possible with VFM heating which, in turn, allows more temperature sensitive devices to be added to the list of WLP candidates.



**Figure 1: The imidization reaction of polyimides**

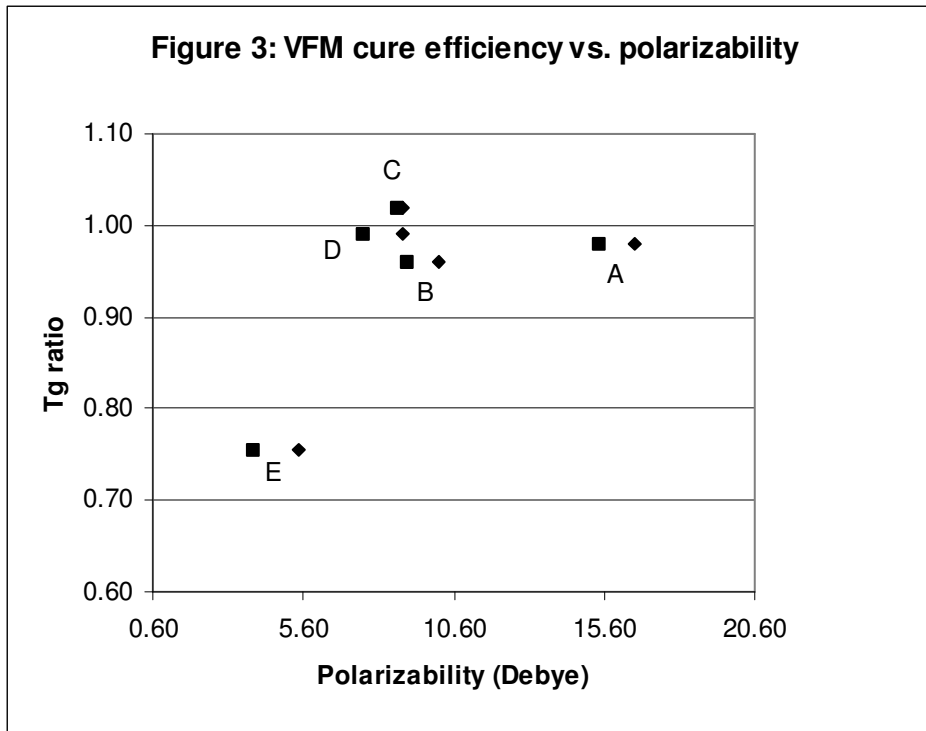


Polyimide	PRCL	No	Cure	T <sub>g</sub>	CTE	Elongation	TS	Modulus	TG-DTA	T <sub>g</sub>	T <sub>g</sub>
			Temp			Max			3%		
			(deg C)	(deg C)	(ppm)	(%)	(MPa)	(GPa)	(deg C)	(deg C)	
D	100	2	200	266.3	26	5.8	157	6.1	355	351	0.76
	100	4	200	268.8	12	4.7	143	5.6	334	351	0.77
	100	5	200	260.7	9	32	296	6.4	470	351	0.74
	100	6	200	263.3	9	43	301	6.8	497	351	0.75
C	76	1	175	299.1	42	120	140	2.9	450	293	1.02
	76	2	175	298.4	45	47	127	2.8	474	293	1.02
	76	3	175	298.9	37	87	128	2.8	474	293	1.02
A	65	1	150	223.6	79	129	127	2.5	443	230	0.97
	65	2	200	225.3	105	137	131	2.3	497	230	0.98
	65	4	200	224.8	93	119	120	2.2	492	230	0.98
B	73	2	175	249.1	30	37	130.2	2.67	489.6	262	0.95
	73	3	175	246.4	35.4	36.7	119.1	2.63	483	262	0.94
	73	4	200	252.3	30.8	88.9	166.6	2.92	496.1	262	0.96
E	81	3	175	243	36.6	2.9	60.9	3.49	469.6	269	0.90
	81	4	175	245.7	48.1	53.5	102.6	3.8	459.1	269	0.91
	81	5	200	267.2	30.6	65.8	159.8	3.36	489.8	269	0.99

**Table 1: Properties of VFM cured polyimides**

Bond	Context	$b_L$	$b_T$	$b_V$
C-H	Alkane	0.65	0.65	0.65
C-C	Alkane	0.97	0.26	0.26
C-C	Cyclopropane			
C-C	Cyclobutane			
C=C	Alkene	2.80	0.73	0.77
C≡C	Alkyne	3.79	1.26	1.26
Ar-Ar	Biphenyl			
C-F	MeF	1.2	0.4	0.4
C-Cl	Mea	3.18	2.2	2.2
C-Cl	<i>t-BuCl</i>	3.94	1.81	1.81
C-Cl	PhCl	4.2	1.9	1.5
C-Br	MeBr	4.65	3.1	3.1
C-Br	<i>t-BuBr</i>	5.98	2.6	2.6
C-Br	PhBr	6.4	2.4	2.2
C-I	MeI	6.7	4.8	4.8
C-I	<i>t-BuI</i>	9.2	3.7	3.7
C-I	PhI	9.1	5.3	3.3
c-o	Ether	0.9	0.46	0.46
c-o	Acetal			
C=O	Ketone	2.3	1.4	0.5
N-H	Ammonia	0.5	0.83	0.83
C-N	Amine	0.57	0.7	0.7
N-N	Hydrazine			
N=N	Azo			
C=N	Imine			
C≡N	Cyanide			
C-S	Sulphide	1.9	1.7	1.7
C-CN	<i>t-BuCN</i>	4.0	1.5	1.5
S-S	Disulfide			

**Table 2: Bond Polarizabilities<sup>13</sup>**



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