High-temperature stability of a polyimide film

by R. Ginsburg
J. R. Susko

Polyimide (PMDA-ODA) films were analyzed by mass spectroscopy to determine their high-temperature stability. Using a high-resolution instrument, the identity of the low-molecular-weight evolved gases was confirmed. With a semiquantitative technique, the effect of a vacuum pre-bake was shown to reduce outgassing appreciably during subsequent treatment at high temperature. Subjection of the films to moisture did not affect their thermal stability. Low-temperature processing (240°C vs 400°C) reduced gaseous evolution by an order of magnitude.

Introduction

Superior mechanical, electrical, and thermal performance of polyimides has led to their widespread use for electronic applications. The material generally serves as a dielectric insulator between metal circuit layers. The application of the metal layers by conventional evaporation or sputtering techniques usually necessitates the use of high temperature and low pressures.

Prior to the deposition of metal, the dielectric layer has generally been exposed to a number of wet chemical processes including immersion in aqueous solutions and organic solvents. It has been shown that polyimide-type materials can readily absorb water vapor to levels as high as two to four weight percent [1, 2]. Unpublished experimental data suggest that chlorinated process solvents can be absorbed to weight percent levels greater than that of water vapor. The physical absorption process is reversible. Diffusion kinetics of thin films dictates that 95 to 99 percent of the physically absorbed solvent will effectively be removed during the first few minutes of a vacuum bakeout process [3]. The question arises as to the tenacity of the residual solvent remaining within the molecular structure of the material.

During a metallization process, one would surmise that outgassing species, if of sufficient quantity and velocity, could adversely affect or interfere with the impact velocity of the metal particles striking the surface of the polyimide. An optimized process requires a reasonable assessment of the quantities of outgassing species as well as an understanding of the origin of the gases.

The technique chosen to address this problem was mass spectroscopy using an instrument equipped with a capacitance manometer for volumetric measurements. From earlier unpublished work, it had been determined that 15–20 minutes at high vacuum [1.33×10^{-4} Pa (10^{-6} torr)] as the sample was raised and maintained at high temperature (400°C) was the time required for the degassing to peak and fall to a steady state. Carbon dioxide was the primary effluent when the mass range greater than 40 atomic mass units (amu) was scanned. This preliminary work also established that solvents used in processing polyimides including n-methyl pyrollidinone, the predominant solvent in the precursor solution, were not detectable if a final cure was interposed between solvent exposure and mass spectroscopy. For this study, we explored the mass range of 2–100 amu for a more comprehensive analysis of outgassing species. To clarify the qualitative data, i.e., to resolve the identity of gases having the same atomic mass number, an initial experiment was performed with a high-resolution instrument. The remaining experiments were designed to

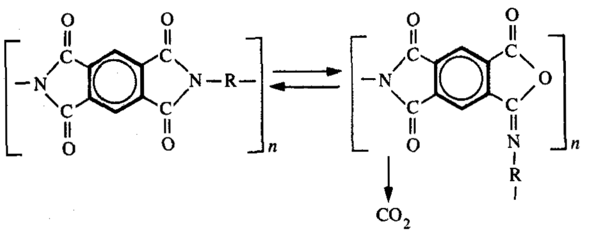

Figure 1

Proposed scheme for CO_2 evolution. Equilibrium between polyimide and polyisoimide maintains concentration of isomer, which heating emits CO_2.

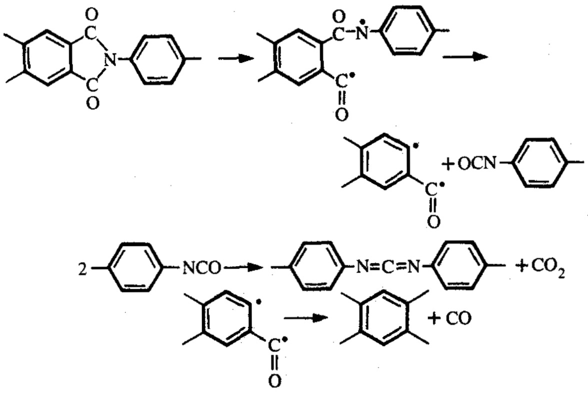

Figure 3

Mechanism suggested for CO_2 and CO emission from polyimide ring opening and formation of isocyanate and carbodiimide. From Ref. [9], reprinted with permission from John Wiley & Sons, Inc.

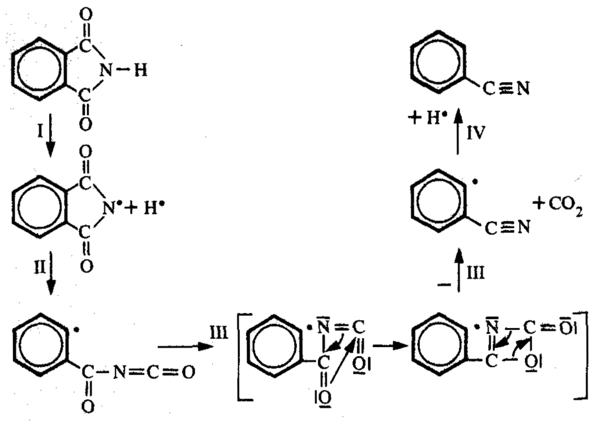

Figure 2

Mechanism proposed for CO_2 generation from model compound via ring opening and rearrangement. From Ref. [8], reprinted with permission from Pergamon Press, Ltd.

provide quantitative estimates of outgases as affected by moisture exposure and reduced process temperature.

Background of previous work

Detection of low-molecular-weight gases from polyimide at high temperature has been reported in several papers. Some sources and mechanisms have been proposed for the generation of these gases. Much of the experimental work has been done with monomeric model compounds or with compounds which are precursors to polyimides. From free acids and anhydrides, CO_2 and CO have been detected, while free amine was shown to emit H_2 [4]. An amide (n-phenyl benzamide) was also shown to emit CO_2, CO, and H_2 at higher temperature. Uncyclized polyamic acid is also a source of CO_2 and, of course, H_2O [5]. Absorbed H_2O must also be considered as a gaseous source. The quantity of water in films equilibrated at varying humidity has been determined for several polyimides [1, 2]. ®Kapton film (E. I. du Pont de Nemours & Co., Inc.), a material chemically the same as the cured pyromellitimide of this study, was shown to absorb up to four percent moisture by weight.

Gay and Berr [6] proposed that the source of CO_2 evolution at high temperature was the degradation of an isomeric form of the imide, isoimide. They suggested that an isoimide concentration is maintained due to an equilibrium between the two forms and that the isomer undergoes a thermolysis on heating, evolving CO_2. A schematic of isoimide degradation is shown in **Figure 1.** In a more recent study, however, synthesized polyisoimide was observed to convert totally to the imide on heating [7].

Mechanisms have been proposed for the generation of CO and CO_2 by imide ring cleavage and molecular rearrangements. With model compounds Zurakowska-Orszagh et al. [8] detected products suggesting the scheme shown in **Figure 2.** Ehlers et al. proposed a degradation of the polymer to form carbodiimide, CO_2, and CO [9], shown in **Figure 3.** This mechanism was based on interpretation of infrared spectra of partially degraded films. Yet another scheme was proposed for thermal degradation when a small amount of moisture is present. It was suggested that the imide could be hydrolyzed to the anhydride which would decompose, releasing CO and CO_2 [8] as suggested in **Figure 4.**

Experimental procedures

Film preparation The polyimide material under investigation was N,N′ bis (phenoxy phenyl) pyromellitimide formed from pyromellitic dianhydride and oxydianiline via a polyamic acid precursor, as indicated in **Figure 5.** Films were prepared by spin-coating a commercially available polyamic acid solution on uncoated silicon wafers. The films were then subjected to a series of thermal treatments beginning with a low-temperature drying step at 85°C and ending with a final high-temperature cure (360°C in N_2 for 30 minutes). This treatment is consistent with general recommendations to achieve optimum film properties.

The average thickness of the films was 10.3 ± 1.1 μm as determined by light section microscopy.

Mass spectroscopy An initial experiment was run to confirm the identity of the atomic mass unit (amu) 28 as either CO, N_2, or a mixture of the two gases. The high-resolution instrument employed was a Vacuum Generators MM 7070-H double-focusing mass spectrometer. The polyimide sample film was peeled from the silicon wafer and inserted via the direct probe of the instrument. The mass resolution was adjusted so that CO, N_2, and C_2H_4 were completely separated (approximately 3000 resolution, M/ΔM, 10% valley). The experiment was run in a multiple ion detection mode so that the monitoring of CO, N_2, and CO_2 was virtually simultaneous. The contribution to CO from fragmentation of CO_2 was calculated and corrected. The correction factor was determined by examining a reference standard. The sample chamber was programmed to heat at a rate of 25°C/min from ambient to 400°C and to remain at that temperature for a total time of 50 minutes. This thermal program was selected to simulate the temperature excursion one might expect in a metallization process. Correction for background was accomplished by subtracting the result of an identical run with an empty capillary tube. The operating pressure of the instrument was measured at 1.33×10^{-4} Pa (10^{-6} torr).

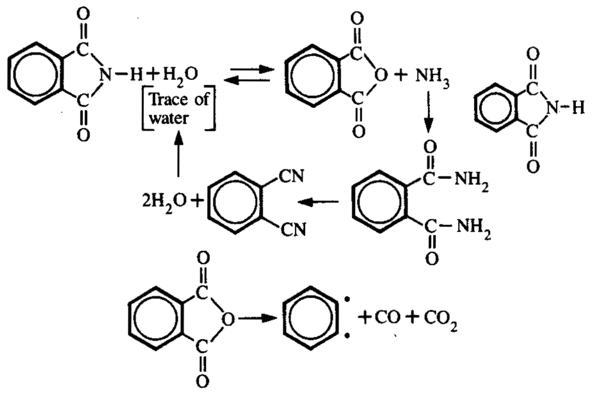

Figure 4

Proposed side reaction for hydrolysis of imide to anhydride which further degrades, releasing CO and CO_2 [8], reprinted with permission from Pergamon Press, Ltd.

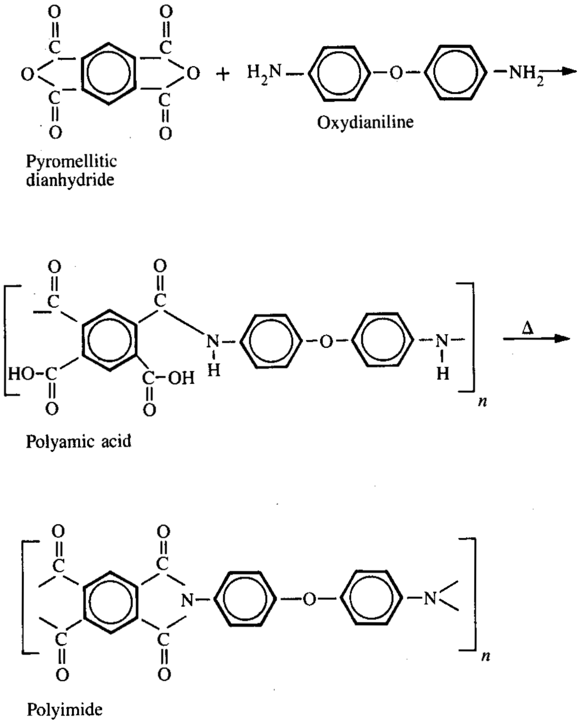

Figure 5

Synthesis of polyimide from starting material via polyamic acid.

For the detection and quantification of the major effluents, experiments were performed on a Consolidated Electrodynamics Corporation Model 21-620 mass spectrometer equipped with a capacitance manometer. The detection range was 2–100 amu and the estimated pressure between 1.33×10^{-3} Pa and 1.33×10^{-4} Pa (10^{-5} and 10^{-6} torr). The experimental program was as follows. Two samples of film were each subjected to an initial thermal program from ambient temperature to 400°C. The temperature was raised at 25°C per minute and maintained at 400°C for 30 minutes. The total outgas from each film was measured in the manometer and then introduced into the spectrometer for analysis. These films were then maintained for an overnight period in two storage

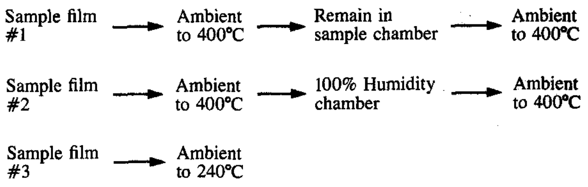

Figure 6

Scheme for low resolution experiment.

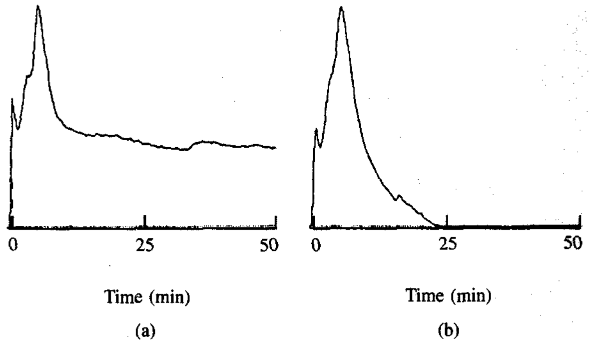

Figure 7

Intensity of CO and CO_2 during high-resolution experiment. CO evolution (a) reached a maximum and declined to low-level steady rate of evolution while CO_2 (b) dropped to detection limit.

conditions. One film remained in the sample compartment at ambient temperature in vacuum, and the other film was maintained at 100% humidity in a sealed container with a beaker of water.

The purpose of this experimental procedure was to determine whether the total outgas declined after an initial thermal excursion and to evaluate the impact of moisture. For example, it was of interest to know whether exposure of the film to humidity would result in hydrolysis of the material, making it more vulnerable to subsequent thermolysis.

Finally, an additional (and equivalent) film sample was analyzed after one thermal run. This sample was taken to a maximum temperature of 240°C and held there for 30 minutes. The purpose of this experiment was to learn if the volume of outgas would be substantially less if the material was processed at reduced temperature. A schematic of this experimental setup is shown in **Figure 6.**

Mass spectrometric data

The high-resolution experiment confirmed that both CO and N_2 evolved from the material. The patterns of evolution for CO_2 and CO are shown in **Figure 7.** The CO evolution reached a maximum and then declined to a steady state, while the CO_2 evolution peaked and then dropped to the detection limit. These patterns suggest that the source of the CO_2 is from defects such as unreacted carboxyl groups, while the CO is from the long-term degradation of the polyimide.

The low-resolution experiment detected CO_2, CO, H_2O, H_2, N_2, and at 240°C, NO, as the major effluents of the film. Small amounts of H_2S and hydrocarbons were also detected. The volume percents of the individual gases were calculated from their respective intensities in the mass spectrometer. Although CO and N_2 could not be resolved in the low-resolution instrument, their levels were evaluated from the intensities of their fragmentation products. The volume percents of evolved gases are shown in **Table 1.** The original sample weights, the weight losses after analyses, and the total volumes of gas emitted are presented in **Table 2.** The volumes of effluents for a 100-mg sample for each run are shown in **Table 3.**

While the results of the low-resolution experiments are presented as numerical data, it should be kept in mind that the technique is not truly quantitative. Particularly when a considerable part of the effluents is water, there is the problem of incomplete detection of gases due to adsorption on surfaces. It is important to note that the data should be interpreted as indicative of trends. It is not possible to calculate a mass balance between sample weight losses and volumes detected.

Nevertheless, the data do show changes in the relative amounts of the major effluents. In the initial run, CO_2, H_2O, and H_2 were predominant, followed by CO and N_2. In the second run of the sample maintained in vacuum, the relative quantities of CO_2 and H_2O decreased, CO decreased markedly, H_2 became the primary effluent, and N_2 remained at the same level. When the film was exposed to moisture, water became the major effluent, the other constituents showing the same trend as in the dry sample.

When the volumes of gas for 100-mg film samples were calculated, a considerable decline in CO_2, CO, and H_2O evolution was observed, while H_2 and N_2 remained at about the same magnitude. With the sample humidified between runs, the same behavior was noted except that moisture was the dominant effluent.

The relative quantities of gases detected when the film was heated to 240°C were comparable to the initial runs at higher temperature for CO_2, CO, and N_2. However, H_2O constituted the major effluent and very little H_2 was generated at the lower temperature. The overall volume showed reduction of about one order of magnitude.

Conclusions

The gases emitted at process temperatures up to 400°C from films of the polyimide, N,N′ bis (phenoxy phenyl) pyromellitimide, were determined. The volumes of gases

Table 1 Volume percent of gases determined by mass spectroscopy for outgases collected from polyimide film samples in the low-resolution experiment.

	No. 1		*No. 2*		*No. 3 (240°C)*
	(1st run)	*(2nd run)*	*(1st run)*	*(2nd run)*	
CO_2	21.68	14.17	23.91	14.91	21.47
CO	9.17	0.21	7.90	1.5	11.33
H_2O	24.17	6.12	39.00	48.31	53.79
H_2	37.60	72.14	20.78	30.16	2.08
N_2	5.15	5.52	4.40	3.25	4.77
CH_4	0.65	0.54	0.46	0.42	0.93
H_2S	0.56	0.56	0.48	0.77	—
C_2H_4	0.12	0.26	0.26	0.38	0.11
C_4H_8	0.57	0.44	2.07	0.1	1.54
C_5H_{10}	0.04	0.03	0.19	0.2	0.98
C_7H_{14}	0.06	—	0.38	—	—
Benzene	0.12	0.01	0.10	—	0.49
Toluene	0.12	—	0.11	—	0.26
NO	—	—	—	—	2.22

emitted from the sample films were very small. By using a high-resolution mass spectrometer, the evolution of both CO and N_2 was confirmed. Based on the patterns of evolution observed, our data would favor a mechanism in which carbon monoxide is generated from the gradual degradation of the polyimide itself, while carbon dioxide may result from the thermolysis of incompletely reacted compounds.

The low-resolution experiments identified CO_2, CO, H_2O, H_2, and N_2 as the major effluents at elevated temperature. The low-molecular-weight gases detected are in general agreement with what has been reported in the literature. Although no explanation was found for large-scale generation of hydrogen from polyimide, we learned that hydrogen is commonly observed as an effluent during thermolysis of many polymers [10]. The source of the small concentrations of hydrocarbon fragments detected is attributed to contamination by ubiquitous ambient organic vapors.

The data indicated that a substantial reduction in effluent occurs if the film has had an initial vacuum bakeout. The gaseous evolution from a thermally conditioned film subsequently subjected to high humidity suggested no real hydrolytic degradation. It is generally accepted that polyimide materials are strongly resistant to chemical interaction with pure water.

The experiment run at reduced (240°C) temperature showed a decline in gaseous effluent by one order of magnitude. Also, the gaseous composition of this effluent suggests that more degassing and less thermolysis occurred in comparison with the high-temperature runs.

In the scope of this experimental effort, we did not collect data over a broad temperature range which would permit the determination of activation energies for thermal degradation. This information would be valuable in understanding the kinetics of the thermal decomposition of the polyimide film.

Table 2 Recorded sample weight losses and total gas evolution as measured by capacitance manometer for low-resolution samples.

	Sample weight (mg)	*Weight loss* (mg)	*Total gas evolved* (ml)	*Sample weight* (ml/mg)
No. 1 (1st run)	86.67	0.73	0.255	0.0029
No. 1 (2nd run)	85.94	0.57	0.105	0.0012
No. 2 (1st run)	68.54	0.33	0.116	0.0017
No. 2 (2nd run)	68.21	0.12	0.116	0.0017

Table 3 Volumes (ml) of major effluents* calculated for low-resolution, 100-mg samples.

Gas	*Sample 1*		*Sample 2*	
	Run 1	*Run 2*	*Run 1*	*Run 2*
CO_2	0.063	0.017	0.041	0.025
CO	0.027	0.0002	0.013	0.003
H_2O	0.072	0.007	0.066	0.082
H_2	0.110	0.088	0.035	0.051
N_2	0.015	0.007	0.007	0.006

* At standard pressure, ambient temperature.

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Rochelle Ginsburg *IBM Systems Technology Division, P. O. Box 6, Endicott, New York 13760.* Ms. Ginsburg is a senior associate chemist in a materials science organization. She joined IBM in 1978 at Endicott. She received a B.A. in chemistry from Temple University, Philadelphia, Pennsylvania, in 1962, and an M.A. in biological sciences from the State University of New York, Binghamton, in 1971. Ms. Ginsburg is currently involved in polymer characterization for packaging applications in Endicott.

John R. Susko *IBM Systems Technology Division, P. O. Box 6, Endicott, New York 13760.* Mr. Susko is an advisory/development engineer currently managing a materials science development group. He joined IBM in 1969 in Endicott and in 1972 received a B.S. in chemistry from Elmira College, New York. Mr. Susko holds several IBM patents and has published many papers in the field of permeation and diffusion of gases and vapors in polymers.