Journal of Thermal Analysis, Vol. 49 (1997) 589-594

THERMAL DECOMPOSITION OF POLY($\alpha,\alpha,\alpha',\alpha'$-TETRAFLUORO-*p*-XYLYLENE) IN NITROGEN AND OXYGEN

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Abstract

The thermal decomposition of poly($\alpha,\alpha,\alpha'\alpha'$-tetrafluoro-*p*-xylylene) (parylene AF-4) films with thicknesses of ca. 7.5 and 10 μm has been studied by both dynamic (10°C min^{-1}) and isothermal TG in either nitrogen or oxygen atmospheres.

In dynamic studies with nitrogen, gross decomposition occurs between 546.7±1.4 and 589.0±2.6°C, with 26.8±4.4% of the initial mass remaining at 700°C. With oxygen as the purge gas, the onset of decomposition shifts slightly to 530.8±4.2°C. The end of the transition at 587.4±2.6°C is within experimental error of the nitrogen value, but no polymer remains above 600°C.

Isothermal data were obtained at 10°C intervals from 420 to 490°C in nitrogen, and from 390 to 450°C in oxygen. Plots of log(Δ%wt/Δt) *vs.* T^{-1} are linear throughout the specified range for oxygen and from 420 to 470°C for nitrogen. The calculated activation energies of (147±16) kJ mol^{-1} and (150±12) kJ mol^{-1} in N_2 and O_2, respectively, are equal within experimental error.

Keywords: decomposition, parylene, poly($\alpha,\alpha,\alpha'\alpha'$-tetrafluoro-*p*-xylylene), TG

Introduction

The desire to enhance the speed of electronic signal transfer has led to the need for new materials for semiconductor devices. To increase the speed of signal movement, the RC product of the interconnection system must be reduced. Because resistances have increased as the dimensions of the metallic lines have become smaller, the only workable variable is the capacitance. Since other factors dictate the dimensions, the capacitance must be controlled by means of the dielectric constant, *K*, of the Interlayer Dielectric (ILD), which is the insulator between the several layers of metallic connections. For over 40 years the ILD material has been silicon dioxide, which has a *K* of about 4. The semiconductor industry is now seeking a material with lower *K* for the ILD in future high-speed devices.

The choice of material will be determined by the ability to satisfy several design considerations. Of particular importance to this study is the need to form several subsequent layers of metallic connections and dielectric. At the present time, these processes are performed at 300–400°C. Thus, the new dielectric must be capable of withstanding repeated exposure to temperatures of this magnitude.

0368–4466/97/ $ 5.00
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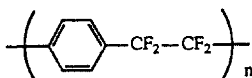
A material which meets these demands, and which is currently being considered by Sematech, the Austin-based research consortium of semiconductor manufacturers, is the polymer of α,α,α′α′-tetrafluoro-*p*-xylylene:



Parylene AF-4

Polymers of *p*-xylylenes are generically referred to as parylenes, and the above compound is conveniently called parylene AF-4. This material has a dielectric constant of 2.35 [1], and can be formed by the Gorham vapor deposition process [2] to give films which replicate submicron features of the underlying layer. The polymer has also been noted for its ability to withstand temperatures in the range mentioned above. A thermal decomposition study has been reported in the literature [3], but the polymer was prepared by gas-phase dehalogenation of the perfluoroxylene, and the TG curves indicate the presence of impurities. For proper evaluation of parylene AF-4 as a semiconductor material, a more controlled study of thermal properties is needed. This paper presents TG results for parylene AF-4 in both nitrogen and oxygen atmospheres.

Experimental

Materials

Parylene AF-4 films (ca. 7.5 and 10 μm) were prepared using the Gorham process by Roger Olson of Specialty Coating Systems, Clear Lake, WI. The films were cut into small pieces (ca. 4 mm^2) to fit into the TG pan. Two to three pieces were used for each analysis to give an initial weight of ca. one milligram.

The nitrogen was supplied as $N_{2(g)}$ from the departmental $N_{2(l)}$ supply, and was passed through a moisture filter between the laboratory valve and the TG flow meters. High-purity oxygen, obtained from Bitec, Tampa, FL, was used without further purification.

Nickel powder and iron wire were obtained from Fisher Scientific and Merck, respectively. Perkalloy wire was purchased from Perkin-Elmer.

Instrumental procedures

All TG measurements were performed using a TA Instruments 2950 Thermogravimetric Analyzer with Thermal Analysis 2000 software. Four temperature calibrations were used: room temperature measured by a mercury thermometer, and the Curie points of nickel (358.0°C [4]), Perkalloy (596.0°C [5]), and iron (780.0°C [6]). Gas flow rates were checked prior to each analysis and were maintained at 20–22 $cm^3 min^{-1}$ in the balance area and 38–40 $cm^3 min^{-1}$ in the furnace. A new platinum TG pan was used solely for this study and was flamed and tared prior to

each analysis. A heating rate of 10°C min^{-1} from room temperature to 800°C was used for all dynamic measurements. For isothermal degradation studies, the samples were heated at 10°C min^{-1} to the desired temperature, held isothermally for 3 h, and then heated at 10°C min^{-1} to 800°C. Separate samples were used for each isothermal study.

Elemental (C/H/N/F) analysis of the residue material was performed by Quantitative Technologies, Inc., Whitehouse, NJ.

Data and results

Figure 1 shows TG curves of parylene AF-4 heated at 10°C min^{-1} to 800°C in nitrogen and oxygen. Data from 16 analyses in N_2 give average values (± standard deviation) of 546.7±1.4°C and 589.0±2.6°C for the temperature limits of the gross decomposition, with 26.8±4.4% of the original weight (evaluated at 700°C) remaining. To determine the chemical content of the remaining material, fourteen samples of AF-4 were heated at 10°C min^{-1} to 700°C, and the residues were collected. Analysis for C/H/N/F gave the following results: 79.47% C, 1.95% H, and 3.56% F. The identity of the remaining 15.02% is not known.

In oxygen the onset for total decomposition shifts to 530.8±4.2°C (8 samples), but the end of the transition at 587.4±2.6°C is within experimental uncertainty of the value obtained in nitrogen. There is no residue above 600°C.

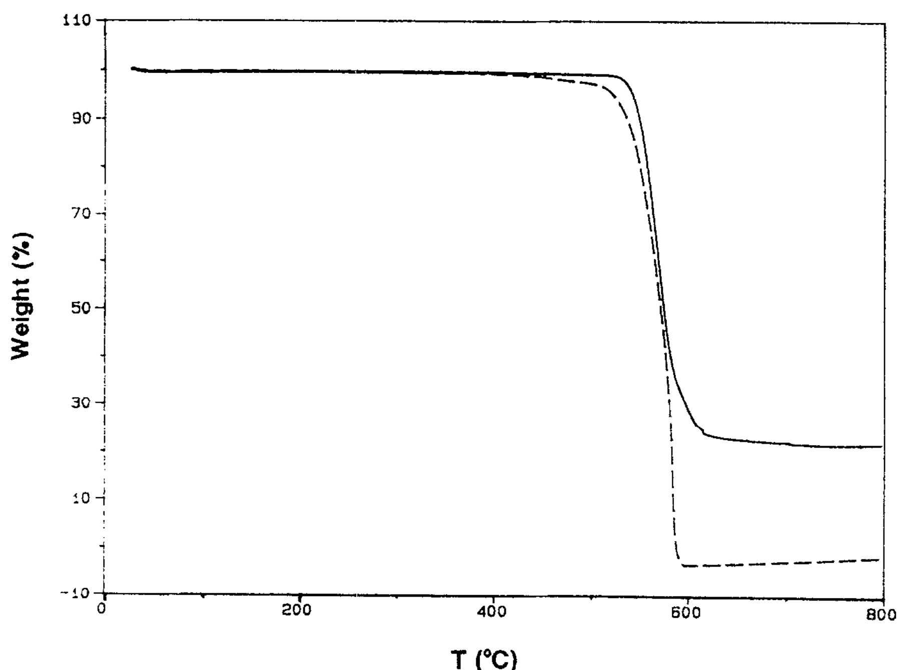


Fig. 1 TG curve of parylene AF-4 heated at 10°C min^{-1} in nitrogen (solid line) and oxygen (dashed line)

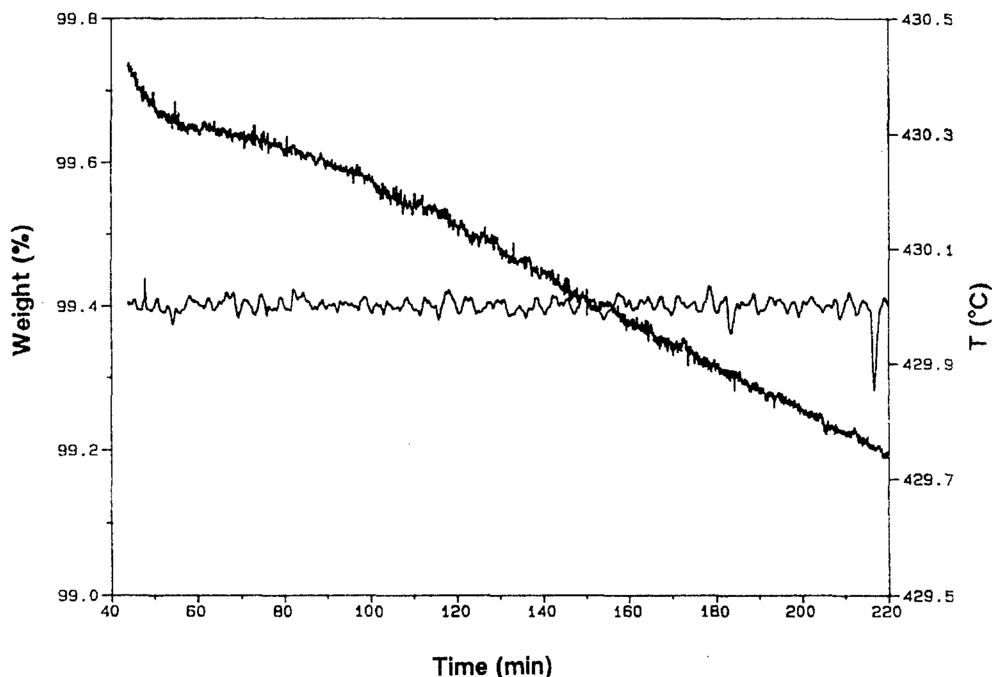


Fig. 2 Plot of %wt *vs.* time for parylene AF-4 heated isothermally at 430°C in nitrogen

Table 1 Decomposition rates for 10 μm parylene films heated isothermally in nitrogen and oxygen

Purge gas	Temperature/°C	Δwt %/Δt(% h^{-1})
Nitrogen	420	0.119
	430	0.199
	440	0.230
	450 (2)	0.289, 0.248
	460	0.546
	470 (2)	0.715, 0.658
	480	1.69
	490	9.56
Oxygen	390 (2)	0.284, 0.242
	400 (2)	0.458, 0.347
	410	0.469
	430	1.400
	450 (2)	3.62, 2.18

To evaluate the effects of prolonged heating at temperatures below the onset of gross decomposition, parylene AF-4 films were heated isothermally for 3 hours. The isothermal temperatures were spaced at 10° intervals from 420 to 490°C in nitrogen and from 390 to 450°C in oxygen. A fresh sample was used for each isothermal temperature. Figure 2 is a plot of both wt% and actual temperature as a function of time for a 0.8240 mg sample heated for three hours at 430°C in nitrogen. The excellent temperature and balance stability are typical of all the isothermal data obtained in the study.

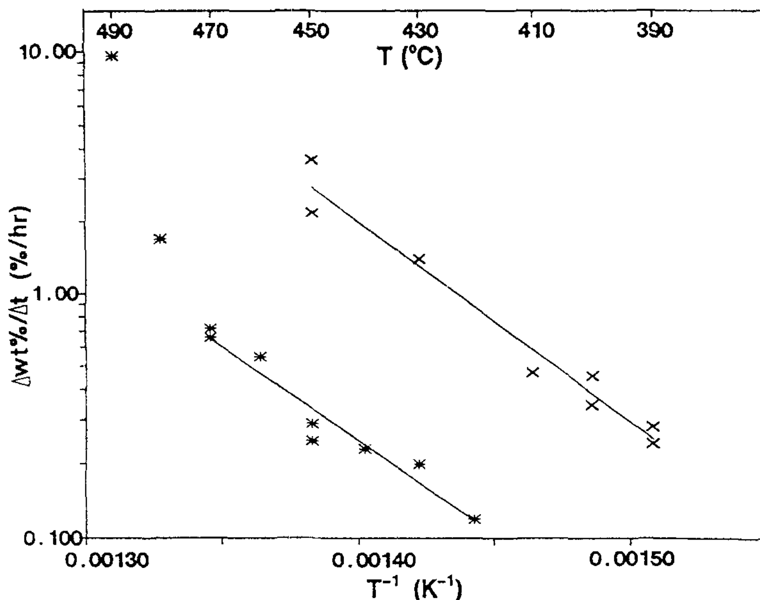


Fig. 3 Plot of log(Δwt%)/Δ*t* *vs.* T^{-1} for parylene AF-4 in nitrogen (*) and oxygen (×)

The values of Δwt%/Δ*t*, which were determined graphically from the slopes of the isothermal data sets, are provided in Table 1, and the corresponding Arrhenius plots are shown in Fig. 3. In oxygen the data demonstrate good linearity throughout the observed temperature range, but the nitrogen plot shows significant upward curvature for the 480 and 490°C values, possibly indicating a change in the decomposition reaction and/or mechanism. The slopes in the linear regions were multiplied by $-2.303R$ to obtain the activation energies. The values, 147±16 kJ mol^{-1} in nitrogen and 150±12 kJ mol^{-1} in oxygen, are equal within experimental uncertainty, indicating that the mechanism of decomposition is probably the same in the two gases in these temperature regions. The pre-exponential factors are $(1.3\pm3.4)\times10^{10}$ in N_2 and $(9\pm19)\times10^{11}$ in O_2. Despite the large uncertainties, it is clear that decomposition starts at a lower temperature in oxygen. This may be due to stabilization of the nascent products by oxygen, thus hindering recombination in the initial stages of degradation.

Conclusion

Careful TG studies have demonstrated the excellent thermal stability of parylene AF-4. When the polymer is heated at 10°C min^{-1}, the onsets for gross decomposition occur well above 500°C in both nitrogen and oxygen. The polymer is somewhat more stable in nitrogen than in oxygen, but the effect is not large. Isothermal decomposition rates less than 0.5 wt% h^{-1} are observed from 390 to 410°C in oxygen, whereas this range is shifted upwards by only about 40° (420 to 450°C) with nitrogen as the purge gas.

* * *

The author thanks Dr. William F. Beach for his guidance throughout the study and Mr. Russell Pierce for careful maintenance of the instrument.

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