

# Structure and Electrical and Magnetic Properties of Polyimide Films Pyrolyzed at High Temperature

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## SYNOPSIS

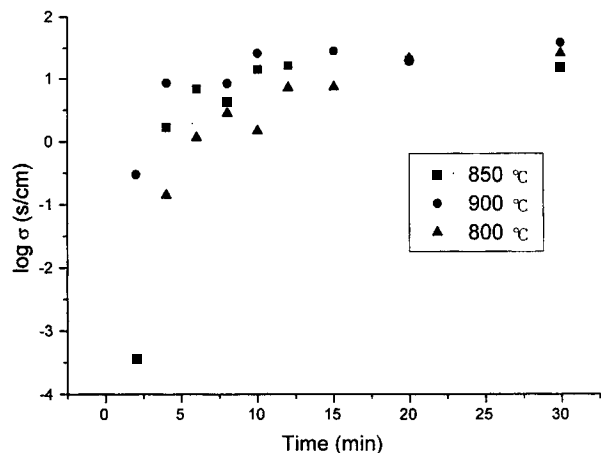
Insulator-to-metal transition of polyimide films can be performed by pyrolysis at high temperature as proposed by the authors. The maximum conductivity of the polyimide pyrolyzed at 950°C for 0.5 h in a nitrogen atmosphere was measured to be 248 S/cm. The structure, electrical, and magnetic properties of the pyrolyzed polyimide depend on the pyrolytic conditions, such as pyrolytic temperature and time. The pyrolysis process consists of carbonization and graphitization processes, and a distinguishable pyrolytic temperature between them was estimated to be about 700°C. In the carbonization process, an increase in conductivity with the pyrolytic temperature may be due to the formation of localized charge carriers. In the graphitization process, on the other hand, it is suggested that the delocalization of charge carriers is responsible for the high conductivity observed from pyrolytic temperature higher than 700°C. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

It has been demonstrated that insulating conjugated polymers, such as polyacetylene (PA), polypyrrole (PY), polythiophene (PT), and polyaniline (PANI), can be converted to the metal regina by oxidation-reduction or protonation doping. Thus, doping as a term for conducting polymers has a very important role in realizing the insulator-to-metal transition. However, the doping method used in the conducting polymers shows some disadvantages as follows: (1) The resulting conducting polymers synthesized by the conventional doping method cannot satisfy the requirement of a metallic energy band. First, the band gap of metal is zero. But for conducting polymers, it ranges between 1.5 and 2.4 eV,<sup>1</sup> which is similar to that of an inorganic semiconductor. Second, the band gap of the conjugated polymers does not change after doping; only a localized state (such as soliton, polaron, and bipolaron) at the middle gap is formed after doping. This is also very similar to an inorganic semiconductor. (2) Doping/dedoping processes in conducting polymers are reversible. This is a unique property for conducting polymers,

which can be used as an excellent electrode material in a rechargeable battery. On the other hand, the instability of conducting polymers in air is always caused by the dedoping process. Therefore, it is expected that the development of conducting polymers synthesized without doping will realize perfect "synthetic metal" needs. This idea challenges the conventional doping method to synthesize conducting polymers. In fact, polymer pyrolysis or high-temperature polycondensation is a simple procedure without doping to synthesize products with graphite-like structure having a high conductivity at room temperature. A typical sample for this method to synthesize conducting polymers is Kapton, in which a conducting polymer forms during a pyrolysis process of Kapton.<sup>2</sup> Recently, interest has been growing with recent studies on the pyrolysis mechanism<sup>3</sup> and laser ablation on the surface of Kapton to fabricate conducting patterns.<sup>4,5</sup> Based on the analysis of the pyrolysis process reported in the literature, an improvement to the pyrolysis method is proposed by the authors. In this method, polyimide films are put into an oven immediately from room temperature to a given pyrolytic temperature in a nitrogen atmosphere, then quickly cooled down to room temperature after pyrolysis for a given time. By this way, the pyrolysis process employed in this article is favorable for the illumination of side products and

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**Figure 1** Effect of the pyrolytic temperature and time on the conductivity of the pyrolyzed polyimide films.

for keeping the resulting structure of the pyrolyzed products. Moreover, the required time for performing the pyrolysis process will be reduced.

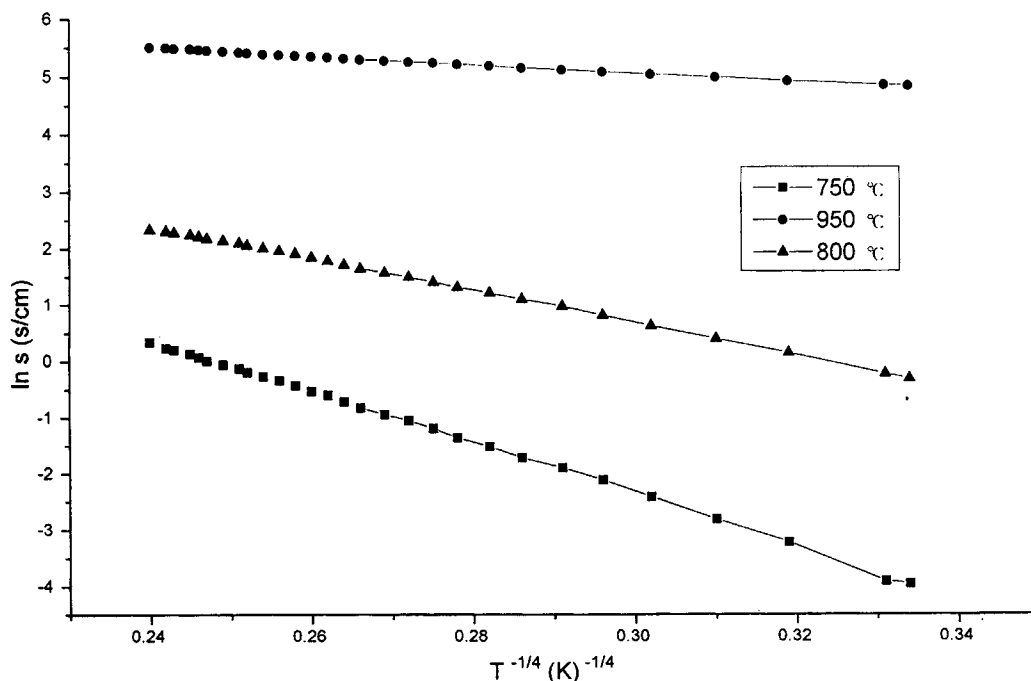
In this article, black film of the pyrolyzed polyimide with a metallic luster and conductivity of about  $10^2$  S/cm was obtained using a method proposed by the authors. The effect of the pyrolysis conditions, such as pyrolytic temperature and time, on the structure and electrical and magnetic properties of the pyrolyzed polyimide was investigated. The mechanism of the insulator-to-metal transition for the pyrolyzed polyimide is discussed.

**Table I** Comparison of the Electrical Properties of the Polyimide Pyrolyzed at Different Pyrolytic Temperatures for 0.5 h in Nitrogen Atmosphere with That of Graphite

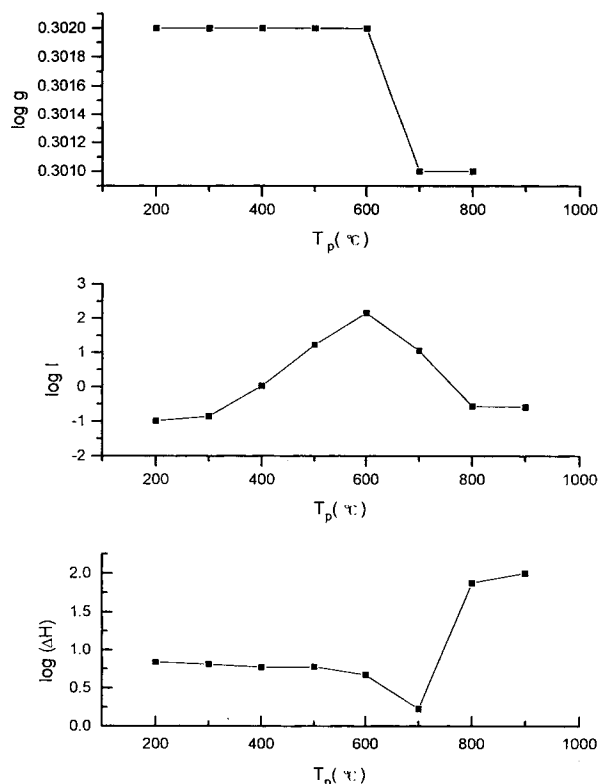
Sample	$T_p$ (°C)	$\sigma_{RT}$ (S/cm)	$\sigma_0$ (S/cm)	$T_0$ (K)
Graphite	—	1000	$3.5 \times 10^3$	$8.3 \times 10^2$
PI-950	950	248	$1.4 \times 10^3$	$2.7 \times 10^3$
PI-800	800	10.0	$9.8 \times 10^3$	$6.4 \times 10^5$
PI-750	750	1.40	$8.0 \times 10^4$	$4.3 \times 10^6$

## EXPERIMENTAL

The polyimide films 20–30  $\mu\text{m}$  thick were synthesized by a reported method.<sup>6</sup> The polyimide films were sandwiched between aluminum foil 0.3 mm thick to avoid deformation of the film during pyrolysis. In our experiment, the sandwiched polyimide film between two sheets of aluminum foil was put into an oven immediately from room temperature to a given pyrolytic temperature in a nitrogen atmosphere, then quickly cooled down to room temperature after pyrolysis for a given time. The resulting pyrolyzed polyimide film is a black film with a metallic luster and reduced flexibility. The pyrolytic temperature and time varied between 500 and 950°C and 12 and 30 min, respectively. The effect of pyrolytic temperature and time on the electrical



**Figure 2** Temperature dependence of the conductivity of the pyrolyzed polyimide films at different pyrolytic temperatures.



**Figure 3** Effect of the pyrolytic temperature on the ESR signal of the pyrolyzed polyimide films.

and magnetic properties of the pyrolyzed polyimide was investigated. The structure of the pyrolyzed polyimide was characterized by elemental analysis, XPS, IR, and SEM to understand the conduction mechanism of the pyrolyzed polyimide. XPS spectra were recorded on a Kratos ES-300 electron spectrometer. SEM images were examined by a Hitachi S-330 scanning electron microscope. The ESR spectra were measured by a Model ES 200B-SRC of Peking University. The conductivity at room temperature was measured by a four-probe method, and the temperature dependence of conductivity at 77–300 K was measured.

## RESULTS AND DISCUSSION

### Electrical and Magnetic Properties

Polyimide films are flexible and with a yellow color before any treatment. Their conductivity at room temperature is about  $10^{-16}$  S/cm. However, pyrolysis treatment leads to a significant variation in electrical and magnetic properties of this material. A black and very brittle film with a high conductivity at room temperature was obtained after pyrolysis at a temperature higher than 700°C. The conductivity

of the pyrolyzed polyimide at room temperature depends on the pyrolytic temperature ( $T_p$ ) and time ( $t_p$ ) as shown in Figure 1. For a given pyrolytic temperature, the conductivity of the pyrolyzed polyimide increases with increase of the pyrolytic time. The maximum conductivity of 248 S/cm at room temperature for polyimide pyrolyzed at 950°C in a nitrogen atmosphere for 0.5 h was obtained, which is enhanced by 18 orders of magnitude compared with that of the original polyimide. This is consistent with the results reported by Murakami et al.<sup>7</sup> and Mory and Chauvet.<sup>3</sup> As shown in Figure 1, for a given pyrolytic temperature, the conductivity increases quickly with increase of the pyrolytic time when the pyrolytic time is less than 15 min. But it increases slowly with the pyrolytic time when the pyrolytic time is greater than 15 min. For a given pyrolytic time, moreover, the conductivity of the pyrolyzed polyimide at room temperature increases with increase of the pyrolytic temperature. Similarly, a critical pyrolytic temperature at about 700°C was observed. This means that the conductivity increases with increase of the pyrolytic temperature when the pyrolytic temperature is lower than this critical temperature. But a change in conductivity with the pyrolytic temperature is slow when the pyrolytic temperature is higher than the critical temperature. This phenomenon is consistent with observations from the variation in the magnetic properties with the pyrolytic temperature, which will be discussed later. These results suggest that the pyrolysis process of the polyimide films consists of two processes, i.e., carbonization and graphitization processes. This conclusion was supported by a structural characterization, which will be discussed in the section on the conduction mechanism.

The temperature dependence of conductivity of the polyimide pyrolyzed at different pyrolytic temperatures for 0.5 h is shown in Figure 2. As one can see, a linear of  $\ln \sigma$  plotted to  $T^{-1/4}$  was observed, which is in agreement with the 3D-variable range hopping (VRH) model proposed by Mott and Davis<sup>8</sup> and it can be expressed as

**Table II** Content of C, N, H, and O Elements in the Polyimide Pyrolyzed at Different Pyrolytic Temperatures for 0.5 h

$T_p$ (°C)	C (%)	N (%)	H (%)	O (%)
Original	66.61	7.17	3.39	20.90
600.0	79.16	7.50	3.34	5.30
950.0	82.80	5.54	1.17	4.08

**Table III XPS Data of the Polyimide Pyrolyzed at Different Pyrolytic Temperatures**

	$T_p$ (°C)	Position (eV)	Intensity (cps)	FWHM (eV)	Relative Intensity (%)
C <sub>1s</sub>	Original	288.511	570	1.337	8.72
		285.754	2411	1.724	36.89
		284.603	2555	1.630	54.38
	600	287.154	1080	3.163	20.93
		285.373	921	1.992	17.85
		283.917	3157	1.829	61.20
	950	287.544	517	1.773	9.15
		285.654	1097	1.931	19.40
		283.791	4037	1.906	71.44
N <sub>1s</sub>	Original	400.429	728	1.694	100
	600	399.671	268	1.606	24.84
		397.867	812	1.727	75.15
	950	399.353	265	1.914	58.51
		397.567	188	1.534	41.48
	O <sub>1s</sub>	Original	533.543	437	1.511
532.195			2339	1.657	84.27
600		532.820	653	2.406	37.42
		530.750	1092	2.155	62.57
950		531.737	809	3.687	35.12
		530.149	1494	2.475	64.87

$$\sigma(T) = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \quad (1)$$

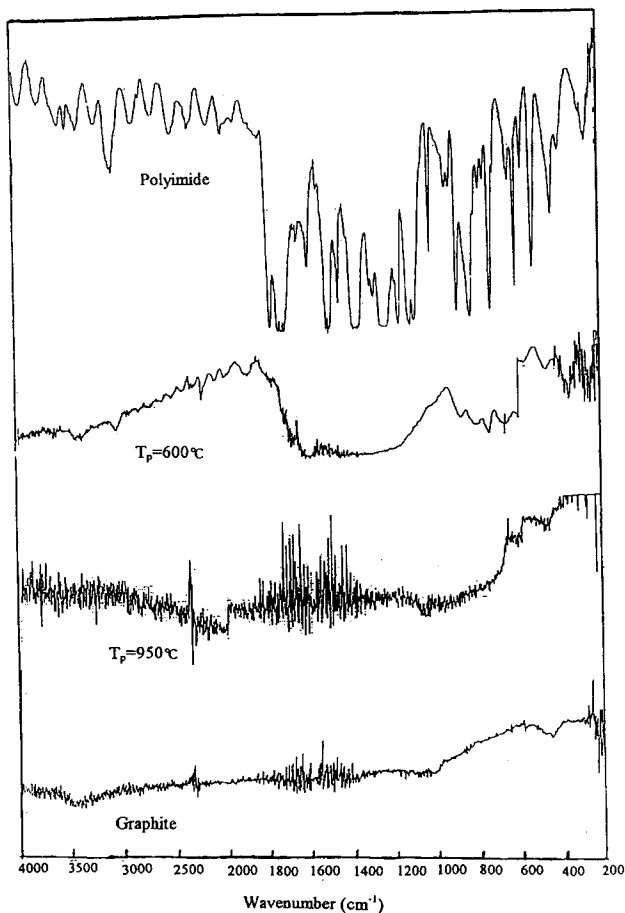
where  $\sigma_0$  is a constant;  $T_0$ , the hopping barrier; and  $T$ , the Kelvin temperature. The  $\sigma_0$  and  $T_0$  can be calculated from the intercept and slope of the linear of  $\ln\sigma$  plotted to  $T^{-1/4}$ , respectively. This result is inconsistent with results reported by Mory and Chauvet<sup>3</sup> and Broom et al.,<sup>2</sup> in which the temperature dependence of conductivity is best fit to the 2D-VRH model. This difference may be caused by a difference in the pyrolysis process used. Moreover, it is very interesting to find that the hopping energies for charge carriers,  $T_0$ , decreases with increase of the pyrolytic temperature. In the VRH model,  $T_0$  is expressed as

$$T_0 = \frac{16\alpha^3}{KN(E_F)} \quad (2)$$

where  $K$  is Boltzmann's constant;  $\alpha^{-1}$ , the radius of the localized state wave function; and  $N(E_F)$ , the density of the localized state at the Fermi level. Thus, the density of the localized state for the po-

lyimide pyrolyzed at 950°C can be calculated to be  $3.6 \times 10^{20} \text{ eV}^{-1} \text{ cm}^{-3}$  when the value of 12 Å for  $\alpha^{-1}$  as in the case of amorphous carbon<sup>7</sup> and a  $T_0$  of  $2.73 \times 10^3 \text{ K}$  (see Table I) were used. In comparison with graphite, the electrical properties of the polyimide pyrolyzed at different pyrolytic temperatures for 0.5 h in a nitrogen atmosphere are given in Table I. For the polyimide films pyrolyzed at 950°C, e.g., its conductivity at room temperature is one order of magnitude lower than that of graphite, but its required hopping energies are one order of magnitude higher than those of graphite.

Before pyrolysis, in addition, polyimide films exhibit typical diamagnetic behavior, i.e., no ESR signal can be detected. On the other hand, a strong ESR signal was observed after pyrolysis, and the properties of the ESR signal, including intensity ( $I$ ), line width ( $\Delta H$ ), and the  $g$  value, depend on the pyrolytic temperature as shown in Figure 3. One can see that the variation of  $I$ ,  $\Delta H$ , and the  $g$  value with the pyrolytic temperature is quite different. However, it is very interesting to find that a turning point at about 700°C for all of the curve of  $I$ ,  $\Delta H$ , and the  $g$  value with the pyrolytic temperature was observed,



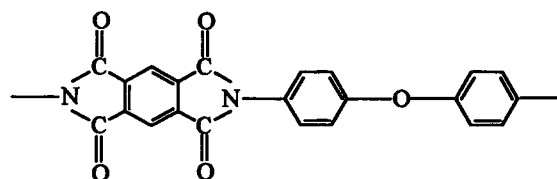
**Figure 4** Dependence of the pyrolytic temperature on the IR spectra of the pyrolyzed polyimide films.

which is consistent with the fact that a critical pyrolytic temperature at about 700°C in a curve of conductivity with the pyrolytic temperature was observed.

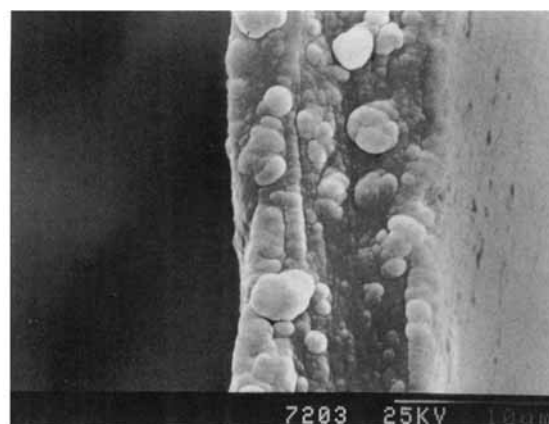
#### Mechanism of Insulator-to-Metal Transition Introduced by Pyrolysis at High Temperature

As described above, an important critical pyrolytic temperature at about 700°C in the electrical and magnetic properties of the pyrolyzed polyimide was observed. This indicates that the pyrolysis process of polyimide is controlled by two distinguishable processes, which are the carbonization and graphitization processes. To support this conclusion, the structure of the pyrolyzed polyimide was characterized by elemental analysis and IR, XPS, and SEM measurement. The structural characterizations of the polyimide pyrolyzed at different pyrolytic temperatures show that a critical pyrolytic temperature at about 700°C was also observed from elemental analysis and IR, XPS, and SEM measurements. Detail discussions about this follow:

The molecular structure of polyimide is shown as



and its molecular formula is  $C_{22}H_{10}N_2O_5$ . The content of C, N, H, and O elements of polyimide pyrolyzed at different pyrolytic temperatures is given in Table II. It shows that the content of C elements increases with increase of the pyrolytic temperature, whereas the content of O elements decreases with increase of the pyrolytic temperature when the pyrolytic temperature is lower than 700°C. However, the content of N and H elements are unchanged when the pyrolysis was carried out at lower than 700°C. The ratio of nitrogen-to-carbon elements of the polyimide pyrolyzed at 950°C was estimated to



a



b

**Figure 5** SEM images of cross section of the pyrolyzed polyimide films at different pyrolytic temperatures: (a) polyimide films; (b) pyrolyzed at 950°C.

be 0.07 by weight, which is higher than that reported by Burger et al.<sup>9</sup> These indicate that the C—H or C—O bonds were broken to create radicals in the materials during this pyrolysis stage. This is consistent with observations from ESR measurement, in which the intensity of the ESR signal increases with increase of the pyrolytic temperature during this pyrolysis stage [see Fig. 3(a)]. For the pyrolytic temperature higher than 700°C, moreover, the variation in C and O elements with the pyrolytic temperature is the same as that of the pyrolytic temperature lower than 700°C, but the content of N and H elements decreases significantly with increase of the pyrolytic temperature when the pyrolytic temperature is higher than 700°C. This suggests that new C=C double bonds are created to lead to dark hardened materials with a graphitelike structure. This is in agreement with the fact that the higher the pyrolytic temperature, the more efficient is the graphitization. XPS measurements show that variation in C<sub>1s</sub>, N<sub>1s</sub>, and O<sub>1s</sub> with the pyrolytic temperature is consistent with the observations from elemental analysis. Furthermore, it was noted that all the binding energies of C<sub>1s</sub>, N<sub>1s</sub>, and O<sub>1s</sub> for the pyrolyzed polyimide were reduced with increase of the pyrolytic temperature (Table III). This indicates that the degree of the electronic delocalization of the pyrolyzed polyimide is enhanced by pyrolysis treatment, which may be responsible for the high conductivity observed from the pyrolyzed polyimide after pyrolysis at high temperature ( $T_p > 700^\circ\text{C}$ ).

A comparison of IR spectra of the polyimide pyrolyzed at different pyrolytic temperatures with graphite is shown in Figure 4. It was found that all the characteristic IR peaks of polyimide disappeared after pyrolysis at a temperature higher than 700°C, and a graphitelike structure for the polyimide pyrolyzed at 950°C was obtained. This suggests that the polyimide pyrolyzed at 950°C exhibits a metal behavior, which is consistent with the higher conductivity of the polyimide pyrolyzed at 950°C. Furthermore, this is also supported by the fact that the SEM image of the cross section of the polyimide pyrolyzed at 950°C shows a planar graphic network. On the other hand, this kind of morphology is not observed for the polyimide pyrolyzed at a temperature lower than 700°C, as shown in Figure 5.

## CONCLUSIONS

Insulator-to-metal transition of polyimide films can be performed by a pyrolysis procedure proposed by the authors. The structure, electrical, and magnetic properties of the pyrolyzed polyimide strongly depend on the pyrolysis conditions, such as pyrolytic temperature and time. The pyrolysis process consists of carbonization and graphitization. The critical pyrolytic temperature between two processes was estimated to be about 700°C. In the carbonization process, an increase in conductivity of the pyrolyzed polyimide with the pyrolytic temperature is due to the creation of a localized charge carrier. In the graphitization process, on the other hand, the delocalization of charge carriers is expected to be responsible for the high conductivity of the polyimide pyrolyzed at 950°C.

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