Pyrolyzed, Conducting Kapton Polyimide: An Electrically Conducting Material

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Synopsis

Polyimide was pyrolyzed in an argon atmosphere at 900°C for 1h. The room temperature conductivity of the polyimide gradually increased from 15 to 100 S/cm with increased pyrolysis time. Further increase in the pyrolysis time did not increase the conductivity. X-ray photoelectron spectroscopy (XPS) showed that the polyimide changed from pure insulator to conductor; detailed XPS spectra of carbon, nitrogen, and oxygen 1s bands showed no further elemental decomposition of the polyimide at 900°C. The high temperature treatment results in internal rearrangement to form a large, dense heterocyclic network. The film probably consists of tiny conductive particles dispersed in an amorphous carbon matrix. The polyimide is placed between two quartz plates during pyrolysis; the resulting film is flat, has uniform conductivity, is nonbrittle, has high chemical resistance, and shows better mechanical strength than films pyrolyzed in free-standing conditions.

INTRODUCTION

The pyrolysis of polyimide results in elimination of all elements except carbon, forming an extended aromatic ring structure similar to graphite. The extended aromatic rings are dispersed in an amorphous carbon matrix. It is believed[1] that in the early stages of pyrolysis defined domains of condensed rings start to form; free radicals are also formed. Later a continuous network of condensed aromatic structure with strong π-orbital overlap is formed. The π-electrons within this aromatic ring network are to a certain degree delocalized (depending on the pyrolysis conditions) and not limited to individual aromatic rings. The strong π-orbital overlapping results in a conductivity in the range of 10^2 S/cm. The free radicals can act as donors or acceptors.

Charge transfer between rings can be described mainly by two mechanisms[2,3] : (a) for small interring distances (less than 10 Å), the tunneling mechanism is available; (b) for large interring distances (greater than 10 Å), the hopping mechanism is available. Under an electric field electrons excited to the empty states can tunnel through the potential barrier between the rings to the empty states of other rings; the hole created can tunnel in the opposite direction. When the distance between rings is large, the electron cannot tunnel from one ring to another, but can transfer by a hopping mechanism.

MATERIALS AND METHODS

The Kapton polyimide free-standing films are products supplied by Du Pont de Nemours and Co. and have the following structure:
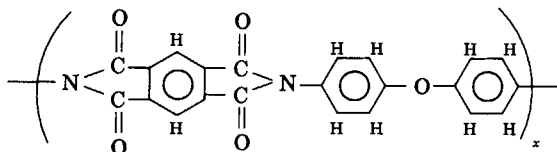
The sample heating system consisted of a high temperature oven, compressed argon gas tank, quartz tube, control valve, and vacuum pump.

Thermogravimetric Analysis (TGA). The polyimide sample is placed inside a small quartz tube oven; high purity argon gas is passed through the inside of the tube at 4 cc/s. At Du Pont 990 Thermal Analyzer records the weight loss as a function of temperature.

X-Ray Photoelectron Spectroscopy Analysis (XPS). XPS analyses of the polyimide samples at different stages of pyrolysis provides information on elemental ratios and bonding environments. Combined with other data, it permits the determination of composition and structure changes during the different stages of pyrolysis. XPS analyses was performed on a Hewlett-Packard 5950B ESCA Spectrometer, using a monochromatic AlKα X-ray source.

Four-Point Probe Conductivity Measurement and Ohmic Contact Test. Four-point probe conductivity methods are described by several authors.[4] The basic principle is the placement of four sharp, equal distance probes on the flat surface of the material. Current is created by a current source and passed through the two outer probes and the voltage created is measured across the inner two probes. If the sample is relatively large compared with the distance between the probes, the resistivity can be calculated. Our four-point probe measurement used an HP 3465A Digital Multimeter, HP 6181C DC Current Source, and Alessi Industries Four-Point Probe. In order to electrically test the sample, an ohmic contact test between the sample and the silver epoxy paint is a must. The silver epoxy paint is coated at the corners of the sample. The current is introduced at each diagonal lead; If $V = IR$ is obeyed, ohmic contact is present.

RESULTS

TGA. The polyimide was heat-treated in two different gas environments: One was heat-treated in an oxygen atmosphere; the other was heat-treated in an argon atmosphere. The heating rate was 5°C/min. The TGA data are presented in Figure 1. Polyimide samples in oxygen started to dissociate at about 425°C; the weight loss continuously increased with temperature to about 525°C, at which point all of the polyimide was gone. Polyimide in an argon atmosphere started to dissociate at about 500°C. The slope of weight loss vs. temperature increased as temperature increased, reached a maximum at 560°C, then started to decrease, and approached zero at about 700°C.
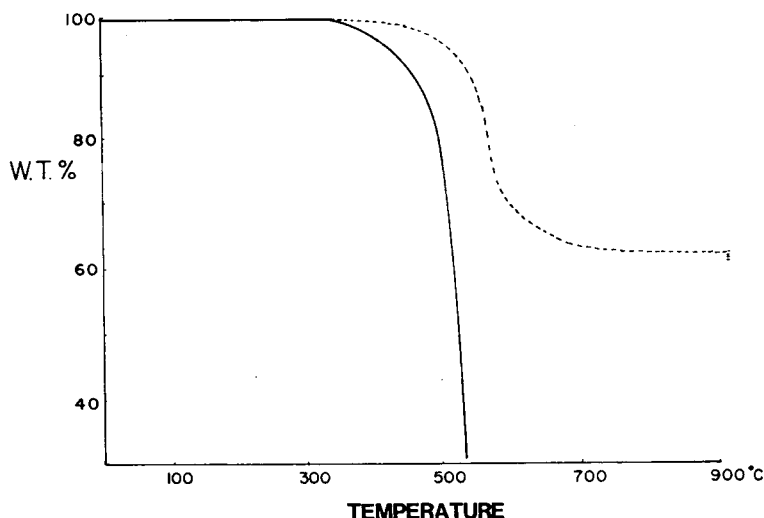
Fig. 1. The thermogravimetric analysis of Kapton polyimide: (————) oxygen atmosphere; (– – – –) argon atmosphere.

At this stage the total weight loss of the polyimide was about 38%; the weight was then nearly constant to 900°C. The polyimide sample was held at 900°C for up to 1 h. For the first 40 min an additional 1-2 wt. % decrease was observed; after 40 min no further weight loss could be detected.

XPS. Wide scans of the polyimide at the different temperature stages are presented in Fig. 2. Nitrogen and oxygen contents decreased as the temperature was increased. Even with the electron flood gun on, the carbon 1s peak position suggests that the 900°C treated polyimide is at least semiconducting. Detailed analyses of carbon, oxygen, and nitrogen are presented in Fig. 3.

The polyimide has three carbon peaks at binding energy 288.4, 286.2, and 284.6 eV, respectively (see Table I). When the temperature is increased to 600°C, the peaks at 288.4 and 286.2 eV were decreased, and the C—C main peak was increased. After heating to 900°C, the peaks at 288.4 and 286.2 eV were not changed and the C—C main peak was increased further. Also, the shape of the C—C main peak was very similar to that of graphite.[5] Further heating at 900°C further reduced the peaks at 288.4 and 286.2 eV; the main C—C peak remained the same.

Two oxygen peaks at binding energies of 534.0 and 532.6 eV, respectively (see Table I), were reduced as temperature increased above 500°C. When the temperature reached 900°C, all the remaining oxygen was of the C—O type. Further heating at 900°C did not further reduce the oxygen.

The nitrogen analyses were most interesting; the peak is at 400.7 eV. After the polyimide was heated to 600°C, a new peak appeared at 398.6 eV (see Table I), suggesting two different nitrogen environments.

Conductivity. The room temperature conductivity of pyrolytic polyimide is presented in Fig. 4, showing the conductivity as a function of pyrolysis time at 900°C. The epoxy silver paint did make ohmic contact with the polyimide samples.
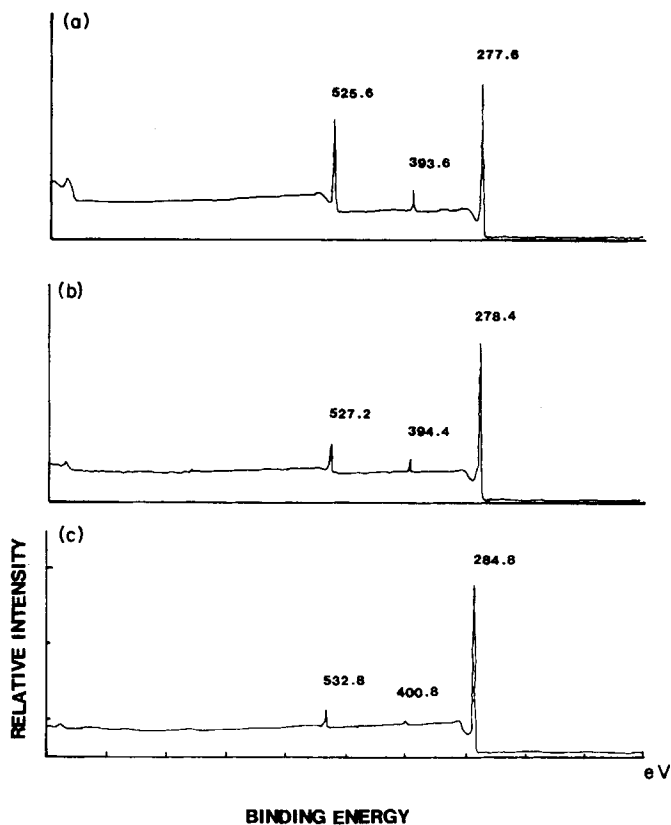
Fig. 2.   XPS wide scan spectra of pyrolyzed Kapton with the electron flood gun on: (a) raw material; (b) pyrolyzed at 600°C; (c) pyrolyzed at 900°C.

Wide Angle X-Ray Analyses. Wide angle X-ray analyses was performed on a General Electric DIANO model. The wide angle X-ray analyses using $Cu_{k\alpha}$ monochromatic radiation showed that there was no long-range crystal structure.

DISCUSSION AND CONCLUSIONS

The TGA and ESCA studies clearly indicate that the polyimide was pyrolyzed. Most of the aliphatic C—N and C—O bonds are broken below 600°C, releasing N_2, CO, and CO_2 gases. At the same time the carbon starts to form a heterocyclic structure. Above 600°C weight loss is insignificant. Some oxygen and nitrogen are incorporated into the heterocyclic rings. It is believed that the structure rearranges or recombines to a larger and denser heterocyclic network, resulting in increased conductivity. This conclusion is supported by both the ESCA and conductivity data. At 900°C, the elemental composition of the polymer stays nearly the same. After 1 h at 900°C, there is no further increase in conductivity, indicating no further structural change.

Wide angle X-ray data indicates that the pyrolyzed polyimide does not have long-term periodic structure. Apparently, the dense aromatic structure consists of small particles uniformly dispersed in a carbon matrix. Small-angle X-ray data are necessary to test this hypothesis. The mechanism of
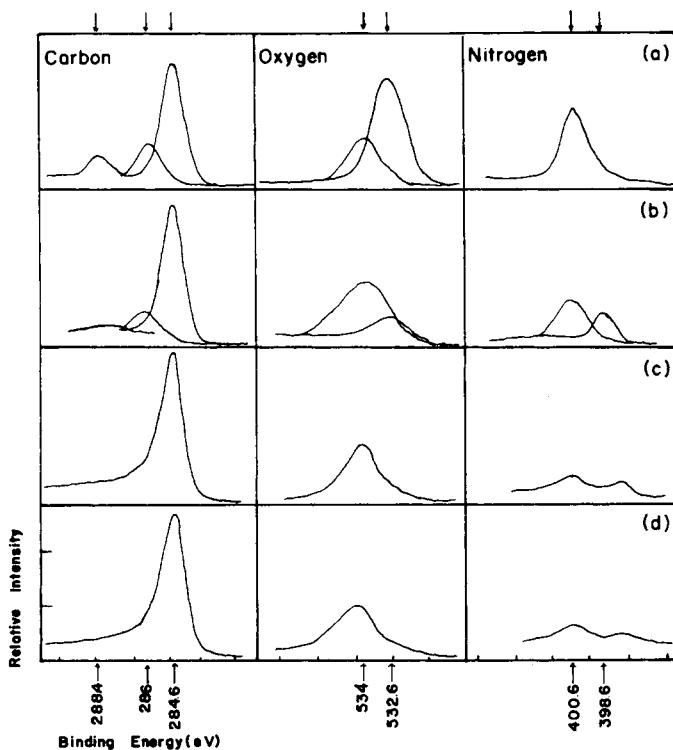
Fig. 3.   XPS narrow scan spectra for carbon, oxygen, and nitrogen 1s peaks: (a) raw material; (b) at 600°C; (c) at 900°C; (d) at 900°C for 1 h.

electron or hole conduction in this material is complex. In each individual particle, the electron requires energy to overcome the intrinsic band gap and create electron and hole pairs. For simplicity, it is assumed that the band gap energy of all particles is approximately the same. The electrical carriers created must jump over or tunnel through the energy barrier between the particles. The average distance between the particles may determine which process is dominant. The energy barrier and structure change can be determined by optical measurements. Such work is in progress.

When the polyimide film is placed between quartz plates, the resulting

TABLE I
Elemental Binding Energy of Polyimide

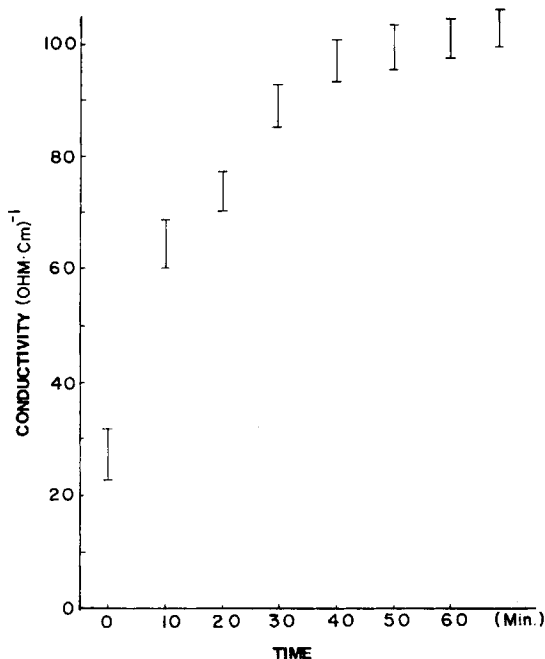| Binding energy (eV) \ Element	C	O	N
C — C	284.6		
C — O	286.2	534.0	
C — N	286.0		400.6
$C{<}^{O}_{N}$	288.4	532.6	
∷ N ∷			398.6

Fig. 4.   Four point probe conductivity measurements of pyrolyzed polyimide. Conductivity vs. time at temperature of 900° C.

pyrolyzed material shows nonuniform conductivity. The conductivity is much lower at the edges than in the bulk. The rest of the sample has a relatively uniform conductivity. When the polyimide starts to dissociate at about 500°C, the volatile gases can only go through the space between the two plates. The large heterocyclic network does not form as effectively at the edges; the result is lower conductivity.

The mechanical strength of the pyrolytic polyimide is greatly improved by putting the polymer film between the quartz plates. Mass transfer of volatile gases is restricted to the direction of arrows in Fig. 5. This restriction causes the formation of a heterocyclic structure more ordered along the arrow directions, resulting in improving mechanical strength.

Pyrolyzed polyimide has conductivity of the order of 10^{20} times greater than the parent polyimide, and it may be doped to produce n-type or p-type material. Pyrolyzed polymers (both doped and undoped) are air stable and can function at very high temperatures without degradation.[6] They show excellent binding to ceramics, metals, silicon, or other semiconductor compounds.[7] The material has dependable and controlled conductivity[8,9] with reasonable mechanical strength. In contrast, polyacetylenes or polydiacetylenes[10-12] are brittle, not air stable, oxidize rapidly when exposed to air; and the dopants often migrate out of the bulk polymer after a period of time.

Electrically conducting pyrolyzed polyimide can be used to produce circuitry on metal or semiconductor substrates by using photosensitive polyimide. Most other means of producing conductive polymers result in insoluble or difficult to process materials.
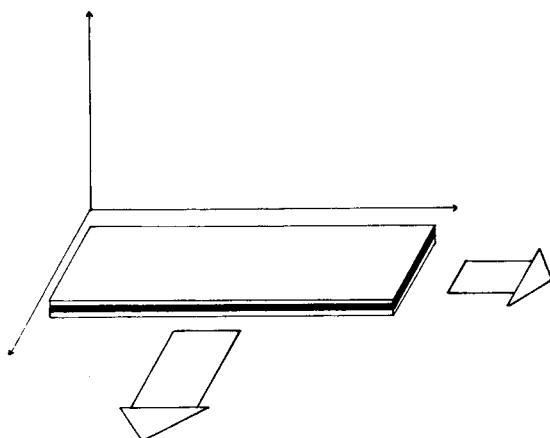
Fig. 5.   The directions of volatile gas transport during pyrolysis, indicated by arrows.

This process of making conductive polymer is simple and cheap. Such materials could replace metal-filled polymer, molecularly doped polyenes,[13] part of semiconductor devices,[14] and has the potential of making some practical photo-devices. Pyrolytic polyimide is easy to fabricate for commercial manufacture.

Pyrolyzed polyimides certainly deserve to be further studied as lightweight materials for unique conductive or semiconductive applications.

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