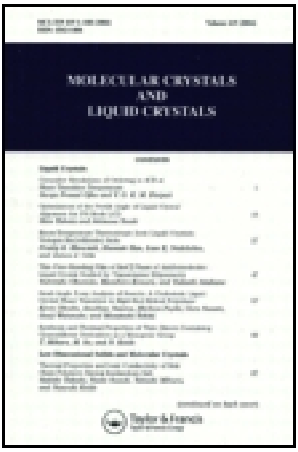

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Electron Energy Loss and Auger Spectroscopies of Conducting Polyimide Produced by Ion Beam Irradiation

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ELECTRON ENERGY LOSS AND AUGER SPECTROSCOPIES OF CONDUCTING POLYIMIDE PRODUCED BY ION BEAM IRRADIATION

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Abstract The appearance of electronic conductivity in polyimide irradiated with ion beams has been attributed to the formation of extended systems of π orbitals. We have studied by reflection energy loss (REELS) and Auger (AES) spectroscopies the electronic properties of PMDA-ODA polyimide films irradiated by N^+ ions. This confirmed the graphite-like electronic structure of the conducting phase. In particular the REELS spectrum shows the plasmon at 7 eV attributed by Taft and Philipp[1] to the collective excitation of π electrons in graphite together with the 25 eV plasmon which results from a $\sigma + \pi$ excitation. These results are in agreement with the evolution discussed by Marletta in BTDA-ODA polyimide[2], but are interpreted by the formation of a graphite-like phase which is known to determine the electronic properties of disordered carbon layers[3]. The insulator-metal transition may be interpreted by a percolation mechanism between conducting blobs which result from radical clustering as shown by the development of a strong ESR signal.

INTRODUCTION

In recent years there has been a growing interest in methods allowing the production of specific properties in bulk materials, as for example the formation of a conducting phase in a polymeric substrate. Many studies have been concerned with the conversion of organic precursors to carbonaceous materials, which exhibit unique electronic properties due to the allotropic nature of carbon,ranging from good insulators (diamond-like phases) to semimetals (graphite-like phases). The electronic properties are in fact determined by the carbon hybridization state and depend in particular on the ratio of sp_2 to sp_3 bonding which weights the two components (graphite-like to diamond-like phases) observed in disordered carbons. Heat treatments of organic polymers have been extensively used for the synthesis of conducting carbons[4]. Methods using ion beams have been more recently developed for the production of diamond like films at low energies, whereas conducting compounds are formed by irradiations at high energies (> 1 keV)[5]. The main interest in ion beams comes from the possibility of producing well defined conducting structures in insulating layers used in electronics. The purpose of this contribution was to discuss the nature of the phase responsible for the appearance of conductivity in high ion fluence irradiated PMDA-ODA polyimide reported in previous papers[6, 7, 8]. A number of complementary techniques have shown that the formation of a carbonaceous material resulted from the ion beam irradiation of polyimide through the loss of the more volatile species : H, N, O (gas evolution studies, RBS, ERD[7]). Structural investigations (IR spectroscopy and XPS[7, 9]) have indicated that the first step in the polymer dissociation was the cleavage of the C-O-C bond between the aromatic rings and scission of the carbonyl group. Electron energy loss (EELS) and Auger spectroscopies (AES) have been used to characterize the proceeding reorganization of the material. The studies were completed with electron spin resonance (ESR).

REELS AND AUGER CHARACTERIZATION

Electron beams of low energy are very sensitive to the electronic structure of solids. In particular the energy lost by primary electrons (50 eV below the elastic diffusion peak) allows the investigation of the states near the valence band whereas the spectroscopy of Auger electrons provides information on the inner electron shells. EELS was developed by Ritsko in the seventies to characterize the electronic states of polymers. He showed in particular the presence of a sharp resonance at 7 eV and a broader one near 22 eV associated to the phenyl group in polystyrene (PS) and poly-2-vinyl-pyridine (PVP)[10]. More recently the modification of the EELS spectrum in the reflection mode (REELS) of different aromatic polymers upon irradiation with ion beams has been studied by Marletta et al.[11],showing the development of a step-like structure in the low excitation energy region attributed to π electrons. This absorption could have the same origin as the weak absorption observed below 5 eV by Ritsko and Bigelow[10] for extended irradiation of PS and PVP and attributed to the production of unsaturation on the polymer backbone. Venkatesan et al.[12] have studied the EELS spectra of ion irradiated carbon films in order to have insight on the evolution of the electronic structure of polymer films irradiated at high fluence. The authors concluded a partial ion beam induced graphitization in film irradiated at high energies, as shown by two peaks at 7 and 25 eV in the EELS spectra,attributed respectively to a plasma resonance of the π electrons (shifted from its normal position by the polarizability of the σ electrons) and of both σ + π electrons[1]. The proportion of trigonally bonded carbons (sp^2) and tetrahedrally bonded carbons (sp_3) may be deduced from the relative weights of the two

	0 ←→ 15 eV	←→ 30 eV	←→ 50 eV	technique	Ref.
Phenyl group	7 eV Interband transition	22 eV $h\omega_p$		EELS	(10)
graphite	7 eV $h\omega_p$ (π)	25 eV $h\omega_p$ ($\pi + \sigma$)		Optical	(11)
diamond			34 eV $h\omega_p$ (σ)	ES	(14)
diamond-like C	6 eV	21.5 eV	33 eV	EELS	(15)
aC: 100 % sp_2	4 - 7 eV	25 eV		EXAFS	(13)
aC : H 1/3 sp_2, 2/3 sp_3	7 eV	22 - 23 eV		EXAFS	(13)

Table 1 : Main excitations in the valence region

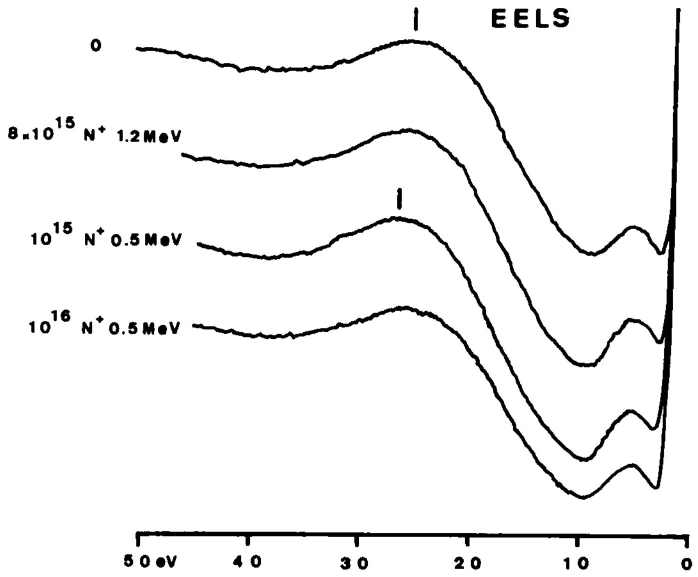

Figure 1 : REELS spectra of irradiated polyimide films at different ion fluences. $E_p = 500$ eV.

resonances. In particular Fink et al.[13] show that an increase of the graphitic ordering in amorphous hydrogenated carbon produces the growth of the resonance at 7 eV. In fact disordered carbon films exhibit most of the features of graphite since the electronic properties are controlled by the sp_2 component in the valence region. Tetrahedrally bonded carbon in diamond gives only a contribution at high energy : 34 eV[14]. The main resonances observed in various carbonaceous materials have been summarized in table 1. Figure 1 shows that most features of the pristine polyimide REELS spectrum are preserved after ion beam irradiation in agreement with the evolution discussed by Marletta et al.[2]. Two main conclusions can be deduced from these spectra :

- Aromatic rings are a stable molecular element,as previously shown by infrared or XPS spectroscopies[7], which remains unaffected in polyimide films irradiated at high ion fluences. However the REELS technique cannot distinguish between organization of the aromatic rings in the polymer backbone or in the graphitic phase.
- The stability of the resonance near 7 eV and lack of the absorption near 33 eV, characteristic of sp_3 bonded carbon, excludes the assumption of progressive formation of an amorphous component which would account for the appearance of the conductivity[11, 2]. Furthermore the shift of the bulk plasmon energy from 24 eV for the pristine polymer to 26 eV for the irradiated one reflects the increase in the valence electron density,N,as indicated by the expression for the plasma frequency:

$$\omega_p = \left(\frac{Ne^2}{m^*\varepsilon_0}\right)^{1/2}$$

in the approximation of free electrons. In fact the valence electron density involves <u>both</u> the effective number of valence electrons per carbon atom and the macroscopic density (in g/cm^3). Weissmantel shows an inverse shift of bulk plasmons towards lower energies when amorphous diamond-like carbon films are formed, in spite of the increase in the material density, because of the drop of the number of free electrons in compounds dominated by sp_3 carbon bonding[15].

The previous modification of polyimide upon ion beam irradiation is indicative of the evolution of the band structure towards dominant graphite-like properties. This interpretation is also supported by the Auger spectra of irradiated polyimide films shown in figure 2. The spectra of sp_2 (in graphite) and sp_3 (in SiC) bonded carbons have also been plotted. The shape of the Auger spectrum appears to be more in accordance with sp_2 bonded carbon atoms than sp_3, but less resolved than in pure graphite, probably due to various carbon bonds, in particular with the residual H, N and 0 atoms. The spectrum becomes more graphite-like when the dissipated power (energy x fluence) increases. We also observe an increase of the ratio of the signal to the background from 0.68 for pristine polymer to 0.92 for the more heavily irradiated one ($8x10^{15}$ N^+ at 1.2 MeV),which shows the increase in carbon proportion and densification of the material.

ESR STUDY OF IRRADIATED POLYIMIDE

According to REELS and Auger spectroscopies the electronic properties of ion beam irradiated polyimide films appear to be mostly governed by the sp_2 component. However pristine polyimide already contains a sp_2 component in its heretocycle, associated with the aromatic rings, which does not allow by itself the long range delocalization of electrons.

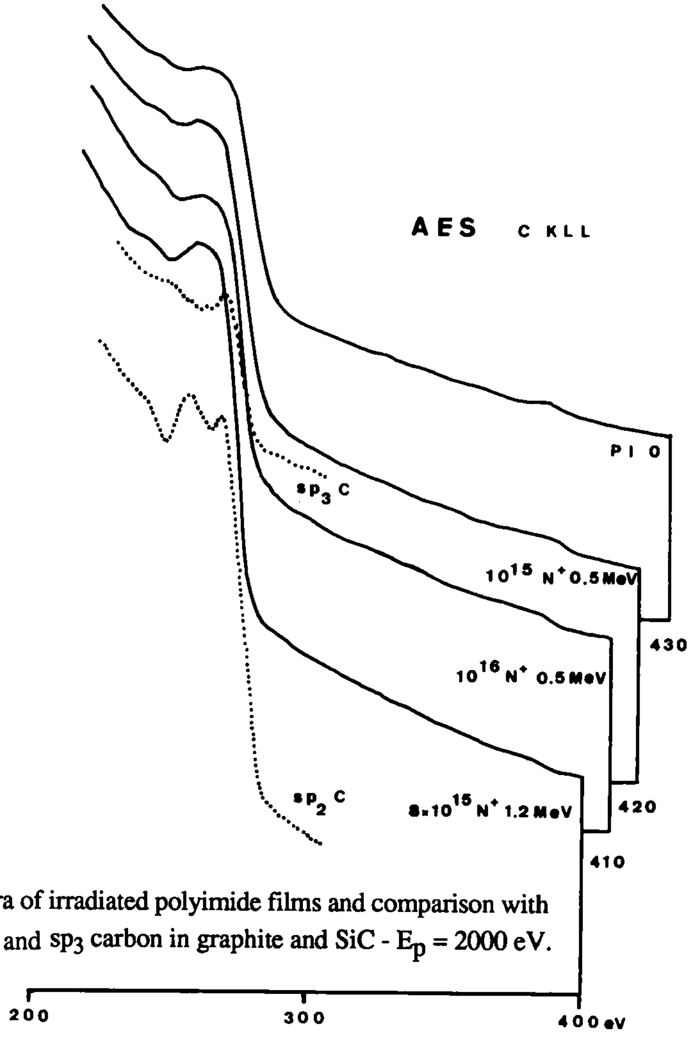

Figure 2 : AES spectra of irradiated polyimide films and comparison with sp_2 carbon and sp_3 carbon in graphite and SiC - E_p = 2000 eV.

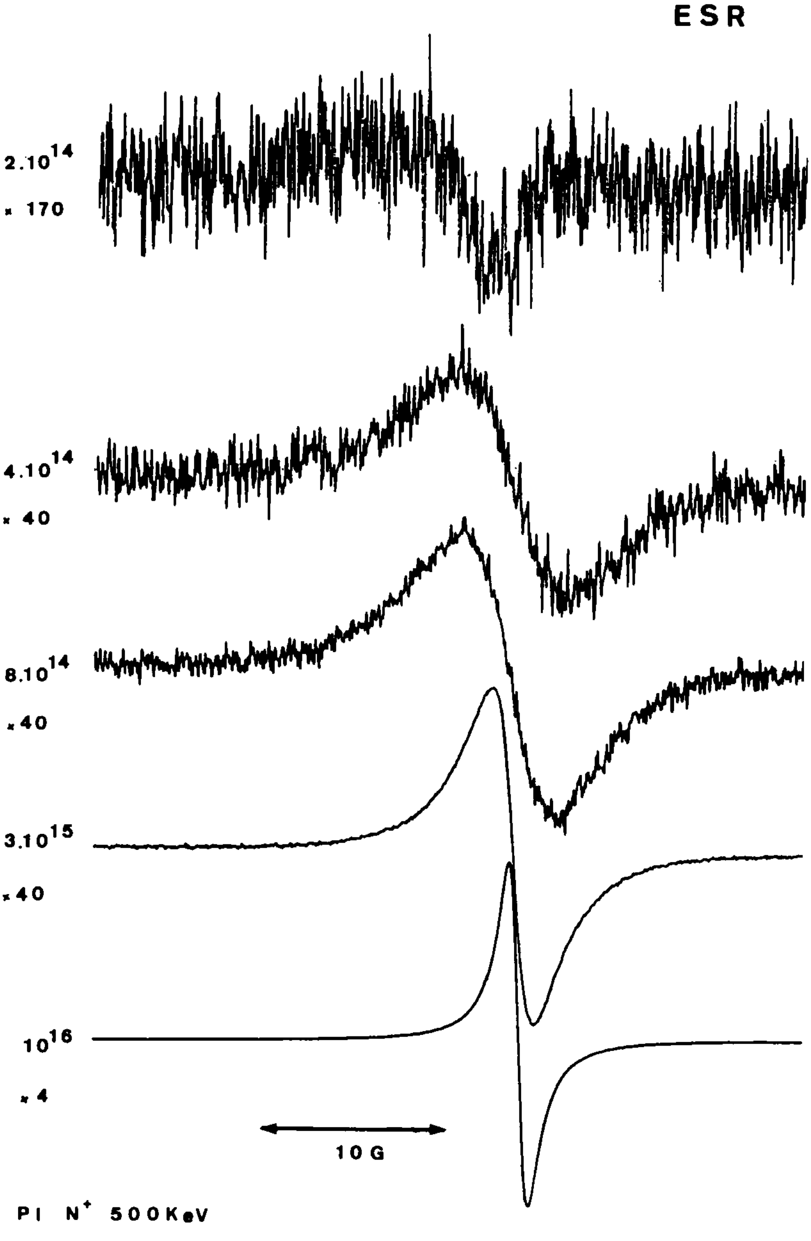

Figure 3 : ESR spectra of 0.5 MeV N^+ irradiated polyimide films for different ion fluences (cm^{-2}). The instrumental multiplication factor is indicated for each spectrum.

The two previous techniques are in fact not very sensitive to the reorganization of the rings during the carbonization process. Electron spin resonance is however very sensitive to spin delocalization. This technique has been used very much to study the formation of radicals which play a key role in the carbonization of hydrocarbons[16,17]. Figure 3 shows the development of an intense ESR signal for increasing ion fluences. The signal appears to be formed by two lines with different widths and g values: one predominant at low ion fluence has a high g value, 2.004, as seen in certain clusters of aromatic rings such as violanthrene[17] and another one, with g value 2.0028, of the minimum linewidth at high ion fluence. The first one is supposedly associated with a precursor state for the formation of an extended system of π delocalized electrons. The sharp decrease of the linewidth observed at high ion fluence is in particular an indication of a large delocalization and mobility of the spins, which could occur through a percolation mechanism when the infinite percolative cluster is formed. The strong correlation between the development of the ESR signal and the drop in resistivity support this type of interpretation and is discussed in another paper[18]. The spin concentration has been estimated to be $1.6 \times 10^{20}/cm^3$ at the maximum of the signal, which may be compared to the surpisingly high value of carrier concentration determined by Wasserman et al. ($\sim 10^{22}/cm^3$) and low mobility in other types of irradiated polymers[19]. These values are substantially higher than the graphite carrier concentrations ($\sim 10^{19}/cm^3$).

CONCLUSION

REELS and Auger spectroscopies of PMDA-ODA polyimide have provided evidence for the domination of the sp_2 hybridization of carbon in the electronic properties of films irradiated with N^+ ions at 0.5 and 1.2 MeV. ESR has shown the development of a strong ESR signal demonstrating a large delocalization of the spins associated to the charge carriers at the insulator-metal transition. Further experiments would be needed to establish definitely wether the finer ESR component can be related to long range mobility. It appears that polymers irradiated at high fluences show strong analogies with disordered carbons as previously pointed out by several authors[2, 7, 12, 19]. However there is a broad variety of carbonaceous materials exhibiting properties[4] ranging from good insulators (diamond-like carbon) to semi-metals (graphite-like carbon). There is now a great deal of evidence that only the long range delocalization of π electron can account for the insulator-metal transition induced by ion beam irradiation. This implies a short range graphitic ordering as observed in the carbonization of polymers upon pyrolysis[4, 17]. In particular the interpretation[2] of the induced conductivity by the formation of purely amorphous carbon is excluded by the lack of delocalized electrons in sp_3 bonded carbon. A model of the insulator-metal transition is discussed in another paper[18].

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