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ABOUT THE FRACTAL INTERPRETATION OF THE INSULATOR-METAL TRANSITION INDUCED BY ION BEAMS IN POLYIMIDE

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Abstract Polyimide films have been shown to become conducting upon irradiation with ion beams. Different analytical techniques have demonstrated that the conductivity resulted from the appearance of a new phase exhibiting a graphite-like electronic structure through the formation of aromatic clusters. The abrupt transition from the insulating to conducting states is interpreted by the formation of random conducting paths according to the model,proposed by Wasserman[1],of percolative phase transition. The conductivity and ESR signal are represented by power laws involving distinct critical exponents in accordance with the evolutions,discussed by Wasserman,for PPO and PAN films. The induced conducting properties are interpreted in the framework of the fractal concepts applied by Stanley[2] to the transport in randomly porous media.

INTRODUCTION

Radiation has been extensively used to induce new chemical bonds in organic solids, in particular in the sixties where the availability of energetic ionizing radiation gave rise to radiochemistry. The use of ion beams to modify the properties of polymers is more recent[3]. However the basic processes remain identical since the energy transfer proceeds mainly through the production of secondary electrons in the solid matter. The high rate of deposited energy leads to tremendous modifications of the materials, in particular in organics,because of the allotropic nature of carbon which allows different recombination schemes of the chemical bonds broken during irradiation. In particular ion beam irradiation of saturated polymers produces the formation of unsaturated bonds which are responsible for the appearance of semiconducting properties[4]. Polymers containing aromatic rings are of particular interest because of the high conductivities reached ($\sim 10 - 10^3$ S/cm), which results from the formation of extended aromatic ring structure similar to graphite. Different techniques have shown that the electronic properties of such modified polymers are governed by the graphitic moieties dispersed in a still dielectric matrix, in particular Auger and Electron Loss Spectroscopies which are discussed in another contribution[5].

The processes involved in the induced modifications of polymers are still in a phenomenological phase. However, Wasserman[1] has recently proposed a model of percolative phase transition which accounts for most of the aspects of the polymer trans-

formation. We have applied this model to polyimide which is a polymer of technological importance, in particular in electronics where it is increasingly used as insulating layer. Excellent agreement with the results of Wasserman on PPO and PAN are obtained.

ION BEAM IRRADIATION

PMDA-ODA polyimide films (kapton H from Dupont de Nemours) have been used in this work. The polymer samples have been irradiated with N^+ or Xe^+ beams at energies between 20 and 200 keV in a Balzers implantor, and between 200 keV and 2 MeV using a Van de Graaff accelerator. The beam density was limited to 1 $\mu A/cm^2$ to avoid excessive heating of the polymer and pyrolytic effects. The intense gas liberation observed at the beginning of the irradiation was studied using a partial pressure gauge (Masstorr FX from VG Instruments). Conventional ESR and four point probe techniques have been used for the characterization of the radicals and free carrier creation.

The incident ions lose their energy in a solid according to electronic processes or atomic collisions until they stop at a depth R_p of the order of several 1000 Å depending on the energy and atomic number (or mass) of the projectile. Because of the statistical character of the involved processes there is a dispersion of the ion penetrations characterized by range straggling ΔR_p, which is of the order of several 100 Å. A large number of chemical bonds are broken during the very short time of particle-matter interaction, but most of them recombine to restore the pristine material. In fact only a part of the transformed energy is converted into the creation of stable defects. We have shown that in polymers the radiation damage resulted mostly from the energy lost by electronic processes[6]. It has been established[7] that the energy is transferred through the ejection of secondary electrons along the path of the incident ion. Energetic ions can then be considered as an internal source of electrons. One of the main problems which appears when trying to establish a model of polymer degradation, comes from the discontinuous conversion of the transferred energy into damage in inorganic materials. Howitt[8] has shown by high resolution electron microscopy the existence of a hierarchy of characteristic damage volumes corresponding to different domains of energy of secondary electrons :

- **spurs** not exceeding 15 Å for energy losses in the range 0 - 100 eV,
- **blobs** of the order of 100 Å in the range 100 - 500 eV,
- **short tracks** of the order of some 1000 Å above 500 eV.

Different authors have attributed the appearance of bulk conductivity in irradiated polymers to the formation of extended carbonized volumes. According to the scheme

proposed by Wasserman[1] the damaged regions will resemble to a "tree structure" incorporated in a blob for ion energies of the order of some 100 keV whereas tracks will be formed at higher energies (typically 1 MeV and above). The formation of an interconnected network of blobs which can be interpreted in the framework of the fractal concept, may be taken as a model of the insulator-metal transition.

RADICAL FORMATION

Figure 1.a. shows the huge rate of hydrogen evolution during the first seconds of polymer degradation. In fact, it is possible to show that only the decreasing part of the partial pressure variation is representative of the gas liberation, the rapidly increasing part of the kinetics being due to the time constant introduced by the pumping speed of the irradiation system[9]. If we assume that the degradation is complete in the irradiated volumes, the overlapping between two volumes will not introduce further depletion. This implies a variation of the total number of hydrogen atoms evolved N_H versus the total number of incident ions N :

$$N_H = n_H [1 - \exp (- VN)]$$

where n_H is the hydrogen deficit at saturation and V the damaged volume. In that case the rate of hydrogen emission Q_{H_2} follows the relation :

$$Q_{H_2} \sim \exp (- VN)$$

which is proportional to the pressure according to the law of perfect gases. The damaged volume is then deduced from the slope of the semilog plot of the partial pressure versus ion fluence. A volume of 1×10^{-19} cm^3 is deduced from figure 1. The main fact is that the previous expressions allow the introduction of a filling factor :

$$p = 1 - \exp (- VN)$$

which relates the probability at a point in an irradiated volume to the total number of incident ions N (or fluence ø when related to a unit area). The product VN would correspond to the porosity introduced by Ruddy et al[10].

The loss of hydrogen corresponds to the formation of radicals, which are best known as dangling bonds by physicists (amorphous silicon). Electron spin resonance is a well suited technique to follow the creation of free radicals. We observe in figure 1.b. the straightforward relation between the loss of hydrogen and the appearance of an intense ESR signal showing a sharp decrease in linewidth, indicating the delocalization of the radicals above the percolation threshold of the conductivity which will be discussed later. The decrease of the ESR signal at high ion fluences has been attributed by Wasserman[1] to induced recombination of the free radicals. The present evolution is in excellent

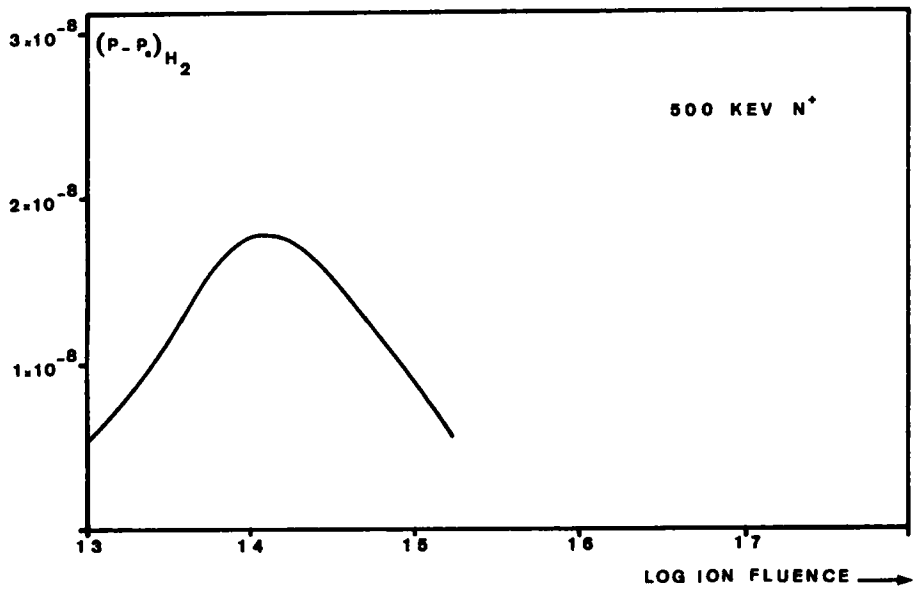

Figure 1a : Rate of hydrogen release versus log ion fluence.

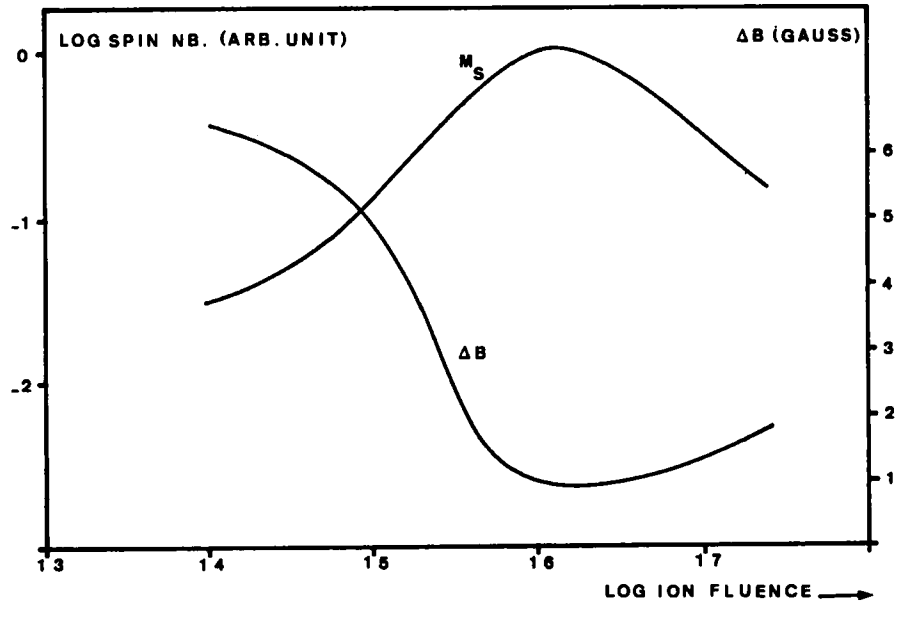

Figure 1b : development of the ESR signal versus log ion fluence (free spin concentration : M_S, ESR linewidth : ΔB).

agreement with the study of Noda and Hioki[11] who have shown that the signal could be decomposed into two different contributions showing two distinct evolutions. If we consider that one contribution is associated with radicals stabilized in isolated blobs and the other to radicals delocalized on the percolation backbone, the decrease of the ESR signal at high fluences could reflect the decrease of the total mass M_S of the isolated radical blobs, above the percolation threshold p_c, according to the relation :

$$M_S \sim \zeta^{d\ell} \sim |p - p_c|^{\upsilon d\ell}$$

where ζ is the correlation length and is related to p by $\zeta \sim |p - p_c|^{-\upsilon}$ in percolation theory[12] and $d\ell$ is the spreading dimension introduced by Stanley[2].

INSULATOR-METAL TRANSITION

ESR reflects the total number of radicals induced by the irradiation. The appearance of the infinite cluster at the percolation threshold can only be extracted from a precise analysis of the signal shape for increasing ion fluences. DC conductivity provides more direct information on the appearance of the infinite cluster. Figure 2 shows the huge drop of the resitivity (more than 18 orders of magnitude) which occurs above 10^{15} ions/cm^2. The onset of the conductivity is quite abrupt and can be attributed to the formation of the infinite cluster. However the interpretation of the conductivity variation requires the use of appropriate order parameters. Wasserman[1] has introduced a power law dependence of the percolation probability p on the ion fluence Ø :

$$p - p_c \sim (Ø - Ø_c)^x$$

In fact the filling factor $p = 1 - \exp(- VN)$ provides a different relation based on more realistic physical bases. The transformation of the lg σ versus lg (ion fluence) plot into conductivity versus the filling factor gives a percolation threshold $p_c \simeq 0.3$ which is reached for $Ø_c = 5.5 \times 10^{14}$ ions/cm^2. This value of the percolation threshold is coherent with the percolation probability predicted by the effective medium theory. The plot of log $(p - p_c)$ as a function of log $(Ø - Ø_c)$ indicates that the power law proposed by Wasserman is a rather good approximation for $Ø - Ø_c < 10^{15}$ with an exponent $x = 0.9$.

The application of the fractal concept to randomly porous media[2], which can be a good model of irradiated polymers, leads to a relation between the mass of the fractal object M and the length scale L, here ζ, at which it is considered : $M \sim \zeta^d$, where the exponent is defined as a fractal dimension. At the percolation threshold the percolative cluster is fractal. In the conjecture described by Stanley, the infinite cluster consists of blobs connected by links. It is formed by a backbone which ensures electronic transport and dead arms which do not participate in conductivity. In ESR experiments all the blobs

contribute to the signal. A spreading dimension $d\ell$ is then introduced and below the percolation threshold we have :

$$M_s \sim \zeta^{d\ell} \sim |p - p_c|^{-\upsilon d\ell} \sim |\emptyset - \emptyset_c|^{-x\upsilon d\ell}$$

A slope about 0.9 is found when plotting log of spin concentration as a function of lg $|\emptyset - \emptyset_c|$ which would give $\upsilon d\ell \simeq 1$, value consistent with $\upsilon = 1/2$ and $d\ell = 2$ taken by Wasserman[1] for branched polymers.

A different exponent arises from the conductivity variation near the percolation threshold since the percolative cluster backbone only contributes to the transport. The conductivity scales like $\sigma \sim \zeta^{df-dw}$ or $\sigma \sim (p - p_c)^t$ according to classical percolation theory. An exponent $t \simeq 8$ is deduced from the plot of log σ versus log $(p - p_c)$. Such values have been experimentally obtained by Wasserman[1] and at higher energies by Venkatesan et al[13]. The largest dimension d_w of a random walk on the percolation backbone is 4 for a dimensionality of the space larger than 6. No convincing interpretation of so high exponents has been proposed up to now. It appears necessary to explore the near vicinity of the percolation threshold, experimentally difficult because of the very low conductivities ($\sim 10^{-18}$ S/cm) in this region, in order to get more reliable experimental values. In case of confirmation, an explanation could come from dynamic effects such as ion beam induced ordering for which there are some experimental indications.

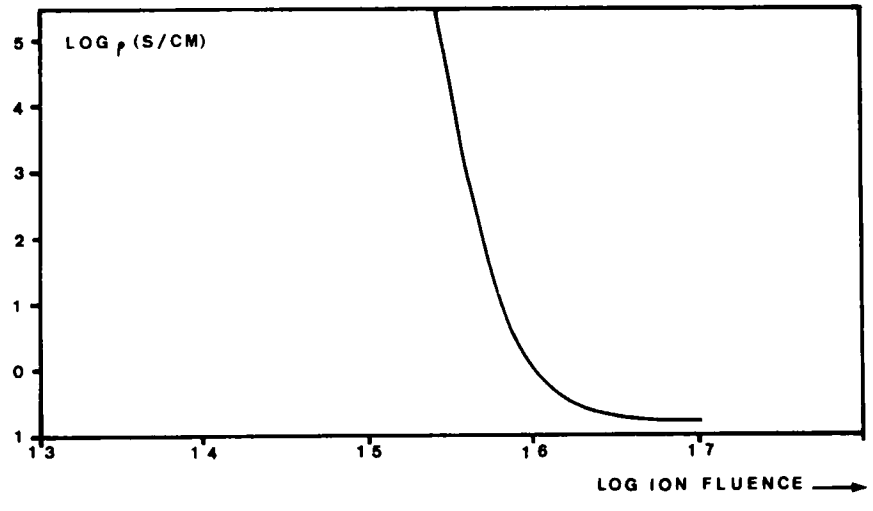

Figure 2 : ion fluence dependence of the conductivity.

CONCLUSION

Conductive properties appear in ion irradiated polyimide according to an insulator-metal tansition. Gas evolution, ESR and conductivity measurements are in accordance with the behaviour of PPO and PAN studied by Wasserman. We have introduced a filling factor, which appears to be a realistic order parameter, in order to describe the transition in terms of a percolation mechanism (percolation threshold at about 0.3). ESR and conductivity have been discussed in the framework of the fractal concepts applied by Stanley to randomly porous media. Complementary experiments will be needed to explain the anomalous critical exponent of the conductivity and to confirm the universality of this interpretation.

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