

Electrical Properties of Ion Implanted Polydiacetylene Crystals

M. Sakamoto, B. Wasserman, M.S. Dresselhaus
and G.E. Wnek
Massachusetts Institute of Technology
Cambridge, MA 02139

Introduction

Conjugated polymers are good candidates for highly conductive polymers. The conductivity of polyacetylene and poly(p-phenylene), for example, increases by more than ten orders of magnitude by chemical doping. Polydiacetylene (PDA) has a conjugated back-bone, but so far no large increase of conductivity has been reported. Though PDA has a single crystal structure and is suitable for the study of one dimensional systems, little is known about the doping mechanism.¹ Recently, a large conductivity enhancement by ion implantation in polymers has been reported.² With ion implantation, the high energy impinging ion comes close to the polymer back-bone and interacts strongly with it. Thus we expect that the conductivity of the PDA will increase greatly with ion implantation.

Experimental

The monomer ($R-C\equiv C-C\equiv C-R$, R : $CH_2OSO_2C_6H_4CH_3$) of PTS polydiacetylene was synthesized, crystallized and polymerized as described by Wegner.³ Ion implantation with 200 KeV As^+ was carried out on cleaved (100) surfaces of polydiacetylene crystals. The ion current of the implanter was 5×10^{-7} A/cm². Chemically doped PTS crystals were prepared using a two-zone method similar to that used for graphite intercalation compounds.⁴ Doping conditions for various dopants are given in Table 1.

Results and Discussion

Chemically doped PTS showed a drastic color change from a golden metallic luster, characteristic of the pristine PTS crystal to mat black. The nominal compositions of the doped materials determined from the weight uptake data are listed in Table 2. Ion implanted samples showed no surface roughening in contrast to chemical doping which greatly damages the surface of the crystals. The sample color changed from greenish-blue to silver-black with metallic luster with increasing fluence of implantation from 5×10^{14} to 10^{16} /cm².

The electrical conductivity (σ) of both the doped and implanted samples are tabulated in Table 2. The sample resistance of the ion implanted PTS with a fluence of 5×10^{14} and 2×10^{15} /cm² was too

high to measure with our techniques. For the sample with 10^{16} /cm² fluence, we could calculate σ assuming a penetration depth of 3000 Å. The electrical resistance of the chemically doped samples, especially Cs-doped-PTS changed very rapidly in air, so all sample handling was carried out in an Ar dry box.

The IR reflectance spectra of the pristine PTS (100) surface showed four very strong peaks at 8.54, 12.1, 14.9 and 18.1 μ m designated as I, II, III and IV, respectively. These peaks are all assigned to the side chain vibrational modes of DPA. The weak broad peak at 18.7 μ m, designated as V is due to the bending motion of the triple bond in the back-bone chain. This triple bond mode appears only in the polymer crystal and not in the monomer crystal. A Raman peak at 18.7 μ m was also observed in the resonant Raman scattering experiment by Bloor et al.⁵ which is assigned as above. The intensity changes of these peaks with doping and ion implantation are summarized in Fig. 1 which shows the relative IR intensity normalized to the corresponding peak intensity of the pristine PTS. The intensity change of the peak at 18.7 μ m was small compared with the other peaks before and after ion implantation and chemical doping with $FeCl_3$. On the other hand, the intensity of the peak at 8.54 μ m decreased significantly. This suggests that both ion implantation and chemical doping introduce damage mainly in the side chain rather than in the back bone chain.

Both ion implantation and chemical doping resulted in a remarkable increase in the EPR signal. The g-value of the spin was nearly 2.00 for all samples. For the ion implanted sample, the spin density calculated from the EPR intensity increased in proportion to the fluence as shown in Fig. 1. From this figure we can readily calculate the "spin yield" of impinging ions as ~ 10 spins/incident ion with a penetration depth of 3000 Å. This value for the implanted sample is much larger than the spin yield per dopant molecule calculated from the nominal composition. Since the number density of the monomeric unit is about 10^{21} /cm³,⁶ each monomeric unit has 0.1 spins compared with 10 spins in the ion implanted samples. This implies that the ion implantation is very effective in introducing spin resonance centers in PTS.

In Fig. 3, the electrical conductivity is plotted as a function of the spin density. At low spin density the conductivity increases dramatically from 10^{-15} to 10^{-4} S/cm, though the spin density increase is only from 3×10^{16} (pristine level) to 3×10^{17} /cm³. Whether this jump results from a percolation threshold or from the conductivity contribution from spinless carriers is not certain at present. In the latter case, the defect spins in the pristine material would be converted to charged but spinless carriers by a redox reaction with the dopant molecules. Further increases in conductivity with doping would be ascribed to the carriers with spins generated by a direct redox reaction between the polymer and dopant. In the case of ion implantation, many radicals are made by a covalent bond scission, because ionization would require more energy than bond breaking in these materials. Thus, a large portion of the radicals remain chargeless and do not contribute to the conductivity. This might be the explanation of the relatively low conductivity of the ion implanted PTS even though the density of spins is very large.

References

1. D.J. Sandman, G.P. Hamill, L.A. Samuelson and B.M. Foxman, *Mol. Cryst. Liq. Cryst.* **106**, 199 (1984).
2. M.S. Dresselhaus, B. Wasserman, G.E. Wnek, *Mat. Res. Soc. Symp. Proc.* **27**, 413 (1984).
3. G. Wegner, *Macromol. Chem.* **145**, 85 (1971).
4. M.S. Dresselhaus and G. Dresselhaus, *Adv. Phys.* **30**, 139 (1980).
5. D. Bloor, F.H. Preston, D.J. Ando and D.N. Batchelder, *Structural Studies of Macromolecules by Spectroscopic Methods*, ed. K.J. Ivin (Chichester; Wiley) p. 91 (1976).
6. D. Kobelt and E.F. Paulus, *Acta. Cryst.* **B30**, 232 (1974).

Table 1: Parameters for chemically doped PTS samples.

Dopant D	T _{dopant} °C	T _{polymer} °C	Doping time (days)	Weight uptake %	Nominal doping x ^(a)
I	80	98	14	19	0.6
FeCl ₃	85	90	20	12	0.3
SbCl ₅	32	40	3	80	1.1
Cs	50	80	18	-	-

(^a) Assuming the formula —[PTS(D)_x]_n—.

Table 2: Properties of doped and implanted PTS.

SAMPLE	Conductivity (S/cm)	SPIN YIELD spins/ion
I-PTS	2×10^{-2}	0.2
FeCl ₃ -PTS	6×10^{-5}	1×10^{-4}
SbCl ₅ -PTS	5×10^{-5}	1×10^{-2}
Cs-PTS	7×10^{-5}	-
5×10^{14} /cm ² (^a)	$< 1 \times 10^{-7}$ (^b)	10
2×10^{15} /cm ² (^a)	$< 1 \times 10^{-7}$ (^b)	11
1×10^{16} /cm ² (^a)	7×10^{-5}	10

(^a) Fluence of As ions in Ion Implanted PTS.

(^b) Too small to measure.

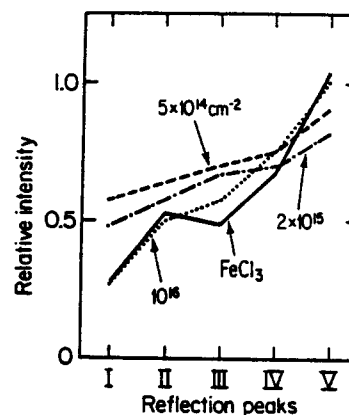


Fig.1. Relative intensity change of IR reflection peak with ion implantation and chemical doping. Each peak intensity is reduced by the corresponding peak intensity of pristine PTS.

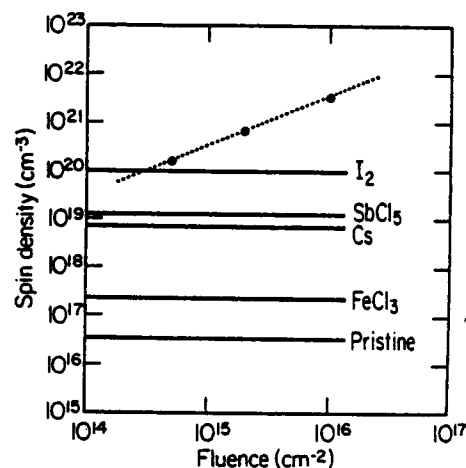


Fig.2. Spin density as a function of fluence. Spin density of chemically doped PTS is also indicated in the figure.

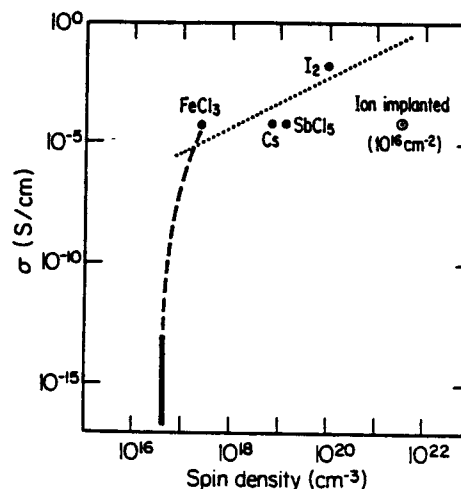


Fig.3. Conductivity plotted against spin density.