The effect of ion implantation on the polymers PAN (polyacrylonitrile), PPO (poly 2,6-dimethylphenylene oxide) and PPS (p-polyphenylene sulfide) is studied using electron spin resonance. ESR measurements on these polymers were performed as a function of ion species and fluence in the temperature range $10 < T < 300 \text{ K}$. The unpaired carrier concentration increases with increasing fluence and is independent of the ion species used for implantation in this study ($^{84}\text{Kr}$, $^{80}\text{Br}$, $^{75}\text{As}$, $^{40}\text{Ar}$ and $^{14}\text{N}$). It is therefore concluded that the carrier concentration is related to the structural damage and not to chemical doping effects. From the shape of the ESR line, the ratio of the relaxation times for one-dimensional to three-dimensional spin diffusion is determined to be larger than 1000. The temperature dependence of the unpaired carrier concentration shows a strong deviation from a Curie law behavior, which can be explained by assuming that a defect band is formed with a bandgap due to strong Coulomb interaction between electrons on the defect sites.

Key words: polymers, ion implantation, electron paramagnetic resonance, lineshape, exchange narrowing
Introduction

A dramatic increase in conductivity by about 14 orders of magnitude can be obtained by ion irradiation of normally insulating polymers (1-4). This remarkable effect has interesting implications from a technological as well as from a fundamental point of view. Possible applications of conducting polymers for interconnections in 2D and 3D integrated circuits and as p-n junctions, combined with a potentially low price, make ion implanted polymers attractive for use in the electronics industry. From a fundamental point of view, the large amount of structural disorder and the high carrier densities caused by the implantation of polymers provide an interesting disordered system where localization and electron correlation effects can be studied in a controlled way (5).

We have previously shown (1,2) that the room temperature electrical conductivity of almost all implanted polymers (except polyvinylcarbazole PVK) exhibits a sharp rise when measured as a function of fluence. For fluences $\phi \gtrsim 5 \times 10^{16}$ ions/cm$^2$, the conductivity reaches a saturation value dependent on the polymer host but independent of the implanted species, indicating that the observed electronic properties are the result of modifications to the polymer structure and not of chemical doping. In addition, strong hydrogen evolution was detected during ion implantation which suggests the creation of free radicals and dangling bonds as well as the formation of new bonding arrangements (for example C = C bonds) leading to carbonization. The temperature dependence of the conductivity of PAN and PPO exhibits a functional form $\ln \sigma/\sigma_0 = -(T_0/T)^{1/2}$ in the temperature interval $80 \lesssim T \lesssim 280$ K with a reasonably large $T_0$ ($T_0 \sim 8 \times 10^3$ K for fluences of $1 \times 10^{16}$/cm$^2$ using $^{75}$As ions at 200 keV). Two conduction mechanisms have been proposed (2,4) to explain the observed temperature dependence of the conductivity: charge hopping between isolated conducting islands or variable range hopping along and between polymer chains.

The thermoelectric power measurements show striking differences between various polymers implanted under identical conditions. Indeed, PAN exhibits n-type electrical conductivity in contrast to PPO and PPS which become p-type (2). These results may indicate that the backbone of the implanted polymer also plays an important role in