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Electronic properties of laser modified poly(bis-alkylthio-acetylene)

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Abstract

The laser-produced permanent electrical conductivity of the modified poly(bis-alkylthio-acetylene), PATAC, lies between 10^{-5} and 200 Scm^{-1} depending on the sample preparation and the laser irradiation conditions. The electrical conductivity of the modified PATAC is long-time stable without any special protection. The converted polymers are *p*-type semiconductors. The Hall mobility has been estimated between 0.01 to 8 $cm^2\,V^{-1}s^{-1}$. The temperature coefficient of the resistance in the highly conducting state is low and lies between 10^{-3} and $10^{-4}\,K^{-1}$.

ESR in the 2 mm and 3 cm waveband was applied for the study of the spin dynamics, and the rates of the intrachain and interchain spin charge carriers were obtained. Depending on the conditions of the conversion and the applied temperature the polymer shows typical properties either of a semiconductor or of a metal.

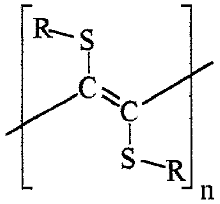
Keywords: Polyacetylene and derivatives, Electron spin resonance, Transport measurements, Hall effect, Schottky barrier

1. Introduction

Conversion of polymers by laser irradiation from the insulating form to a conducting form is reported for several polymers like polyimide [1-3], polyvinylchloride [4] and poly(bis-alkylthio-acetylene) [5-7]. Based on this effect it is possible to create a laser patterning technology for printed circuit board production or for interconnection of micro devices.

2. Sample preparation

Poly(bis-alkylthio-acetylene) (PATAC) is a conjugated polymer synthesised according to the method described in [8]. It appears as a brown powder which is soluble in a variety of organic solvents. Thin films of 0.5 to 5 μm thickness were casted or spin coated from solution on several substrates like glass, polymers, ceramics, metals or silicon. The unmodified PATAC layers are well insulating. The samples were irradiated either by an focussed Ar^+-laser (λ=488 nm) with illuminations of 5 to 80 J/cm^2 or by an KrF-excimer laser (λ=248 nm) with 20 pulses of 0.1 J/cm^2. The result is a black insoluble material with an increase in conductivity of about 16 orders of magnitude up to 200 S/cm.



$8 \leq n \leq 53$
R = methyl, ethyl, propyl

3. Electronic properties

The conductivities reached by Ar^+-laser irradiation depend not only on laser incident energy but are a rather complicated function of laser power and scan velocity. The conductivity increases extremely sharp with incident laser energy after passing a certain threshold and then reaches a saturation value. Additionally the conductivity is influenced by the film thickness and the substrate. The conductivity is relatively independent on temperature and frequency and is long time stable even under extreme environmental conditions. The linear temperature coefficient is between $4\cdot10^{-4}\,K^{-1}$ and $2\cdot10^{-3}\,K^{-1}$.

Hall measurements indicate that laser converted PATAC is a *p*-type semiconductor with charge carrier mobilities of 0.01 to 8 $cm^2\,V^{-1}s^{-1}$ [5].

By variation of irradiation conditions (e.g. wave lengths, laser power, intensity, pulse rate) we can realise not only different conductivity levels but we can also influence the type of conductivity. The high conducting PATAC shows predominantly metallic properties and ohmic behaviour. If semiconducting PATAC is in contact with certain metals Schottky barriers are formed at the metal-polymer interface.

4. ESR spectroscopy

ESR investigations were carried out at 3 cm and 2 mm wave bands. The spectra (Fig. 1) show two types of radicals. The more asymmetric spectrum (g_{xx} =2.04331, g_{yy} =2.00902, g_{zz} =2.00243) is attributed to polarons R_1 located on short conjugated chain segments and the more symmetric one (g_{xx} = 2.00551, g_{yy} =

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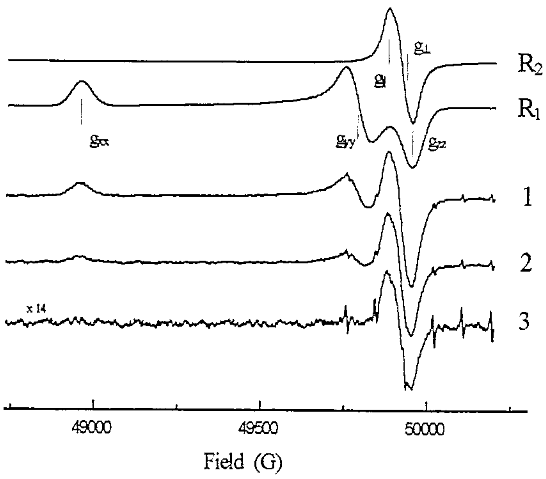

Fig. 1. 2 mm waveband ESR spectra of the PATAC samples, treated by laser with a dose 5 (*1*), 20 (*2*) and 80 (*3*) J/cm^2 registered at 100 K. The calculated spectra of R_1, R_2 are shown.

2.00380, g_{zz}= 2.00232) is attributed to polarons R_2 moving along longer conjugated chains.

At 2 mm wave band ESR the dispersion spectra with the saturation of the spin packets are also recorded [9]. As in the case of other conducting polymers [10], this leads to an appearance of a bell-like contribution in both in-phase and $\pi/2$-out-of-phase components of dispersion spectra that allows to determine spin-lattice T_1 and spin-spin T_2 relaxation parameters of the samples. The rates of spin diffusion along and between the polymer chains were calculated using the equation [11]

$$T_1^{-1} = \langle\omega^2\rangle\left[2J_1(\omega_e) + 8J_2(2\omega_e)\right] \quad (1)$$

$$T_2^{-1} = \langle\omega^2\rangle\left[3J(0) + 5J_1(\omega_e) + 2J_2(2\omega_e)\right] \quad (2)$$

where $<\omega^2>$ is the second momentum of the line, $J(\omega_e)$ is the appropriate spectral density function for 1D semiconductor at the spin precession frequency ω_e. From experimental data the temperature dependences of polaron diffusion rates in slightly treated PATAC sample were estimated [9]. By means of the well known Einstein relation the contribution of the polarons to the *a.c.* (140 GHz) conductivities was calculated as well. These temperature dependences are presented in Fig. 2.

Superslow macromolecular reorientation in the samples was determined [9] by means of the saturation transfer (ST-EPR) method [12] from the analysis of the shape of $\pi/2$-out-of-phase dispersion signal term. Pinned polarons was proved to move together polymer segments near their *x*-axis with correlation time τ_c^X=6.3·10^{-6}exp(0.04 eV/*kT*) in slightly modified polymer and τ_c^X=3.1·10^{-6}exp(0.06 eV/*kT*) in moderately and highest laser treated PATAC samples.

5. Conclusions

The investigations show that the polaron conductivity derived from the ESR measurements contribute only to a small fraction to the conductivities observed. Additionally the polaron conductivity shows a much stronger temperature dependence as the conductivity observed by electrical methods does [5]. This gives rise to the conclusion that the conductivity is dominated by spinless bipolarons which do not contribute to the ESR signal. The relatively low temperature dependence of *d.c.* conductivity is a result of compensating behaviour of charge carrier mobility and concentration.

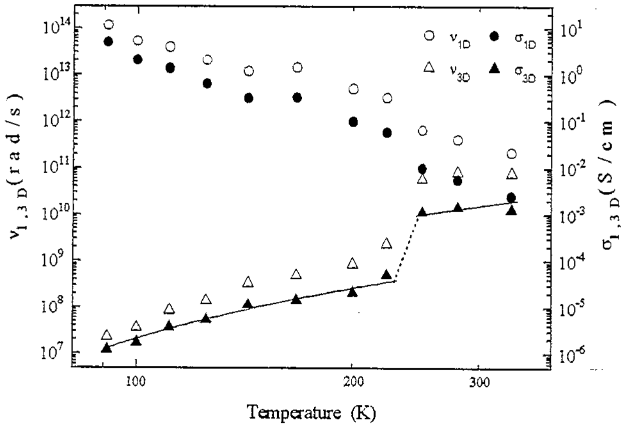

Fig. 2. Temperature dependences of intrachain and interchain diffusion rates of mobile polarons in PATAC sample treated by laser with a dose 5 J/cm^2 and of polaron contribution to *a.c.* conductivity calculated from Einstein equation. Additionally the dependence of the 3D conductivity calculated in the frames of activation spin hopping with E_a=35 meV is shown by solid line.

Due to the ability of conductivity tuning, fine patterning, environmental stability and nearly temperature independent conductivity the laser converted PATAC is an interesting material for application in electronics.

Acknowledgements

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