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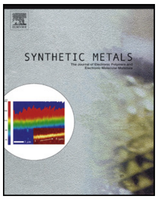

Decay in spin diffusion length with temperature in organic semiconductors—An insight of possible mechanisms

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ABSTRACT

This article presents a comparison of spin transport mechanism in two π-conjugated organic polymers namely, regiorandom and regioregular poly (3-hexyl thiophenes) with same elemental composition but different regioregularity of the constituent atoms leading to different crystallinity and charge carrier mobility. Spin-valve devices made with both polymers show substantial low temperature giant magnetoresistance (GMR) response. However, the GMR signal decreases drastically at higher temperatures where charge carrier mobility is higher. Our results suggest that in both the polymers spin diffusion length at low temperature is almost similar, but, temperature dependence of spin diffusion length is greater in the disordered polymer compared to the more structured one. Comprehensive analysis of our experimental data suggest that at low temperature, in the VRH hopping regime (5–50 K), spin relaxation due to hyperfine interaction and Elliot-Yafet momentum scattering is the dominant spin relaxation mechanism while in the thermally activated regime Dyakonov–Perel mechanism contribution becomes significant. However, mobility dependence of spin scattering rate in both systems differ from traditional Dyakonov–Perel model signifying that there are coexisting contributions from several spin scattering effects present in the system. Proper understanding and careful modification of spin–orbit coupling in organic semiconductors can be very useful for organic based spin devices.

1. Introduction

Since the emergence of organic spintronics, spin injection and transport in many organic spin valve structures have been reported by different groups [1–5]. Different electrodes as well as spacer materials were used in these stacked structures, however, none of these electrode–spacer–electrode trilayers showed promise for improved spin response at higher temperature. In 2009, Drew et al. [6] reported that spin diffusion length (λ_S) in organic semiconductor (OS) small molecule Alq_3 decreases rapidly as a function of temperature, but what causes this large decrease of spin diffusion length at increased temperature remained an open question. In our recent work with in π-conjugated polymer regio-regular poly (3-hexylthiophene) (RRP3HT) based spin injection devices, we have found that charge and spin transport has a clear correlation and transition from variable range hopping (VRH) to thermally activated nearest neighbor hopping marks the most significant decrease in spin diffusion length in RRP3HT [7]. However, if this crossover in transport regime and decrease in λ_S is universal for all OS and whether the crystalline or amorphous structure of the OS play a role in the decay of λ_S with temperature, needs further clarification. Also, the spin relaxation mechanisms in the two different transport regimes need further careful analysis.

In the present work, we have compared the transport and magneto-transport properties of two π-conjugated polymers RRP3HT and regio-random poly (3-hexylthiophene) (RRaP3HT) based spin valve devices. The reason behind choosing RRP3HT and RRaP3HT is to investigate the role of structural disorder and mobility without modifying the other parameters influencing spin relaxation. As the elemental composition is similar in both RRP3HT and RRaP3HT, spin–orbit (SO) coupling and hyperfine interaction (HFI) is supposed to be similar in these two materials. However, RRP3HT forms a two-dimensional lamellae structure on the substrate and due to delocalization of charge carriers within the lamellae RRP3HT has a much better charge carrier mobility ($10^{-5}\,cm^2\,V^{-1}\,s^{-1}$) than RRaP3HT. In comparison, RRaP3HT has a completely disordered structure and the charge transport in this system is slow and dispersive. Comparison between these two systems will definitely provide deeper insight of the spin relaxation phenomenon in different OS systems.

2. Experimental

The vertical $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)/P3HT/Co/Al device structure is fabricated using the following technique. First, the LSMO films were made using pulsed laser deposition technique as

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reported earlier [8]. After cleaning the LSMO films with acetone and isopropyl alcohol, RRP3HT or RRaP3HT films were spin-coated on top of them from a 10 mg/ml chloroform solutions and annealed at 800 °C for 10 h in a nitrogen-filled glove-box. Finally Co and Al were vacuum-evaporated on top of the polymer film using a shadow mask without breaking the vacuum. The polymer film thickness was kept 70–80 nm, confirmed by the Charge Extraction by Linearly Increasing Voltage (CELIV) measurements [9]. The MR of the SVs was measured using four probes, one pair of current and voltage leads connected to the LSMO while the other pair to the Al, varying the in-plane magnetic field between +300 mT and -300 mT and the temperature between 5 K and 300 K.

3. Results and discussion

Fig. 1 shows schematic structural diagram of the two polymers. In RRaP3HT, the alkyl chains are randomly oriented while in RRP3HT all the alkyl chains are oriented in a certain direction. Moreover, RRaP3HT forms a one dimensional chain structure on the substrates with poor orientation of conducting π-stacks in a certain direction while RRP3HT forms a two dimensional lamellae structure perpendicular to the substrate plane with a preferential orientation of conducting π-stacks (as shown in Fig. 1). This well-organized two-dimensional structure in RRP3HT leads to improved charge carrier delocalization resulting in better mobility [10].

Fig. 2(a) shows spin valve MR response of a typical RRaP3HT based spin-valve device at 10 nA bias currents. The device resistance showed almost similar value as the RRP3HT devices however the giant magnetoresistance (GMR) signal was significantly less in this case (Fig. 2(b)). Also the switching field (≈100 mT) exceeds the LSMO coercive field value (≈25 mT) significantly, as also observed before [11]. This higher switching field in the polymeric spin valve devices can be attributed to the modification of the coercive field of LSMO surface in different chemical surroundings i.e. by binding with different organic molecules. With increasing bias current, the GMR signal dropped off significantly in the lower bias regime, however for higher bias regime the GMR response was almost saturated.

Fig. 3(a) shows temperature dependence of resistance and magnetoresistance of a typical RRaP3HT based spin valve device. Also temperature dependence of RRP3HT based spin valve device is shown (Fig. 3(b)) for comparison. From the figures, it becomes clear that, like in previously reported RRP3HT devices [7], in RRaP3HT devices also temperature dependence of both GMR and the device resistance is similar. Hence we can conclude that charge and spin transport has a clear correlation in both these polymeric spacers. We have also calculated the spin diffusion length (λ_S) in RRaP3HT using modified Júlliere formula [7] from the measured GMR value,

$$\frac{\Delta R}{R} = \frac{R_{AP} - R_P}{R_{AP}} = \frac{2p_1p_2e^{-(d-d_0)/\lambda_s}}{1 + p_1p_2e^{-(d-d_0)/\lambda_s}} \tag{1}$$

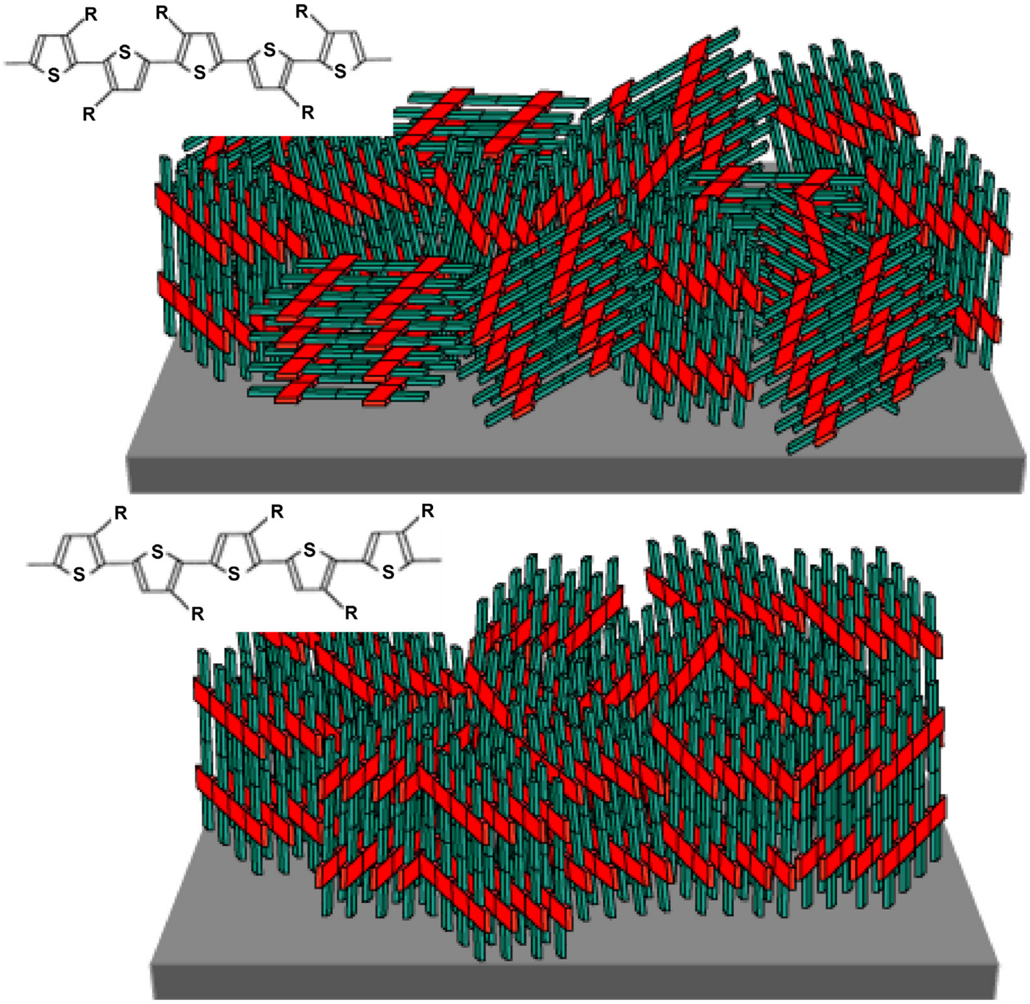

Fig. 1. Schematic diagram (reproduced from R. J. Kline et al., Nature Mater. 5 (2006) 222–228) of the structure and organization of region-random (top) and regio regular poly (3-hexyl thiophene) (bottom) forming either a poor orientation or a preferentially oriented crystal structure on the substrate. Conducting π-stacking planes are shown in red while the insulating hexyl chains are in green. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)