New advances in organic spintronics

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Abstract. The basic components of spintronic devices are spin polarized ferromagnets and spin transporting non-magnetic spacers. Exploiting carbon-based materials for these components promises to extend functionality of information storage and processing as well as to improve device integration and fabrication. Here we present the magnetoresistance of organic semiconductor rubrene (C\textsubscript{42}H\textsubscript{28}) used as a spacer in La\textsubscript{2/3}Sr\textsubscript{1/3}MnO\textsubscript{3} (LSMO)/organic semiconductor (OSC)/Fe heterojunctions. Efficient spin polarized tunneling through the thin layer of rubrene spacer (5 nm) was observed. As the thickness of rubrene layers is increased, device current is strongly limited by carrier injection resulting in strong temperature dependent device resistance. The carrier injection is described with thermionic field emission at the metal/OSC interface. As a next step toward organic spintronics we used an organic based magnet vanadium-tetracyanoethylene (V(TCNE)\textsubscript{x}, x\textapprox{}2) in tandem with LSMO in a spin-valve with 5 nm rubrene spacer. V(TCNE)\textsubscript{x} is the earliest developed room temperature molecule-based magnet (T\textsubscript{c} \textapprox{} 400 K). Due to strong on-site Coulomb interaction and weak intermolecule overlapping their magnetic state can be described with a model of half-semiconductor in which valence and conduction bands are spin polarized. The magnetoresistance data for bulk V(TCNE)\textsubscript{x} is in agreement with the model of spin polarized valence and conduction bands. We demonstrated that an organic-based magnetic semiconductor V(TCNE)\textsubscript{x} functions very well as an electron spin polarizer in the standard spintronic device geometry.

1. Introduction

An emerging field of “spintronics” based on the control of electron “spin” degree of freedom introduces a number of new phenomena and applications [1]. The principal spintronic device, a “spin valve”, consists of soft and hard magnetic layers separated by a non-magnetic spacer. Using of organic materials for these components potentially enables to improve functionality and processability [2, 3]. Here we present our recent progress in this organic spintronics.

The application of organic semiconductors (OSCs) as a spacer was motivated by anticipated long spin lifetime in OSCs. However, efficient spin polarized carrier injection and transport in OSC films are rather complicated [4]. Definitely, the spin valve effect was measured in thin layers of OSC (< 10 nm) as tunneling magnetoresistance (TMR) [5, 6]. But the previous reports [7, 8] on giant magnetoresistance (GMR) with thick OSC layers (> 100 nm) have been very controversial [9-11]. The low and temperature/voltage independent resistance as well as wrong sign of magnetoresistance for those devices suggest that the charge transport in the spacer represents tunneling through a random network of metallic (Co) nanoparticles. The OSC plays a role of supporting dielectric matrix for those metallic granular networks.
Here we describe real GMR in OSC films due to injection and transport through the OSC channel [4]. We used rubrene as a prototype of OSC because rubrene consists of only hydrogens and carbons and has the highest mobility among OSCs and a low energy gap \( \sim 2.3 \text{ eV} \) (for Alq3 \( \sim 2.8 \text{ eV} \)). Varying thickness of rubrene film from 5 to 50 nm we observed the crossover from TMR to GMR. In the GMR regime the rubrene devices show strong exponential temperature and electric filed dependence of the current and sign of GMR remains the same as TMR one. The maximal thickness of rubrene film for which we detect MR is 30 nm at temperature less than 100 K.

Another advance we introduced was the use of a molecular based magnet V(TCNE)_x as spin injector/detector for a spin valve [12]. It is widely spread that the spin transfer between semiconductor spacers and magnetic contacts can be improved by using magnetic semiconductors typically obtained by doping conventional semiconductors with transition metals [1]. However the application of such diluted magnets is restricted because of their low Curie temperature. The organic V(TCNE)_x is a semiconductor with \( T_c \sim 400 \text{ K} \) [13]. Here we report that V(TCNE)_x can be used as spin injector/detector in a spin valve with a 5 nm rubrene film as spacer. The device demonstrates excellent performance and its operation at high temperatures is limited to spin polarization of LSMO which is used as the second magnetic contact.

2. Giant Magnetoresistance with OSC, Rubrene

Fig. 1a illustrates the schematics of our LSMO(50nm)/LAO(1.2nm)/Rubrene/Fe(30nm) heterojunction with rubrene (C_{42}H_{28}) film as a spacer. The epitaxial 50 nm of LSMO was grown by pulse laser deposition. Thin layer (1.2 nm) of LaAlO_3 (LAO) was employed to improve interfacial quality between LSMO and rubrene. The thickness of the rubrene layer in our devices was varied from the TMR regime \( (d \leq 5 \text{ nm}) \) to the giant magnetoresistance limit \( (d \geq 20 \text{ nm}) \). The temperature dependence of MR curves for 5 nm rubrene device at bias voltage 10 mV is presented in Fig. 1b. Device exhibits positive MR over all biases and temperatures and the steps of MR show excellent correspondence with each other as well as the coercivity of Fe (30 nm) and LSMO (50 nm) electrodes.

![Figure 1](image_url)

**Figure 1** (a) Schematic view on the device structure. (b) Tunnel magnetoresistance of LSMO(50 nm)/LAO(5 nm)/Ru(5nm) /Fe(30 nm) heterojunction. Reproduced in part with permission from Yoo et al., Phys. Rev. B 80, 205207 (2009) Copyright © 2009 American Physical Society.
As the thickness of rubrene is increased, the device current strongly relies on carrier injection resulting in strong temperature and voltage dependent device resistance [4]. Fig. 2a displays $T$ dependent device resistivity for the 5, 20, 50 nm rubrene devices and 50 nm LSMO film at bias 0.1 V. Strong nonlinear $I-V$ curves are shown in Fig. 2b for 5, 20, 30, and 50 nm Ru devices.

The strong $T$ and $V_b$ dependent current for devices with space thickness less than 100 nm originates mainly from activation at the metal/OSC interface barriers rather than bulk resistance. To explain the voltage and temperature dependence of current in our organic-based spin valve devices, we use the theoretical model developed by Kiveris and Pipinys [14]. This model describes carrier injection at the metal/semiconductor interface by equally putting multiphonon activation and field emission of electrons from defect states at the interfaces to the conduction band of semiconductors. The phonon assisted tunneling rate of electron under the electric field at the metal/semiconductor interface is as follow [14, 15]

$$W_T = eE \left(8m^*\epsilon_T\right)^{1/2} \left(1 + \gamma\right)^{1/2} \left[1 + \gamma\right]^{-1/4} \exp\left[-\left((32m^*\epsilon_T)^{1/2} \left(3eE\right)\right)^{-1}\left[1 + \gamma\right]^{-1/4} \left[1 + \gamma\right]^{1/2} + \gamma\right]^{1/2},$$

where $\gamma = (2m^* \Gamma^2 / 8\hbar eE)^{1/2} \epsilon_T$. Here $\epsilon_T$ is the energetic depth of defect states from the conduction band of semiconductor, $E = V_b / d$ is the applied electric field, $\Gamma^2 = 8a (\hbar \omega)^2 (2n + 1)$ is the width of the defect states broadened by the interaction with optical phonons, $n = 1/\left[\exp(\hbar \omega / k_B T) - 1\right]$, and $a$ is the electron-phonon coupling constant ($a = \Gamma/\hbar \omega$).

![Figure 2](image)

**Figure 2 (a).** $T$-dependence of resistance of 5, 20, 50 nm rubrene devices and 50 nm LSMO film at bias 0.1 V. (b) $I-V$ curves for 2, 20, 30 and 50 nm rubrene devices at $T = 10$ K. Reproduced in part with permission from Yoo et al., Phys. Rev. B 80, 205207 (2009) Copyright © 2009 American Physical Society.

The dashed lines in Fig. 3 show fits to 20 nm rubrene device current with Eqn. (1). Qualitatively good fitting can be achieved over all $T$ and $V_b$ with fixed parameter of $a = 1.4$, $\hbar \omega = 0.034$ eV, $m^* = 1.2 m_e$ and $\epsilon_T = 0.678$ eV (for $V_b = 0.1$ V), and 0.660 eV (for $V_b = 0.1$ V). The results show that 20 nm rubrene device currents crucially depend on the carrier injection. The phonon assisted carrier injection start to increase dramatically above 100 K. Below 100 K the temperature independent but strongly voltage dependent elastic tunneling dominates.
As the thickness of rubrene layer is increased further ($d > 30$ nm), the effects of carrier transport in the bulk on the device current become stronger. As it was suggested by Ruden and Smith [15], in order to transmit spin polarized carriers through the thick amorphous OSC channel, applying high bias is essential to promote field emission and support higher drift mobility (e.g., $\mu = \mu_0 \exp(E/E_0)^{1/2}$). However, the conductivity mismatch problem could be more serious in electrical detection of MR [17] as $d$ increases further. The MR of 20 nm rubrene film is shown on Fig. 4a at different temperature. Fig. 4b shows the MR for spin valves with different thickness of rubrene spacer. No any MR signal was detected for thickness larger than 30 nm.

**Figure 3.** Temperature and bias dependencies of the current for 20 nm rubrene device. The dashed lines show the fit to the phonon-assisted tunneling model. Reproduced in part with permission from Yoo et al., Phys. Rev. B 80, 205207 (2009) Copyright © 2009 American Physical Society.

**Figure 4 (a).** MR of 20 nm rubrene device for different temperatures and bias 1 V. (b) Temperature dependence of MR for 5, 20, and 30 nm rubrene devices. Reproduced in part with permission from Yoo et al., Phys. Rev. B 80, 205207 (2009) Copyright © 2009 American Physical Society.
3. Molecular based Magnetic Semiconductor, V(TCNE)$_2$

Vanadium-tetracyanoethylenes (V(TCNE)$_x$, $x\approx 2$) represents a room-temperature molecule-based ferrimagnet with ordering temperature $T_c \approx 400$ K and a small coercive field $H_c = 4.5$ G. V[TCNE]$_2$ is a semiconductor with conductivity $\sim 10^{-4}$ S/cm and gap $\sim 0.5$ eV at 300 K. It can be prepared at 40 °C using chemical vapor deposition [18].

Nature of magnetic state and semiconductor charge transport of V(TCNE)$_2$ can be understood within the model of half semiconductor [13]. From average stoichiometry V(TCNE)$_2$ and because of the [TCNE]$^-$ is the radical anion, it can conclude that the vanadium is in the V$^{ill}$ oxidation state [19]. The spins of three electrons at the 3d level of V$^{ill}$ are parallel with a total spin of 3/2. Fig. 5a represents a one-dimensional “cartoon” for the spatial distribution of energy levels in V(TCNE)$_2$. The orientation of electronic spins in the $\pi^*$ state is opposite of the 3/2 spin of V$^{ill}$ due to the large antiferromagnetic exchange coupling, $J$.

The relevant model for description of electronic state on TCNEs is the Hubbard model with nearly half filling $\pi^*$ band [13]. According to this model due to the Coulomb repulsion $U_c$ between electron sitting on the same site the initial $\pi^*$ band is split into two non overlapping subbands provided $U_c >> t$, where $t$ is the electronic transfer integral between neighboring TCNEs. The spins of electrons in the lower filled Hubbard subband should have antiferromagnetic order, but the corresponding exchange constant, $J' = 2\hbar^2/3U_c$ is much less than the antiferromagnetic exchange constant, $J$ between 3/2 spins of V$^{ill}$'s and spin ½ of [TCNE]$^-$. Therefore, in the magnetic phase the electronic spins of lower subband are parallel and their orientation is opposite to the spin of V$^{ill}$. According to the exclusion principle, the upper empty subband may be occupied by electrons with spins polarized in the direction which is opposite to the lower subband, i.e., along the direction of the V$^{ill}$ spins.

The one-site Coulomb repulsion $U_c$ or the gap between $\pi^*$ and $\pi^*$ levels of TCNEs in analogy with known organic materials is estimated to be 2 eV [20]. According to Tengstedt et al. [20-21], the 3d level of V is located inside the Hubbard gap. Therefore, the temperature dependence of conductivity is determined by thermal activation of electrons from 3d levels of Vs to $\pi^* + U_c$ levels of TCNEs (see Fig. 5a). The corresponding activation energy, $E$, besides the energy separations between the two levels, $E_0 = E(\pi^* + U_c) - E(3d) \sim 0.5$ eV, includes the change of magnetic energy associated with this electronic transition.

Taking into account the opposite spin polarizations of $\pi^*$ subbands and their antiferromagnetic coupling with V$^{ill}$ spins, the magnetic contribution to the activation energy, $\Delta E$, is approximated as $\Delta E = -4J\langle S \rangle < \sigma >$ [3, 22], where $< S >$ is the spin 3/2 polarization of V$^{ill}$ and $< \sigma >$ is the spin 1/2 polarization of the lower $\pi^*$ subband. Applying the magnetic field changes the spin polarization, and hence the activation energy. In this way, the magnetoresistance can be estimated from the relation

$$MR = (-4J/k_B^2)[< S(H)> - < S(0)> + < \sigma(H)> - < \sigma(0)>].$$  

In the paramagnetic phase the spin polarizations are induced by an external magnetic field and become noticeable only upon approaching $T_c$. Within the mean field theory [12] $< S >\sim -< \sigma >\sim \chi h$, where $\chi$ is the Curie-Weiss susceptibility per spin, $\chi \sim 1/|\delta|$, with $\delta = (T - T_c)/T_c$ being the “distance” from $T_c (k_B T_c \approx 3.2 J)$. Here $h = \mu_B g H/(k_B T_c) << 1$ and $h^{3/2} << |\delta| << 1$. As a result, the gap widens with the applied field and $MR \sim (h/\delta)^2$.

In the critical region, $|\delta| << h^{3/2}$, the induced polarization obeys the scaling law $< S >\sim -< \sigma >\sim h^{3/2}$ and MR $\sim h^{3/2}$. Below $T_c (|\delta| >> h^{3/2}, |\delta| < 0)$, there is the spontaneous spin polarization $< S >\sim -< \sigma >\sim |\delta|^{1/2}$, with field-dependent corrections $\sim \chi h$, where $\chi \sim 1/|\delta|$. Therefore, in the ferrimagnetic phase the MR is proportional to the external field, MR $\sim h/|\delta|$

To check these predictions on the $H$ and $T$ dependencies of MR, the $T_c$ was decreased by exposition of a sample on air. Fig. 5b shows up the magnetic field dependence of magnetoresistance below and above $T_c = 240$ K. Linear and quadratic dependence of magnetoresistance on a magnetic field clearly can be identified. As a function of temperature, the MR has its maximum near $T_c$. For $H = 6$ kG and $T_c = 230$ K the model predicts the MR maximum $\sim h^{2/3} \sim 2\%$, which is of the order of the observed value.
Thus, the experimental results for resistance and MR of organic-based magnet \( V(\text{TCNE})_x \) support the existence of spin-polarized subbands. This is a very desirable property for utilizing organic-based magnetic semiconductors in spintronic applications.

Figure 5 (a). Energy diagram for \( V(\text{TCNE})_2 \). (Reproduced with permission from Prigodin et al., Adv. Mater. 14, 1230 [2002]. Copyright © 2002 John Wiley and Sons.) (b) The magnetoresistance of \( V(\text{TCNE})_2 \) as a function of magnetic field above and below \( T_c \). Reproduced with permission from Prigodin et al., Adv. Mater. 14, 1230 (2002). Copyright © 2002 John Wiley and Sons.

4. Organic based Spin Valve \( V(\text{TCNE})_x(500 \text{ nm})/\text{Rubrene}(5 \text{ nm})/\text{LAO}(1.2 \text{ nm})/\text{LSMO}(80 \text{ nm}) \)

Here we demonstrate that the organic-based magnetic semiconductor \( V(\text{TCNE})_x \) functions well as the ferromagnetic layer in a hybrid magnetic tunnel junction device [12]. The rubrene thin film was used for organic semiconducting barrier as it was shown to be highly efficient for spin polarized tunneling. Fig. 6a shows typical magnetoresistance curves for in-plane magnetic field in the hybrid magnetic tunnel junction \( V(\text{TCNE})_x(500 \text{ nm})/\text{Rubrene}(5 \text{ nm})/\text{LAO}(1.2 \text{ nm})/\text{LSMO}(80 \text{ nm}) \) at 100 K with an applied bias of 0.5 V. The magnetization curves for individual magnetic layers of \( V(\text{TCNE})_x \) and LSMO films were recorded by SQUID magnetometry and are overlaid on the same plot of Fig. 6a. Blue line and symbols (△) represent the data recorded during positive sweep of magnetic field. Red line and symbols (◇) represent the data collected during negative field sweeping.

With sweeping of the magnetic field, the device resistance becomes higher when the magnetizations of two magnetic layers become antiparallel. The magnetoresistance curves well
correspond to the magnetization steps of both V(TCNE)x and LSMO films and clearly represent the shape of hysteresis curves of each individual magnetic layer. This unambiguously demonstrates spin filtering through a V(TCNE)x magnetic semiconductor film, wherein spin polarized carriers tunnel through the hybrid rubrene/LAO barrier while effectively conserving their spin polarization.

The MR as a function of temperature (Fig. 6b) shows a maximum at ~ 100 K. The decrease of MR, as temperature increases above 100 K, is attributed to the decrease of surface spin polarization of the LSMO film. This suggests that MR at higher temperature can be achieved in magnetic tunnel junctions with organic-based magnet V(TCNE)x, in tandem with other ferromagnets. The MR of our devices decreases as temperature decreases below 100 K because the semiconductor bulk resistance of V(TCNE)x film starts to dominate the total device resistance as T decreases below 100 K [12].

The bias dependence of MR in our hybrid magnetic tunnel junction is similar to the behavior of tunnelling magnetoresistance in typical inorganic magnetic tunnel junctions. At lowest bias, data are noisier as the device resistance becomes high at low T and low Vb. The observed bias-induced suppression of MR by the application of high-voltage could be also related with the bulk resistance of V(TCNE)x film. At low bias, the barrier resistance controls the device currents. As the applied bias increases, the bulk resistance of V(TCNE)x starts to control the total device resistance, which reduces the effectiveness of electrical detection of spin dependent scattering at the interface.

5. Conclusion

In summary, we presented the GMR with an OSC (Rubrene) spacer. In contrast to the previous reports the GMR for our devices shows strong Vb and T dependence as a result of the activation processes of carrier injection and transport in amorphous OSC layer. We explained the carrier injection and
transport into/in OSC and their impact on the GMR in OSC-based spin valves in terms of phonon-assisted tunneling and hopping in the presence of strong electric field.

We have shown that the magnetotransport of organic based magnet V(TCNE)₂ can be explained in terms of discrete spin polarized bands with hopping mechanism transport. Spin valve used V(TCNE)₂ as one of magnet confirms the presence of these spin polarization bands.

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