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New method of spin injection into organic semiconductors using spin filtering tunnel barriers

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ABSTRACT

In an organic light emitting diode, injection of spin-polarized current can be expected to influence the light emission. For the emission to occur, the bias voltage must exceed the device turn-on voltage. However in magnetic junctions with conventional ferromagnetic electrodes, the magnetoresistance decreases as bias increases. This response limits the use of such ferromagnets for spin injection in organic light emitting diodes where high bias is needed. A way out of this limitation is shown here, by utilizing the spin-filter phenomenon to generate current spin polarization, and inject into an organic semiconductor. Europium sulfide was used as the spin-filter layer with rubrene as the barrier to form a quasi-magnetic junction. The junctions showed magnetoresistance which increased as bias voltage was increased, with a high value of 6% at 1.8 V. These results show the potential to use spin-filter systems for investigating electroluminescence in organic light emitting diodes with spin-polarized electrons. Ferrite compound spin-filters with Curie temperature much above room temperature are a potential class of materials to realize room temperature spintronics devices.

The use of organic semiconductor (OS) as a tunnel barrier or a spacer layer between two ferromagnetic electrodes has attracted significant attention in the last few years towards the development of organic spintronic devices [1,2]. Due to the weak spin–orbit and hyperfine interactions, spin information in these materials is expected to be preserved for a relatively long time, ~ hundred microseconds to few milliseconds [3]. In literature, both tunneling magnetoresistance (TMR) in thinner [4,5] and giant magnetoresistance (GMR) in thicker [6–8] OS as a barrier/spacer layer have been realized. Recently, isotope substitution in OS has shown reduction in the spin scattering hyperfine fields within the molecule, with concurrent enhancement in the magnetoresistance (MR) signal [9]. In these studies, the ferromagnetic injector/detector was based on inorganic ferromagnets (FMs) like lanthanum strontium manganese oxide (LSMO), iron (Fe), cobalt (Co) or Permalloy. Recently, progress has been made towards using a chemically synthesized organic FM as a spin injecting material: Yoo et al. [10] reported TMR in rubrene using an organic ferromagnetic semiconductor, $V(TCNE)_x$, as the spin polarized electrode.

Here, we present results obtained using an inorganic ferromagnetic insulator europium sulfide (EuS) as the spin-filter (SF) tunnel barrier replacing the normal FM electrode for injecting spins into rubrene [11]. The exchange splitting (ΔE_{ex}) of the conduction band in ferromagnetic semiconductor, below its curie temperature ($T_{c,bulk}$ = 16.6 K), create spin filtering properties. The energy difference of ΔE_{ex} (see Fig. 1) leads to different barrier heights for the spin-up and spin-down tunneling electrons. Since the tunneling probability depends exponentially on the barrier height, the spin-up electrons tunnel easily giving rise to highly spin polarized tunneling electrons: in the case of EuS, the spin polarization has been shown to be >80% [12]. Thus, spin filtering approach has the potential

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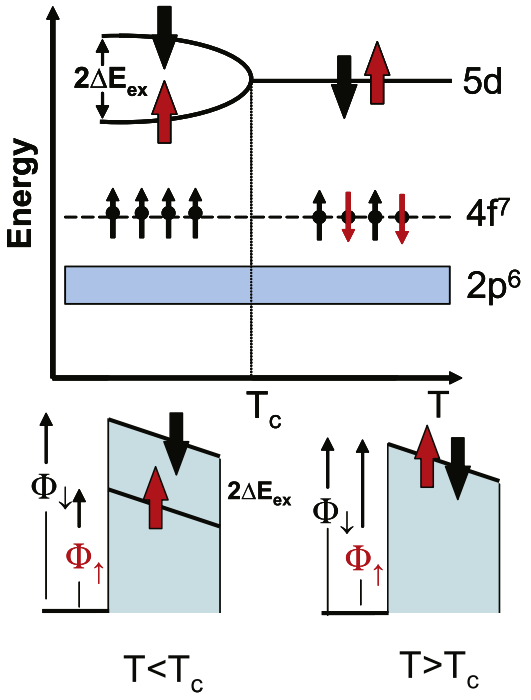

Fig. 1. Energy levels of EuS showing the splitting in the 5d conduction band below T_c (16.6 K) by the exchange energy, $2\Delta E_{ex}$ ($\sim$ 0.36 eV in bulk). When used as a tunnel barrier, it leads to lowering of the barrier height for spin-up electrons ($\Phi_\uparrow$) relative to the spin-down electrons ($\Phi_\downarrow$).

to serve as a good source for injecting spin-polarized electrons into an OS. There has been a recent report of utilizing a spin filter (EuO) for spin injection into rubrene [13]. However, in this preliminary study the interface and device stability was a significant issue. In the present work, we show that the use of SF barrier does not only provide spin injection, but also leads to enhanced spin injection at high applied voltage biases. Recently, chemically synthesized organic ferromagnetic semiconductor, $V(TCNE)_x$, has also been used to inject spins in OS. However, its stability especially in thin film form and high resistance as an electrode need to be addressed.

In the current study, the quasi-magnetic junction (QMJ) devices were fabricated using an *in situ* shadow mask technique in a vacuum chamber with a base pressure of 7×10^{-8} Torr. The geometry of the device (junction area: $200 \times 200\ \mu m^2$) is shown in Fig. 2. A thin film of EuS (2 nm) was grown at room temperature over Al, followed by the deposition of rubrene. Different thicknesses of the rubrene layer were grown ranging from 5 to 12 nm. A thin film of Fe (12 nm) was used as the top FM electrode and the whole structure was subsequently protected by 8 nm of Al_2O_3. The growth of rubrene, as seen in previous studies, has been shown to be influenced by the local surface electronic properties of the bottom seed layer [7,14]]. The insulating property of EuS can be expected to lead to azimuthal growth of rubrene at the interface, as in the case with alumina seed layer. Such interface ordering has been reported to improve the spin injection efficiency in rubrene [7].

MR measurements were performed at 1 K to achieve full exchange splitting of the conduction band in EuS, below its T_c, for higher spin filtering efficiency. MR was measured for different rubrene film thicknesses ranging from 5 to 12 nm. For 5 nm thick rubrene, the bulk of the junction resistance was coming from EuS and the anti-parallel state of the magnetization between EuS and Fe layer was not observed, whereas for 7 nm rubrene, although there was magnetic coupling between EuS and Fe, independent switching of EuS and Fe magnetizations could be seen (see Fig. 2a). Here, the large background non-saturating MR signal observed might be attributed to the magnetic field dependent resistance of the EuS barrier. With increasing rubrene thickness, the device showed a transition from a EuS dominated to a rubrene barrier dominated junction resistance. For 9 nm rubrene, higher MR was seen with a well-defined parallel and anti-parallel magnetization state of the EuS and Fe layer (see Fig. 2b). In these devices, the resistance was observed to increase at zero fields before reaching the anti-parallel state of the two FM electrodes. This could be caused by the dipolar coupling of EuS and Fe layer. The coercivity of bottom EuS layer was confirmed to be $\sim$90 Oe by SQUID measurements. A MR of 6% was

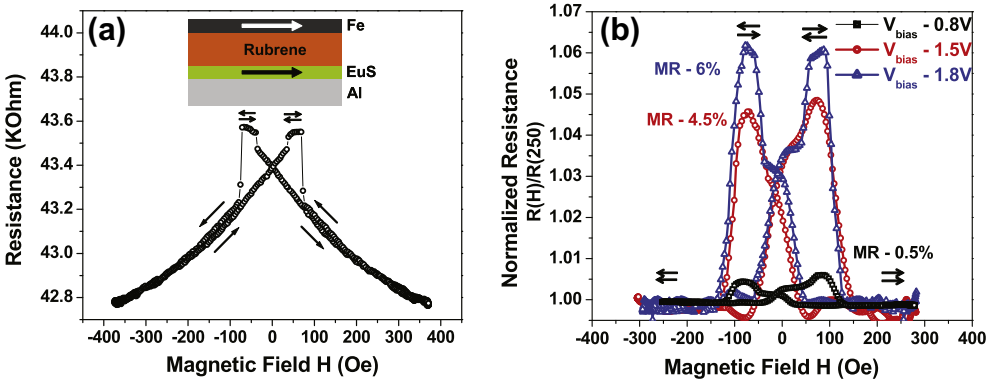

Fig. 2. (a) MR measured for rubrene barrier thickness of 7 nm at 1 K in a quasi-magnetic junction (schematically shown in the inset) having the layer structure: Al (8 nm)/EuS (2 nm)/Rub (x nm)/Fe (12 nm). (b) Increase in MR with applied voltage bias, for a junction with 9 nm rubrene barrier, measured at 1 K. The DC resistance of the device reduced from $\sim$12 MΩ at 0.8 V to $\sim$300 KΩ at 1.8 V.