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Citation: *Appl. Phys. Lett.* **101**, 022416 (2012); doi: 10.1063/1.4737008

View online: <http://dx.doi.org/10.1063/1.4737008>

View Table of Contents: <http://aip.scitation.org/toc/apl/101/2>

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Manipulating spin injection into organic materials through interface engineering

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(Received 27 April 2012; accepted 26 June 2012; published online 13 July 2012)

The correlation of spin injection efficiency and interfacial resistance is investigated in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO)/ Alq_3 /Co organic spin-valve devices. When a thin layer of copper phthalocyanine (CuPc) is inserted between LSMO and Alq_3 , the magnetoresistance (MR) of the device decrease to only $\sim 0.4\%$ at 50 K, in sharp contrast to $\sim 6\%$ MR ratio at the same bias voltage for the device without CuPc interlayer. Meanwhile, the electrical resistance decreases by one order of magnitude, indicating that the interface barrier height is reduced. These results reflect that a strong correlation between the significant decrease of spin injection efficiency at LSMO/CuPc interface and the reduced interfacial resistance. The findings indicate that the conductivity mismatch problem is applicable to organic materials and the interfacial resistance has important impact on the spin injection efficiency. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4737008>]

Recently, the study of spin transport in organic semiconductors has attracted considerable interest due to their long spin-relaxation time, which is several orders of magnitude longer than that of metals and inorganic semiconductors, stemming from very weak spin-orbit coupling and hyperfine interaction.^{1,2} This allows one to utilize spin to transport and manipulate information in organic electronic devices. After the initial reports of the experimental demonstration of spin transport through sexithienyl (T_6) in the in-plane organic spin-valves (OSVs) and tris-(8-hydroxyquinoline) aluminum (Alq_3) in the vertical OSVs,^{3,4} a wide variety of organic semiconductors such as rubrene,^{5,6} copper phthalocyanine (CuPc),⁷ and 3,4,9,10-perylene-teracarboxylicdianhydride (PTCDA)⁸ have been examined to show sizable magnetoresistance (MR) effects. Strikingly, a MR of up to 300% was observed in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO)/ Alq_3 /Co OSVs at low temperature.⁹ These results suggest the high spin injection efficiency from a ferromagnetic (FM) electrode into an organic semiconductor can be achieved even though the reason of high spin injection efficiency is not well understood.

The conductivity mismatch problem, which is a fundamental obstacle for efficient spin injection by electrical means from a FM metal into an inorganic semiconductor, has been generally recognized in the field of the inorganic semiconductor spintronics.¹⁰ It was suggested by inserting a tunnel barrier or Schottky barrier between the FM metal and semiconductor to circumvent this problem.¹¹ This approach was demonstrated in GaAs, Si, and graphene by a number of groups.^{12–14} Similarly, the resistance of organic semiconductors is usually much larger than that of FM electrodes and dominates the total resistance of the OSV devices. The conductivity mismatch problem could be also applicable to organic semiconductors. However, the large MR effects have been frequently reported without interface engineering.^{3,4,9} This is recently explained by considering that the spin or charge carriers in organic semiconductors are supplied from

the electrodes to form space charge like a capacitor, in contrast to inorganic semiconductors acting as a simple resistor.¹⁵ On the other hand, according to Ruden and Smith's theoretical calculation, the interface barrier is crucial to achieve significant spin injection into organic semiconductors.¹⁶ The validation of the conductivity mismatch problem in organic semiconductors, however, has not been experimentally presented.

In the present work, we show that the spin injection efficiency strongly depends on the interfacial resistance, which is controlled by inserting an interfacial organic layer between a FM electrode and an organic semiconductor. We specifically chose copper phthalocyanine (CuPc) [its molecular structure is shown in Fig. 1(a)] as the interface layer. CuPc is one of the typical high mobility p-type organic semiconductors, which is widely used as an interface layer to improve the hole injection efficiency in organic light emitting diodes (OLEDs), due to its relatively high highest occupied molecular orbital (HOMO).^{17,18} We have carried out systematic studies on the following two types of comparable OSV devices, LSMO/CuPc/ Alq_3 /Co (device A) and LSMO/ Alq_3 /Co (device B). The resistance of device A is found to be more than one order of magnitude smaller than that of device B, reflecting that the interface resistance at the LSMO/CuPc interface is smaller than that at the LSMO/ Alq_3 interface and the resistance of device B is dominated by the interface resistance. The MR of device A is about 0.42% at 50 K, which is much smaller than that of device B. These results show that the conductivity mismatch problem have important impact on spin injection into organic semiconductors.

LSMO thin films were chosen as the bottom electrodes, which were grown by pulsed laser deposition on SrTiO_3 (001) substrates and wet-etched to be 1 mm in width. The LSMO films have been cleaned and reused for more than 15 times without any apparent degradation. The purified Alq_3 and CuPc films were thermally evaporated at deposition rates of 0.6 Å/s and 0.2 Å/s, respectively. To prevent the penetration of the FM atoms into organic layer to form the so-called

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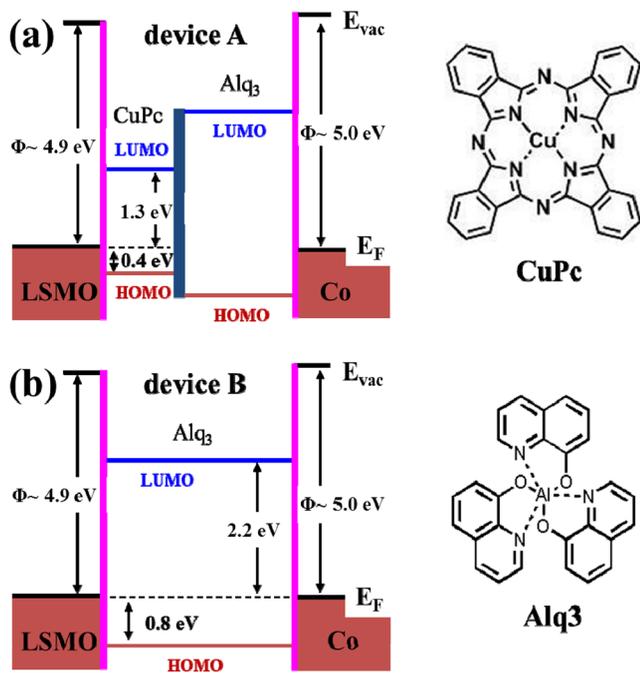


FIG. 1. Schematic energy level diagrams of (a) device A and (b) device B, respectively. The right side is the molecular structure of CuPc and Alq₃.

ill-defined layer, the top FM electrode is deposited with a newly developed approach named indirect deposition method.¹⁹ Before deposition Co, the LSMO/organic bilayers were faced away from the deposition source and covered with a shadow mask, which defined the active area of the devices to be $1 \times 1 \text{ mm}^2$. The Co films were deposited by electron beam evaporation after the vacuum chamber was purged with Ar gas to a pressure of $3 \times 10^{-3} \text{ Torr}$ from a base pressure of $< 2 \times 10^{-7} \text{ Torr}$. The Co atoms released their kinetic energy by scattering with Ar atoms and softly landed onto the organic material. Finally, a 20-nm-thick Al film was deposited to prevent the oxidation of the Co film.

The schematic energy-level diagram of the devices is illustrated in Figs. 1(a) and 1(b). The work function of LSMO and Co is ~ 4.9 and ~ 5.0 eV, respectively, which is in the energy gap of CuPc and Alq₃. The barrier heights for electron and hole injection at LSMO/CuPc interface are estimated to be 1.3 and 0.4 eV, respectively, which are 0.9 and 0.4 eV lower than that at LSMO/Alq₃ interface, respectively. With an additional interface layer of CuPc, the energy barrier height is significantly reduced to facilitate the charge injection. At the metal/organic interface, the interface dipole formation or band bending should be considered to estimate the interface barrier height.²⁰ According to the experimental results measured by x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS), the barrier heights for electron and hole injection at LSMO/CuPc interface are 1.0 and 1.1 eV, respectively,²¹ in comparison to the corresponding barrier height of 1.26 and 1.7 eV at LSMO/Alq₃ interface, measured by photoelectron spectroscopy (PES).²² These results are in qualitative agreement with the simple band estimation that CuPc layer reduces interface barrier height.

The current-voltage (I - V) curves of the two types of devices LSMO (70 nm)/CuPc (5 nm)/Alq₃ (55 nm)/Co (25 nm)/Al

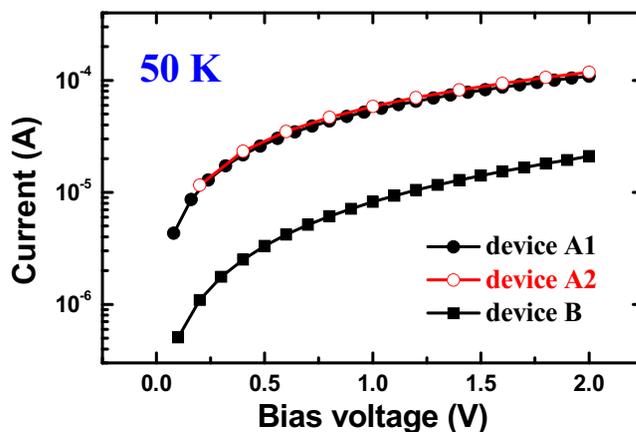


FIG. 2. The I - V characteristic response of device A1 (black circle) and A2 (red open circle) and device B (black square) at 50 K.

(20 nm) (device A) and LSMO (70 nm)/Alq₃ (60 nm)/Co (25 nm)/Al (20 nm) (device B) are shown in a semi-log plot in Fig. 2. To check the reliability of devices, we fabricated and measured the same structures of device A and device B several times. The results are essentially similar (see curves of device A1 and A2 for type A device). Note that, for comparison, the total thickness of organic layer is kept the same and for device A the thickness of Alq₃ is much thicker than that of CuPc. The bulk transport properties are dominated by Alq₃ and expected to be the same in both devices. The current of the device with CuPc layer, or device A, is more than one order of magnitude larger than that of the device without CuPc, or device B. The CuPc layer between LSMO and Alq₃ is the only difference between device A and B. The morphology of CuPc and the following grown Alq₃ is similar to Alq₃ grown on LSMO with the rms roughness of 1-2 nm (not shown here). And the parameters of Alq₃ in both devices are expected to be the same. Therefore, we attribute the current increase of the device with CuPc layer to the reduction of the barrier height at LSMO/CuPc interface, which promotes the carrier injection efficiency. This is consistent with the expectation given above. In addition, this result indicates that the I - V characteristics of device B is dominated by injection limited rather than transport properties of the bulk Alq₃.

Based on the above results that the interface resistance can be tuned by the CuPc interfacial layer, we continue to study the correlation of spin injection and interface resistance. In Figs. 3(a) and 3(b) we show the typical magnetic field dependence of the resistance for the device A and B, measured at 50 K with a dc bias voltage of 100 mV. The MR ratio is defined as $MR = (R_{AP} - R_P)/R_P$, where R_{AP} and R_P are the resistance of the two FM electrodes in the antiparallel and parallel configurations, respectively. Obviously, both OSVs show an inverse or negative spin valve effect, $R_{AP} < R_P$, in good agreement with previous reports in similar OSVs.^{4,9,19} The MR ratio of device B is similar as previous reports.^{4,19} The coercivity of LSMO is slightly different between device A1 and A2, which can be understood as the coercivity is sensitive to fabrication process, such as deposition temperature and oxygen pressure. Although the resistance of device A is significantly decreased by inserting a CuPc interlayer between LSMO and Alq₃, quite strikingly, the MR ratio, which is normalized by the resistance, is still

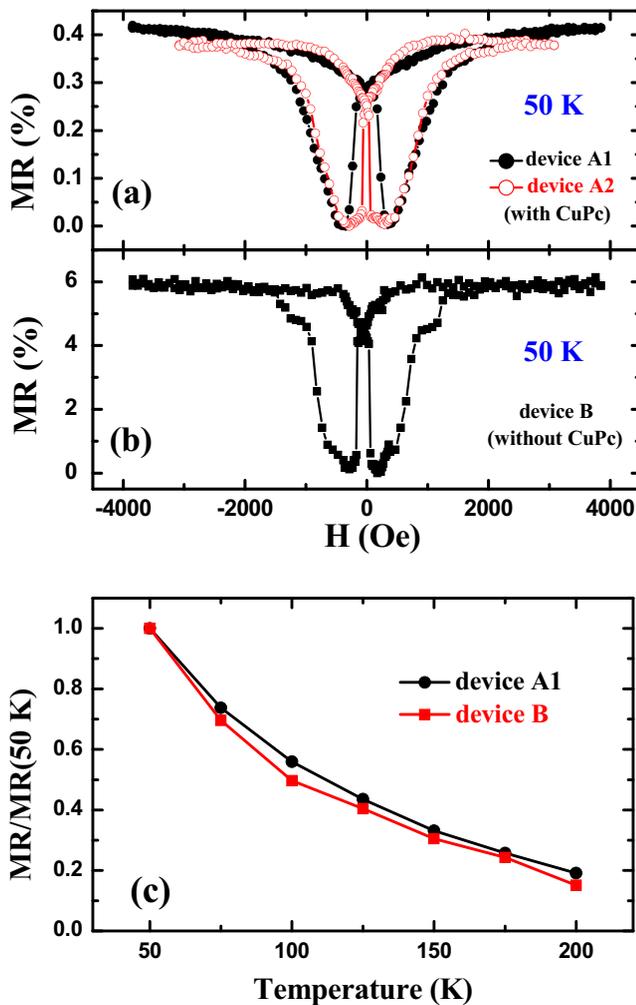


FIG. 3. MR response of (a) device A1 and A2, with CuPc interlayer, and (b) device B, without CuPc interlayer, at a bias voltage of 100 mV at 50 K. (c) Normalized MR as a function of temperature for device A1 and device B at bias voltage of 100 mV (black circle) and 30 mV (red square), respectively.

one order of magnitude smaller than that of device B at the same bias voltage. In addition, the stability of the OSVs is improved by the CuPc interlayer and evidenced by the much smaller signal-to-noise ratio of device A in MR measurements compared with that of device B, even though the data of device A is measured only one time and the data of device B is averaged from five scans [see Figs. 3(a) and 3(b)]. This improved device stability by CuPc interlayer was also found in the OLEDs.¹⁷

Figure 3(c) shows the temperature dependence of the normalized MR ratio measured at the minimum applied bias voltage for the two devices. The MR ratio monotonically decreases with increasing temperature. The temperature dependence of the surface spin-polarization of LSMO (Ref. 23) and the increase of spin-lattice relaxation rate with increasing temperature²⁴ have been invoked to explain the temperature dependent MR. Although our experiments cannot distinguish these mechanisms, each of them should give the same MR response as a function of temperature for device A and B. Therefore, the observation of the similar temperature dependent MR, in spite of the distinct MR ratio difference, is a confirmation that the spin transport in Alq₃ in device A is not altered by the CuPc interlayer.

Since the spin relaxation mainly occurs in the Alq₃ layer and is demonstrated to be the same, regardless of CuPc buffer layer, the MR ratio directly reflects the spin injection efficiency. Comparing with device B, the observed lower MR ratio of device A indicates the lower spin injection efficiency at LSMO/CuPc interface than that at LSMO/Alq₃ interfaces. The spin injection efficiency related with the interface barrier height suggests that the conductivity mismatch problem is still applicable to organic materials, namely the interfacial resistance determines the spin injection efficiency.

In most of OSVs the MR ratio decreases strongly with increasing bias voltage, but decreases less at negative bias voltage.^{4,9,23} Our devices exhibit similar behaviors, which are shown in Figs. 4(a) and 4(b) after normalization. Obviously, the MR value of device A decreases much slower with increasing the bias voltage than that of device B, which can be characterized by the bias voltage value $V_{1/2}$ for which the MR value decrease to half of its maximum value. The $V_{1/2}$ for device A is 1.8 and -3.0 V for a positive and a negative bias voltage, respectively, which are one order of magnitude larger than the corresponding value for device B, 0.17 and -0.20 V, respectively. For organic spintronics, an interesting application is to enhance the electroluminescence efficiency by controlling the injected spins, called spin-OLEDs.¹ These devices have not been experimentally demonstrated yet²⁵ partially due to the fact that the threshold voltage for electroluminescence is in excess of a few volts, whereas the reported MR effect or effective spin injection disappears above about 1 V.^{4,9,23} Our experiments demonstrate apparent spin injection above ~ 5 V by reducing interface barrier

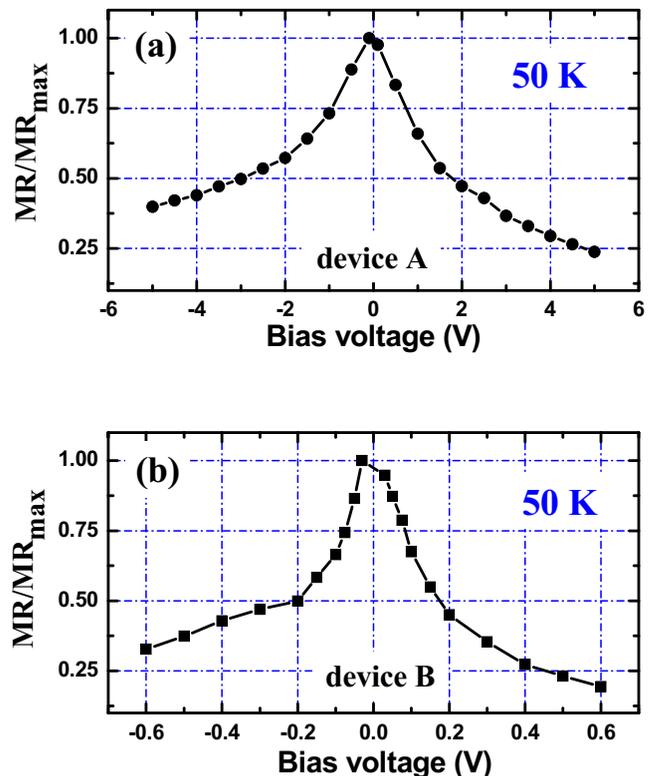


FIG. 4. Normalized MR as a function of bias voltage for (a) device A and (b) device B, respectively, at 50 K.

height at FM/organic interface, which make it possible to realize spin-OLED.

In summary, we successfully utilize the organic semiconductor CuPc to tune the interfacial barrier height and thereby the spin injection efficiency. The current increase one order of magnitude with inserting a CuPc interfacial layer between LSMO and Alq₃ manifests the reduced interface barrier height. And the corresponding MR ratio significant decrease reveals the lower spin injection efficiency, indicating the presence of the conductivity mismatch problem. The observation of MR effect at relatively high bias voltage may shed light on the realization of spin-OLEDs.

This work is supported by NSF of China (10974084 and 11023002), National Basic Research Program of China (2010CB923402), NCET project (NCET-08-0266), the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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