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Spin diffusion in fullerene-based devices; morphology effect

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Abstract

The buckminsterfullerene C₆₀ molecules are composed of ~99% naturally abundant ¹²C carbon atoms having spinless nucleus and thus zero hyperfine interaction. Therefore it was assumed that the spin diffusion length in C₆₀-based spin-valves is large. We fabricated spin-valves based on C₆₀ and studied the magnitude of the giant magneto-resistance (GMR) as a function of bias voltage, temperature and C₆₀ layer thickness. Surprisingly, we found that GMR first increases as the C₆₀ layer thickness increases, reaching a maximum at ~35 nm, then exponentially decreases with thickness from which we extracted a small spin diffusion length of ~12 nm at 10 K. From our data we obtain two important conclusions. First, morphology related disorder that originates from the C₆₀ nano-crystalline grains embedded into an amorphous phase of C₆₀ is responsible for an unusual spin diffusion process that results in short spin diffusion length. Second, we identify the main spin relaxation dynamics in the fullerene to be the grain boundaries in which spin-orbit coupling is enhanced by the local electric field.

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I. **Introduction**

Spintronics utilizes the electron’s spin degree of freedom in addition to its charge in electronic devices for advanced approaches to information storage and processing. For efficient spintronics devices it is necessary to achieve spin *injection, detection and manipulation* of spin polarized carriers. Organic semiconductors (OS) have recently become the center of attention in the spintronics community, because of the presumed long spin relaxation time, and the additional functionality of these materials such as electroluminescence. The prototype organic spintronics device, namely the organic spin-valve (SV) is based on an organic semiconductor spacer placed in between two ferromagnetic (FM) electrodes having different coercive fields, where the magneto-resistance (MR) changes upon sweeping the magnetic field, $B$. When the active layer shows electroluminescence then a spin-organic light emitting device can be fabricated. Organic semiconductors are composed of light elements that are supposed to possess weak spin-orbit coupling (SOC) leading to small spin relaxation rates. Indeed, giant MR (GMR) has been measured in OSV devices based on small molecule and polymer spacers, both as thick films and thin tunnel junctions. Clear proof of spin injection into organic spacer was also provided by muon spin rotation and two photon photoemission spectroscopy.

The hyperfine interaction (HFI) has been recently shown to play a significant role in limiting the spin diffusion length in polymer organic SV devices. In addition, the SOC, which has been a useful tool in manipulating the injected spin aligned carriers in inorganic spintronics devices, should be considered also in organic SV devices, in spite of the light atoms comprising the organic materials. In fact, the weak SOC is the reason that organic spintronics has been attractive in the first place.

The buckeyball $C_{60}$ molecule is composed of 60 carbon atoms (see Fig. 1d inset), of which 98.9% are the natural abundant $^{12}$C isotope having spinless nucleus, and thus zero HFI; and ~1.1% $^{13}$C isotope having nuclear spin $\frac{1}{2}$ with estimated HFI constant of ~0.2 μeV. Therefore the HFI constant averaged on the 60 carbon atoms of natural $C_{60}$ molecule should be ~3 neV, which is too small to play any significant role in magneto-transport. It has therefore been assumed that the spin diffusion length in fullerene-based spin valve (SV) devices is relatively large. However since the $C_{60}$ molecule is strongly curved, significant hybridization may occur.
between the π and σ electrons, and this might enhance the SOC. Recent calculations\textsuperscript{20} estimated the SOC in C\textsubscript{60} to be less than 1 µeV; this is a relatively small value but is larger than the HFI in this molecule, and thus may be a key factor in limiting the spin diffusion length in C\textsubscript{60} spin-valves.

A 9\% MR at room temperature has recently been reported\textsuperscript{21} for a C\textsubscript{60} SV device with thickness \(d=5\) nm, that diminishes to 5.5\% at \(d=28\) nm. The spin transport mechanism was attributed\textsuperscript{21} to a multi-step tunneling process through the C\textsubscript{60} buckyballs. In another recent report\textsuperscript{22} on C\textsubscript{60} SV devices, a 13\% GMR at \(T=15\) K and \(d=25\) nm was obtained. From the thickness dependent GMR(\(d\)) it was estimated\textsuperscript{22} that the spin diffusion length is several tens of nanometers, comparable to other organic SV devices.

In this work we studied GMR of C\textsubscript{60} based SVs and correlated the results to the morphology of the active layer. We found that evaporated C\textsubscript{60} films contain micro-crystalline domains of diameter \(D\approx10\) nm in size, that grow in density and size with the film thickness, \(d\), followed by saturation at \(d=40\) nm. The measured GMR(\(d\)) response shows a peculiar maximum at \(d_0=35\) nm that obscures spin diffusion length measurements. Nevertheless, we determined the spin diffusion length, \(\lambda_{C60}\) for C\textsubscript{60} SV devices with \(d>d_0\); we obtained \(\lambda_{C60}\approx12\) nm at 10 K that strongly depends on the temperature. We discuss the unusual GMR(\(d\)) response in terms of the unusual film nano-morphology coupled with the ensuing energy disorder. In particular we identify the main spin relaxation in the fullerene to occur at the grain boundaries, where the SOC may be enhanced due to the strong local electric field.

\textbf{II. Experimental}

The fullerene SVs were fabricated using C\textsubscript{60} evaporated films as spacers with various thicknesses in between two FM electrodes\textsuperscript{3} namely La\textsubscript{0.67}Sr\textsubscript{0.33}MnO\textsubscript{3} (LSMO) [bottom electrode, FM\textsubscript{1}], and cobalt (Co) [top electrode, FM\textsubscript{2}]. The LSMO films having thickness of \(\approx200\) nm and area of \(5\times5\) mm\textsuperscript{2}, were grown epitaxially on \(<100>\) oriented SrTiO\textsubscript{3} substrates at 735° C using dc magnetron sputtering technique, with Ar and O\textsubscript{2} flux in the ratio of 1:1. The films were subsequently annealed at 800° C for \(\approx10\) hours before slow cooling to room temperature\textsuperscript{13}. The LSMO films were
patterned using standard photolithography and chemical etching techniques. LSMO is stable against oxidation, and thus the films were cleaned and reused *multiple times* as substrates without visible degradation \(^3\). Following the LSMO substrate cleaning using toluene and chloroform, we evaporated the \(C_{60}\) layer in an evaporation chamber with base pressure of \(5 \times 10^{-7}\) torr. Subsequently, we deposited a thin (5 - 7 nm) Co film capped by an aluminium (Al) film using a shadow mask. The obtained active device area was typically about 0.2 x 0.4 mm\(^2\). \(C_{60}\) is quite robust against Co clusters penetration, and this eliminated the problem of an ‘ill defined’ film thickness encountered before using OSV with Tris(8-hydroxyquinolinato)aluminum (Alq\(_3\)) organic interlayer \(^3\). The \(C_{60}\) film thickness \(d\) was controlled by a quartz crystal thickness monitor, and calibrated against measurements using thickness profilometry methods (KLA Tencor). \(C_{60}\) SV devices with various \(d\) were measured and compared at several bias voltages, \(V\), and temperatures, \(T\). Typical device resistance was in the range of 5 k\(\Omega\) (for \(d=20\) nm) to 500 k\(\Omega\) (for \(d=90\) nm).

The \(C_{60}\) SV devices were placed on a cold finger end in vacuum in a closed-cycle helium refrigerator. The SV GMR response was measured in the temperature range of 10 to 300 K using the ‘four probe’ method, while varying an external in-plane magnetic field. The magnetization properties of the FM electrodes were measured by the magneto-optic Kerr effect (MOKE). From these measurements we determined typical low temperature coercive fields for the unassembled electrodes \(B_{c1}\sim4.5\) mT and \(B_{c2}\sim16.5\) mT, for the LSMO and Co (covered by 15 nm \(C_{60}\)) films, respectively.

Transmission electron microscopy (TEM) images of clusters in \(C_{60}\) films were studied using a FEI TEM machine operating at 80 kV. For measuring the nano-crystalline (NC) grain size and density as a function of the film thickness we evaporated several films on Formvar carbon films placed on copper grids, with the same overall effective film thickness normalized to a 90 nm film. For films with small \(d\) values we measured several films put together in series separated by \(\sim2\) nm organic thin films (Alq\(_3\)) to preserve the effective \(d\). For the x-ray diffraction (XRD) pattern we used a \(CuK\alpha\) X-ray machine with \(\lambda=0.154\) nm; each scattering pattern was collected for 6 hours to attain good signal to noise (S/N) ratio. For obtaining the various Bragg bands from the \(C_{60}\) crystalline grains we removed from the film scattering pattern the scattering pattern of the
substrate, which was measured separately. The Bragg scattering bands were translated into crystal plane-spacing, \(d_{hkl}\), using the Bragg relation \(2d_{hkl}\sin2\theta_{hkl}=\lambda\), where \(2\theta_{hkl}\) is the scattering angle for the hkl planes with \(d_{hkl}=a/(h^2+k^2+l^2)^{1/2}\), where \(a\) is the cubic lattice parameter and hkl are the cubic Miller indices. The NC grain size, \(D\), was estimated using the Scherrer’s equation:

\[
D = 0.9\lambda/\Delta_2\theta\cos\theta,
\]

where \(\Delta_2\theta\) is the full-width-at half maximum of the (111) Bragg band at \(2\theta_{111}=10.6^\circ\). For the dependence of \(D\) on the film thickness we evaporated \(C_60\) on a glass substrate and kept constant the XRD scattering S/N ratio by using the same technique as described above for the TEM measurements, namely keeping constant a normalized effective \(d\) of \(\sim 155\) nm.

III. Experimental Results

A. \(C_{60}\) film Morphology

Figure 1a is a TEM image of a \(d=90\) nm thick \(C_{60}\) film grown on a thin metal grid. The TEM image clearly shows the formation of domains having higher \(C_{60}\) density than that of the surrounding matrix, which we thus identify as NC grains. From the TEM image we estimate an average grain size, \(D<30\) nm. We found, however, that the grain size and their number density increase with the film thickness. The NC domains formed in the film are also clearly seen in the phase atomic force microscope (AFM) image of a 50 nm thick \(C_{60}\) film grown on LSMO substrate, as shown in Fig. 1b. In addition, the AFM study shows good film roughness of \(\sim 0.9\) nm that is crucial for fabricating high quality \(C_{60}\) SV devices.

Figure 1c shows the grazing incidence XRD pattern from a 155 nm thick \(C_{60}\) film deposited on a glass substrate, using the \(CuK\alpha\) X-ray line at \(\lambda=0.154\) nm. Four Bragg scattering bands are clearly seen above the scattering background that is due to the glass substrate. \(C_{60}\) is known to crystallize in a fcc Bravais lattice (BL) structure with lattice constant, \(a=1.42\) nm (Ref. 24); we therefore analyze the obtained Bragg scattering bands using this natural BL structure. We could fit the three obtained Bragg bands at large scattering angle, \(2\theta\) as originating from fcc NC grains in the film with \(a=1.41\) nm having (hkl) Miller indices of \((111), (220)\) and \((311)\) at \(2\theta_{hkl}=10.8^\circ, 17.8^\circ\) and \(20.9^\circ\), respectively. We note, however, that the (200) Bragg band, which is allowed in fcc
BL structures, is not present in the XRD pattern (Fig. 1c). This is due to the room temperature rotational motion of the C\textsubscript{60} molecules around one of their central axes, which renders their scattering symmetry to that of spheres; this enhanced symmetry eliminates the (200) band\textsuperscript{24}. In addition, we also estimated the average NC grain size $D \approx 10 \text{ nm}$ from the full width at half maximum (FWHM), $\Delta_{2\theta}$ of the (111) Bragg band (Fig. 1c inset) using Eq. 1. In contrast, the Bragg band at $2\theta = 6.6^\circ$, denoted “disordered cubic” (dc), cannot be accounted for using the most abundant fcc BL structure. We note, however, that there is another C\textsubscript{60} crystalline structure which is somewhat disordered but stable at high temperatures. This structure has a distorted fcc BL with $a = 1.36 \text{ nm}$ (Ref. 24). We thus identify the obtained dc band as due to (100) Bragg scattering band coming from a fcc BL with $a = 1.34 \text{ nm}$, that is allowed here due to the disorder resulting from the relatively small NC grain size in the film.

Figure 1d shows the film thickness dependence of the grain size and intensity, $A$, under the (111) Bragg scattering band, which were measured on a variety of C\textsubscript{60} films having normalized thickness. It is clearly seen that both $D$ and $A$ increase with the thickness $d$, followed by a saturation above $d_s = 45 \text{ nm}$. The increase of the film crystallinity with $d$ complicates the analysis of spin transport and spin diffusion measurements in C\textsubscript{60} SV devices at small $d$ values, because it may influence carrier mobility that should be larger in the crystalline domains. This, in turn increases the device GMR with $d$ (at small $d$) due to the expected increase in the spin diffusion length of the injected carriers for C\textsubscript{60} SV devices fabricated with $d \leq 40 \text{ nm}$ (see below).

**B. Giant magneto-resistance measurements of C\textsubscript{60} spin valves**

We used C\textsubscript{60} SV devices in which the fullerene film was sandwiched in between LSMO and Co as the two FM electrodes having different coercive fields (Fig. 2a). These FM electrodes have high nominal spin injection polarization degree, $P_1(\text{LSMO}) = 98\%$ that is strongly temperature dependent above ~150K (see Fig. 2d, inset), and $P_2(\text{Co}) = 30\%$ that is essentially temperature independent in the temperature range up to 300 K; but its sign depends on the environment\textsuperscript{13, 25}. Since $B_{c1} \neq B_{c2}$, then it is possible to switch the relative magnetization directions of the FM electrodes in the SV device between parallel (P) and anti-parallel (AP) alignments upon sweeping $B$; whereby the device resistance, $R$ is dependent on the relative magnetization orientations. The SV device resistance was measured using the four-probe technique at constant current. Figure 2b
shows typical GMR hysteresis response of a C\textsubscript{60} SV fabricated with the layer configuration LSMO/C\textsubscript{60}(35nm)Co/Al, measured at various temperatures. It is seen that $R(\text{AP})<R(\text{P})$, i.e. a sign opposite to that of inorganic spin-valves, but in agreement with many other organic SV devices based on LSMO and Co electrodes\textsuperscript{3,4}. The ‘turn-on’ and ‘turn-off’ GMR($B$) response are quite sharp, similar to the best spin-valve devices\textsuperscript{4,11}. Bobbert \textit{et al.} (BWOKW)\textsuperscript{26} attributed the sharpness of the ‘turn on’ and ‘turn off’ GMR response in organic SV devices to the HFI of the organic interlayer, being sharper for smaller HFI constant. This model is in agreement with our results, since the HFI in C\textsubscript{60} film is indeed very small, and this leads to a superior GMR response. In addition, we also see (Fig. 2b) that the coercive fields $B_{c1}$ and $B_{c2}$ decrease strongly with the temperature; this is in agreement with our MOKE measurements (not shown here). In general, both $B_{c1}$ and $B_{c2}$ are much larger for the C\textsubscript{60} SV than in many other organic SV devices based on LSMO and Co FM electrodes\textsuperscript{3,12}. We do not exactly know the reason for this behavior, but it is conceivable that the coercive fields depend on the specific organic interlayer. When $R(\text{AP})<R(\text{P})$ the maximum GMR value, $[\Delta R/R]_{\text{max}}$ (or MR\textsubscript{SV}) is given by the ratio: $\text{MR}_{\text{SV}}=[R(\text{P})-R(\text{AP})]/R(\text{AP})$. We notice that $\text{MR}_{\text{SV}}$ decreases with temperature (Fig. 2b); however, the temperature decrease is not as steep as in other organic SV devices\textsuperscript{3,4}.

Figure 2c shows the bias voltage dependence of MR\textsubscript{SV}($V$) at various temperatures. First, we note that MR\textsubscript{SV}($V$) response is rather symmetric about $V=0$. Second, it is not as steep as in other reported organic SV devices\textsuperscript{4,12}; this may indicate a superior contact surface between the C\textsubscript{60} film and the two FM electrodes. In addition, it is clear that MR\textsubscript{SV}($V$) response is less steep at elevated temperatures, and this is good news for Organic Spintronics. From the weaker MR\textsubscript{SV}($T$) and MR\textsubscript{SV}($V$) responses we conclude that C\textsubscript{60}-based SV have excellent qualities. Indeed, we found that such devices are sufficiently stable that we could readily measure the GMR hysteresis loop also at room temperature, with MR\textsubscript{sv} ~0.16% at $V=200$ mV reaching 0.3% at $V<5$ mV (Ref. 27); we note, however, that a 9% MR\textsubscript{SV} value at room temperature was reported\textsuperscript{21} in C\textsubscript{60} SV having the configuration Co/AlO\textsubscript{x}/C\textsubscript{60}(5nm)/Py, where Py denotes permalloy, Fe\textsubscript{80}Ni\textsubscript{20}. The obtained MR\textsubscript{sv} in those devices was interpreted\textsuperscript{21} as due to tunneling MR rather than GMR that involves spin transport through the C\textsubscript{60} layer. The flatter MR\textsubscript{sv}($V$) response with increasing temperature (Fig. 2c) shows that it cannot be entirely due to a decrease in the polarization degree $P_1$, or $P_2$ with $V$, as suggested before\textsuperscript{3,6}. 

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We also plot in Fig. 2d the temperature dependence of MRsv at various \( V \)'s extracted from Fig. 2c. It is clearly seen that although MRsv\((T)\) response decreases with increasing \( T \), it does not follow the moderate temperature decrease of the LSMO magnetization, M\((T)\) that is shown in Fig. 2d (inset). In addition, MRsv\((T)\) response is clearly voltage dependent (Fig. 2c), and the response is symmetric about \( V=0 \). These characteristic properties show that MRsv\((V,T)\) response cannot be explained solely by the dependence of the FM injecting capability through \( P_1(V,T) \) of the LSMO electrode\(^6\), because it is difficult to understand that \( P_1(V) \) (or \( P_2(V) \)) is completely symmetric for injecting either electrons or holes. We therefore conclude that the decrease in MRsv at high \( T \) and \( V \) reveals an \textit{intrinsic spin relaxation mechanism} which reduces the spin diffusion length at high temperature and/or electric field \( (|V|/d; \text{symmetric about } V=0) \), as measured in Alq\(_3\) films\(^14\), and discussed for Alq\(_3\) SV devices\(^28\).

Next, we tried to estimate \( \lambda_{C_{60}} \) from the SV device performance at various C\(_{60}\) thickness at \( V=100 \text{ mV} \), as shown in Fig. 3a for \( T=10 \text{ K} \). For these measurements we used the same LSMO substrate but different interlayer thickness, since LSMO is relatively stable in air, and its spin injection properties were found to be quite robust\(^3\). According to the modified Jullière formula\(^3, 29\), when MR\(_SV\) <<100% (see Figs. 2b,e) it should be a monotonic decreasing function of \( d \):

\[
\text{MR}_{SV} \approx 2P_1P_2\exp\left[-d/\lambda_{C_{60}}\right], \quad (2)
\]

where \( \lambda_{C_{60}} \) is the spin diffusion length in the fullerene interlayer. \textit{Surprisingly}, the obtained MR\(_{SV}(d)\) first \textit{increases} with \( d \), reaches a maximum at \( d_0=35 \text{ nm} \), and decreases thereafter with the C\(_{60}\) interlayer thickness for \( d>d_0 \). This rather peculiar behavior may be explained taking into account the film morphology at increasing \( d \). As discussed above, the film crystallinity increases with \( d \) at small \( d \)-values, but saturates at \( d_S=45 \text{ nm} \), approximately where MR\(_{SV}(d)\) starts decreasing (Fig. 3a). The less disordered the C\(_{60}\) layer becomes with increasing \( d \) (at \( d<d_0 \)), the higher is the charge carrier mobility, thereby increasing \( \lambda_{C_{60}} \)\(^26\). We thus conclude that the unusual MR\(_{SV}(d)\) increase at small \( d \) arises from the increase in the spin diffusion length because of the increase in carrier mobility with \( d \). Since the increase in film crystallinity saturates at \( d_S=d_0 \), then \( \lambda_{C_{60}}(d) \) also saturates, i.e. \( \lambda_{C_{60}}(d>d_0) = \lambda_{C_{60}}(d=d_0) \equiv \lambda_0 \), resulting in an exponential decrease of MR\(_{SV}(d)\) for \( d>d_0 \) that shows a constant \( \lambda_{C_{60}}=\lambda_0 \). In order to extract \( \lambda_0 \) from our GMR measurements we fit MR\(_{SV}(d)\) decrease for devices with \( d>d_0 \) using Eq. (2) obtaining \( \lambda_0=12 \text{ nm} \) (Fig. 3a).
Surprisingly, this value is smaller than $\lambda_S$ reported for Alq3 (~45 nm, Ref. 3), and $\lambda_S$ obtained in $\pi$-conjugated polymers (~30 nm, Ref. 12), even though the HFI is much smaller in C$_{60}$. The HFI in C$_{60}$ is too weak to explain such a small $\lambda_{C60}$; we thus conclude that other spin relaxation mechanisms limit the spin diffusion length in the C$_{60}$ film.

C. Discussion

(i) The short C$_{60}$ spin diffusion length. We propose that carrier spin dynamics in C$_{60}$ film is composed of both hopping in the disordered C$_{60}$ matrix and ballistic transport in the C$_{60}$ NC crystalline grains. Injected carriers inside the grain may bounce back and forth many times before escaping into the disordered matrix that surrounds the grains, resulting in an overall reduced spin diffusion length that is related with spin relaxation mechanism at the grain boundaries. The obtained $\lambda_{C60}=12$ nm (for $d>d_0$) is very similar in magnitude to the average grain size $D$ (~10 nm), and this lends support for this hypothesis. We note that if not for the relatively small grain size, $\lambda_{C60}$ might have been much larger because the intrinsic spin relaxation mechanism is indeed weak in this material. As mentioned above, the HFI is unlikely to play an important role in C$_{60}$ because 99% $^{12}$C with zero nuclear spin; thus we consider the SOC as the most dominant spin relaxation mechanism in the fullerene, similar as in graphene (which is in fact another carbon allotrope). Carbon is a light atom with relatively small atomic SOC of the order of ~6 meV$^{30}$; this is too large to explain our results. However, since the orbital angular momentum is mostly quenched for $\pi$-orbital electron or hole carriers in planar organic molecules$^{31}$, then the atomic SOC is expected to be substantially reduced to less than ~0.1 $\mu$eV in carbon based organic molecules, including graphene and possibly also C$_{60}$ (Ref. 20). We showed above that C$_{60}$ films are composed of NC grains of various sizes and shapes. Consequently, upon the application of a bias voltage, substantial electric fields may form at the grain boundaries that, in turn, may enhance the SOC through the Stark effect$^{20,30}$. Nevertheless, given the applied voltage employed here, we expect the SOC to be quite small, giving rise to relatively long spin relaxation times. Another boundary spin relaxation mechanism may be due to finite surface spin flip probability, as suggested recently for mesoscopic systems$^{32}$. Therefore, it is conceivable that the obtained short spin diffusion length in C$_{60}$ SV devices is limited by the grain size dimension. Although the effective SOC gives rise to relatively long spin relaxation times, carriers inside the grain bounce back and
forth many times before escaping the grain, thereby decreasing the spin diffusion length. It is thus expected that SV devices based on smooth, mostly crystalline C\textsubscript{60} would have much larger spin diffusion length.

(ii) The MR non-monotonic thickness dependence. As the thickness increases from \(d=20\) nm, the C\textsubscript{60} film becomes more crystalline, and the disordered regions shrink. BWOKW\textsuperscript{26} introduced a model in which the spin diffusion in disordered organic semiconductors is controlled by a combination of incoherent carrier hopping together with coherent spin evolution around a local effective magnetic field. BWOKW considered disordered organic matrix with random site energies distributed having a Gaussian density of states with a width \(\sigma\), and local effective magnetic field caused by the vector addition of a random hyperfine field combined with the static external applied magnetic field. We believe that this model is not necessarily limited to random local fields caused by the HFI, but is equally applicable to random local fields that originate from other mechanisms; e.g., the SOC. According to BWOKW, \(\lambda_S\) increases as the disorder is reduced; this is mainly due to the increase in carrier mobility when the layer becomes less disordered. BWOKW therefore concluded\textsuperscript{25} that the bottleneck mechanism that limits the spin diffusion length, \(\lambda_S\), is not the spin relaxation time (which may be long) but rather the waiting time between consecutive hops.

Using this model we may explain the non-monotonic MR\textsubscript{SV}(\(d\)) response displayed in Fig. 3a as follows. At \(d_1=20\) nm (the thinnest layer studied here), where the disorder in the film is relatively large, the parameter \(\lambda_{C60}(d_1)\) is small (\(~8-9\) nm); as \(d\) increases above \(d_1\) the disorder in the film decreases and in turn \(\lambda_{C60}\) increases up to a maximum value reached at \(d=d_0\). For \(d>d_0\) the film disorder stays put and the energy distribution width \(\sigma\) does not decrease anymore with \(d\), and thus \(\lambda_{C60}\) remains unchanged at \(\lambda_0=\lambda_{C60}(d_0)\). Consequently, MR\textsubscript{SV}(\(d\)) for \(d>d_0\) follows the dependence expected by Eq. (2) with fixed spin diffusion length parameter, \(\lambda_0\). Fitting MR\textsubscript{SV}(\(d\)) for \(d>d_0\) (Fig. 3a) with Eq. (2), we find MR\textsubscript{SV}(\(d>d_0\))=MR\textsubscript{0}exp(-\(d/\lambda_0\)) with \(\lambda_0\approx12\) nm and MR\textsubscript{0}=0.6. According to BWOKW model the spin diffusion length \(\lambda_S\) increases dramatically even with a slight decrease of \(\sigma\); e.g., at an electric field \(F=\sigma/ea\) (\(a\) is the lattice constant), \(\lambda_S/a\sim(\sigma/k_BT)^{-\alpha}\), with \(\alpha=4\) for \(\sigma\) in the range \(3\leq\sigma/k_BT\leq6\) (deduced from Fig. 1b in Ref. \textsuperscript{26}). We therefore conclude that even a slight variation in the disorder width, \(\sigma\), brings about a large change in
the spin diffusion length. Assuming that Eq. (2) holds also for \( d<d_0 \) with \( d \)-dependent disorder-limited spin diffusion length, we have \( \lambda_{C60}(d)=\ln(MR_0/MR_{SV}(d)) \), with \( MR_0=0.6 \) as above; this dependence is shown in Fig. 4 (blue symbols) as the ratio \( \lambda_{C60}(d)/\lambda_0 \) vs. \( d \). Using the relation between \( \lambda_S \) and \( \sigma \) obtained from BWOKW model, we also plot in Fig. 4 the ratio \( \sigma(d)/\sigma(d>d_0) \) (red symbols) vs. \( d \). It is clearly seen that a mild \(~40\%\) variation in \( \sigma \) is sufficient to explain the unusual MR\(_{SV}(d) \) functional dependence shown in Fig. 3a.

(iii) The MR temperature dependence. For the MR\(_{SV} \) temperature dependence we consider the Elliott-Yafet (EY) mechanism\(^{33, 34} \), which is most suitable for hopping transport. According to EY, the spin randomization rate is due to carrier scattering events, and therefore is inversely proportional to the momentum relaxation time, \( \tau \). Since \( \tau \) decreases at elevated temperatures, then the spin relaxation rate increases and consequently \( \lambda_S \) decreases at high temperatures\(^{14, 28} \). We note that if not for the EY mechanism, then \( \lambda_S \) would have increased with the temperature, since the carrier diffusion constant in organic semiconductors is higher at elevated temperatures\(^{28} \). But such an increase is contrary to the obtained MR\(_{SV}(T) \) shown in Fig. 2d, where MR\(_{SV}(T) \) sharply decreases with temperature, steeper than the decrease of LSMO magnetization \( M(T) \) (see Fig. 2d, inset). Since MR\(_{SV}(V) \) analysis presented above showed that it is determined by a bulk spin scattering mechanism in the C\(_{60} \) layer rather than the LSMO \( P_1 \) value, it is reasonable to assume that MR\(_{SV}(T) \) response is substantially influenced by the temperature dependence of the relevant spin relaxation mechanism in the organic layer. To understand MR\(_{SV}(T) \) we extract the dependence of the spin relaxation rate on temperature by dividing MR\(_{SV}(T) \) by \( P_1(T) \) response (Eq.(2)), assuming that \( P_1(T) \) is represented by \( M(T) \) of the LSMO electrode. \( M(T) \) shown in Fig. 2d (inset) can in fact be very well fit by a Brillouin function, \( B_J(T/T_c) \) with \( J=5/2 \) and \( T_c=307 \) K. We thus obtain \( \lambda_0(T) \) using the relation \( \lambda_0(T)=d/\ln(MR_0 B_{5/2}(T/T_c) /MR_{SV}(T)) \) (with \( MR_0=0.6 \)) from the data in Figs. 2c,d; this is shown in Fig. 3b (symbols). Interestingly, the obtained \( \lambda_0(T) \) at \( V=0 \), can be very well fit with an activated function: \( [1/\lambda_0(T)-1/\lambda_0(0)]<<\exp(-\Delta/k_B T) \), with \( \Delta=16\pm3 \) meV (solid line, Fig. 3b). The obtained thermally activated behavior indicates a parallel behavior of the spin relaxation rate.

**D. Summary**
We have studied the GMR in C\textsubscript{60} based spin valves, in which the hyperfine interaction is nearly absent and does not play any important role in limiting the spin diffusion. Surprisingly, we found that the GMR value first increases as the C\textsubscript{60} layer thickness increases, reaching a maximum at \~35\:nm, then exponentially decreases with thickness showing a small spin diffusion length of \~12\:nm at 10\:K. We show that morphology related disorder which originates from the combination of C\textsubscript{60} crystalline grains embedded within an amorphous phase of C\textsubscript{60} is responsible for the unusual GMR thickness dependence and short spin diffusion length. We then explain the obtained spin diffusion length in C\textsubscript{60} films as due to a spin relaxation mechanism at the grain boundary, which we identify to be SOC enhanced by the local electric fields at the NC grain boundaries.

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References

**Figure Captions**

**FIG. 1** (color on line) Morphology characterization of C$_{60}$ films grown by evaporation. (a) Electron transmission microscope image of a 90 nm thick C$_{60}$ film grown on a metal grid. The darker domains are due to C$_{60}$ crystalline grains ~20-40 nm in diameter. (b) Typical AFM image (shown in phase mode) of a C$_{60}$ film; the C$_{60}$ clusters are clearly evident. (c) X-ray diffraction (XRD) pattern using CuK$_{\alpha}$ line vs. the scattering angle, 2$\theta$ measured off a 155 nm thick C$_{60}$ film grown on a glass substrate. The inset shows the four pronounced Bragg scattering peaks after removing the scattering background due to the glass substrate; they are denoted $dc$ (disordered cubic), and three (hkl) Miller indices of the fcc Bravais lattice from the crystalline grains. (d) The C$_{60}$ NC grain size and the area under the (111) Bragg scattering peak in the XRD pattern (see inset in (c)), plotted vs. the film thickness, $d$. Note the grain size initial increase with $d$, followed by saturation at $d$>$\sim$45 nm.

**FIG. 2** (Color on line) Magnetic field response of C$_{60}$-based SV. (a) Schematics of a C$_{60}$ SV device and the magneto-resistance measurement configuration. The C$_{60}$-based SV device consists of two ferromagnetic electrodes (namely LSMO and cobalt) and a C$_{60}$ interlayer of thickness, $d$. (b) Typical GMR loops of a LSMO/C$_{60}$(30nm)/Co/Al SV device measured at bias voltage $V$=100 mV and four different temperatures, as shown. (c) The GMR magnitude, $\text{MR}_{SV}$ vs. $V$ at various temperatures up to 240 K, as obtained from the I-V device characteristics at AP and P magnetization directions of the FM electrodes. The solid lines through the data points (for $V$>0) are fits to guide the eyes. (d) The $\text{MR}_{SV}(T)$ response at various $V$'s extracted from (c); the lines serve as guide to the eyes. Inset: The LSMO magnetization vs. $T$, and its fit using the Brillouin function, $B_{1}(T/T_{c})$ with $J$=5/2 and $T_{c}$=307 K.

**FIG. 3** (Color on line) (a) MR$_{SV}$ of C$_{60}$-based SV devices measured at $V$=10 mV and $T$=10 K vs. the interlayer C$_{60}$ thickness, $d$, showing a pronounced maximum at $d_0$~35 nm. The line through the data points for $d$>$d_0$ shows a fit of MR$_{SV}$ to Eq. (2) with spin diffusion length, $\lambda_0$=12 nm. (b) The temperature dependence of $\lambda_0$ at $V$=0 extracted from the fits to the data shown in Fig. 2(b), corrected for the temperature dependence of the LSMO magnetization, $M(T)$ [see text]. The line through the data points is a fit with a thermally activated spin diffusion, $[1/\lambda_0(T)-1/\lambda_0(0)]\sim\exp(-\Delta E/k_{B}T)$, with $\Delta E$=16±3 meV.

**FIG. 4.** (Color on line) Blue square symbols: thickness dependence of the disorder limited spin diffusion length, $\lambda_{C60}(d)$, plotted as the ratio $\lambda_{C60}/\lambda_0$, with $\lambda_0$=12 nm. Red round symbols: The
thickness dependence of the extracted disorder width, $\sigma$, plotted as the ratio $\sigma/\sigma_{d0}$, where $\sigma_{d0}$ is the energy disorder width for $d \geq d_0$. The solid lines serve as guide to the eyes.

FIG. 1
FIG. 2

FIG. 3
FIG. 4