Invited Paper

Electron transport and noise spectroscopy in organic magnetic tunnel junctions with PTCDA and Alq_3 barriers

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ABSTRACT

The possible influence of internal barrier dynamics on spin, charge transport and their fluctuations in organic spintronics remains poorly understood. Here we present investigation of the electron transport and low frequency noise at temperatures down to 0.3K in magnetic tunnel junctions with an organic PTCDA barriers with thickness up to 5 nm in the tunneling regime and with 200 nm thick Alq_3 barrier in the hopping regime. We observed high tunneling magnetoresistance at low temperatures (15-40%) and spin dependent superpoissonian shot noise in organic magnetic tunnel junctions (OMTJs) with PTCDA. The Fano factor exceeds 1.5-2 values which could be caused by interfacial states controlled by spin dependent bunching in the tunneling events through the molecules.[1] The bias dependence of the low frequency noise in OMTJs with PTCDA barriers which includes both $1/f$ and random telegraph noise activated at specific biases will also be discussed. On the other hand, the organic junctions with ferromagnetic electrodes and thick Alq_3 barriers present sub-poissonian shot noise which depends on the temperature, indicative of variable range hopping.

Keywords: organic spintronics, shot noise, spinterface, two-level systems, variable range hopping

1. INTRODUCTION

Downscaling of inorganic electronics has currently become increasingly difficult due to both physical limitations such as the modification of the electronic structure due to increasing relation between surface and volume as well as increasing fabrication costs of top-down structures. Since the last decades, interest has been gradually building up in alternative qualitatively different concepts of building electronic devices at reasonable prices. Among the most promising candidates to create future devices capable of substituting traditional silicon based electronics is the concept of molecular electronics[2] with single molecules or small groups of molecules conducting electrical current between two electrodes.[3] It has been now realized that electron transport in molecular or organic tunnel junctions (OTJs) is much more complex than initially thought. Besides, in organic magnetic tunnel junctions (O-MTJs) the electron spin could become relevant for transport.[4] Last, but not least, the magnetic state of the interfacial molecules in O-MTJs could be qualitatively changed by the electron coupling at spinterfaces.[5]

Here we describe some initial steps in the direction beyond the previously explored conductance spectroscopy and monitor both conductance and voltage fluctuations as a function of applied bias voltage in two different types of macroscopic O-MTJs with efficient heat transport away from the molecules so that the junction's structure

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is not jeopardized. We observe superpoissonian shot noise and indications on the resonant enhancement of the low frequency noise for some specific biases which could be due to vibrational heating.[6] The shot noise and temperature dependence of conductance molecular junctions with thick Alq_3 barriers are indicative of variable range hopping through Alq_3.

2. SAMPLES WITH PTCDA BARRIER

The upper left part in Figure 1 sketches a typical OMTJ with PTCDA barrier, where the molecules have a 13° inclination with respect to the bottom electrode plane. The upper right part sketches the expected molecular order with small part of the molecular bonds to the electrodes being broken due to molecular bending and surface roughness. The bottom left and right graphs in Figure 1 show typical tunneling magnetoresistance curves measured at 10K and low (few mV) applied bias as well as the dependence of TMR on PTCDA thickness. Details about the sample preparation can be found in Refs.[1,7]

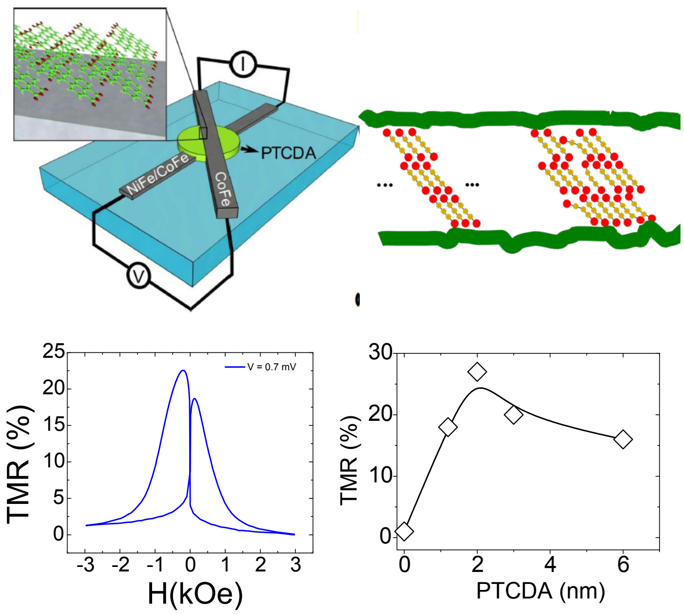

Figure 1. Upper left part sketches the O-MTJs with PTCDA barrier. Upper right part presents zooms pointing out some broken bonds contacting the molecules. The bottom left part shows typical tunneling magnetoresistance (TMR) curve measured at low (0.7mV) bias and T=10K. The bottom right part shows TMR vs PTCDA thickness at measured T=10K.

3. CONDUCTANCE, TUNNELING MAGNETORESISTANCE AND NOISE IN MTJS WITH PTCDA BARRIER

Figure 2 shows bias dependence of conductance of O-MTJs with PTCDA barrier measured at 0.3K and in the P state for different set of PTCDA thickness. While the control sample (with 1.2 nm AlOx barrier only) shows a quasi-metallic bias dependent conductance $G(V)$, strongly nonlinear curves, which could be related to presence of inelastic tunneling mediated by vibrational modes are observed for the junctions with finite PTCDA thickness.

Figure 3 summarizes our results of shot noise in O-MTJs with PTCDA barriers.[1] In order to explain the observed superpoissonian shot noise (Figure 3a) a simple model (see Figure 3b) considering tunneling through two level system of Coulomb interacting electrons with lower level much weaker connected to the leads has been suggested.[1] In these conditions, tunneling statistics are expected to be dominated by bunching processes which would also provide different Fano values in the parallel and antiparallel states. This Fano asymmetry increases with spin asymmetry represented in the model by the parameter β. More details on the model can be found in[1] and will be published soon elsewhere.

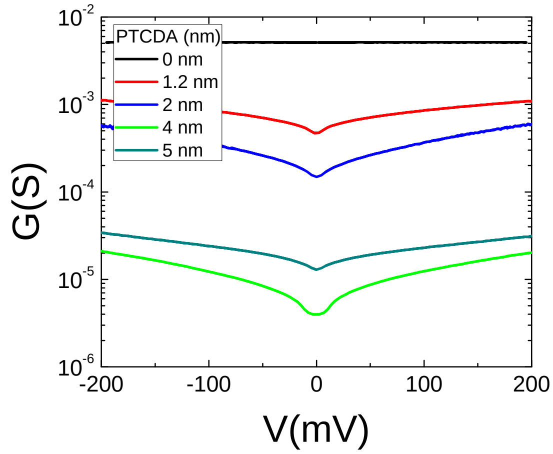

Figure 2. Bias dependence of conductance in O-MTJs with PTCDA barrier measured at 0.3K and in the P state

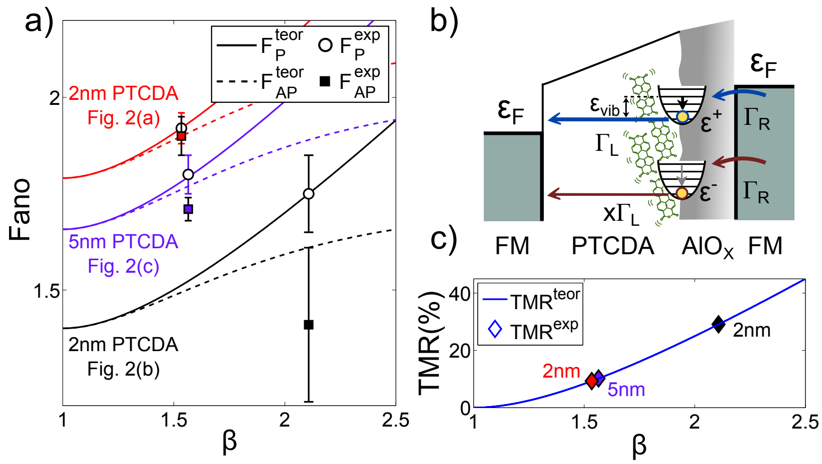

Figure 3. Part (a) shows experiment on Fano as well as fits of Fano as a function of spin asymmetry parameter β of the model. Part (b) explains model of superpoissonian shot noise as due to correlated electron tunneling through the two-level system (see Ref.[1] More details will be published soon by Szczepanski et al.). The following factors are introduced in the model: $\alpha^{\pm} = \Gamma^{\pm}_{R\uparrow}/\Gamma^{\pm}_{L\uparrow}$ to describe left-right asymmetry, $\beta_{L(R)} = \Gamma^{\pm}_{L(R)\uparrow}/\Gamma^{\pm}_{L(R)\downarrow}$ to describe spin asymmetry on the left and right sides and $x_{L(R)} = \Gamma^{+}_{L(R)\uparrow}/\Gamma^{-}_{L(R)\uparrow}$ to account for asymmetry in the bare tunneling to the two levels. Part (c) shows TMR vs. spin asymmetry parameter β of the model.

Finally, we mention that preliminary results on the bias dependence of the low frequency noise (LFN) indicate rather reproducible strong enhancement of the Hooge factor (α) $S_V = \alpha V^2/Af$ (here V is voltage, f - frequency and A - sample area) at specific biases. We have found (now shown) that these low frequency noise anomalies are relatively strongest for the smallest barrier thicknesses of 1.2-2 nm. The LFN anomalies survive heating up to 100K and the strongest features could correlate with anomalies observed in inelastic tunneling spectroscopy (IETS). We tentatively attribute these excess noise features to a vibrational heating of the molecules situated near the disordered interfaces, which could result in periodic closing/opening of a small part of the electron transport channels. Details on the anomalous low frequency noise vs. bias will be published separately.

4. CONDUCTANCE, TUNNELING MAGNETORESISTANCE AND NOISE IN JUNCTIONS WITH 200 NM THICK ALQ$_3$ BARRIER

Thanks to shot noise measurements the previous section reveals correlated tunneling through thin (1.2-5 nm) PTCDA organic tunnel barriers, which provide superpoissonian tunneling statistics. Organic spin valve devices with 200 nm thick, Alq_3 organic spacers present the chance to go beyond the tunneling regime where hopping process could take place.

4.1 Growth and sample characteristics

Figure 4 sketches O-MTJs with thick Alq_3 barrier. The layer sequence of the organic spin valves with Alq_3 is: $La_{0.7}Sr_{0.3}MnO_3$(20nm)/Alq_3(200nm)/Al_2O_3(2nm)/Co(20nm).

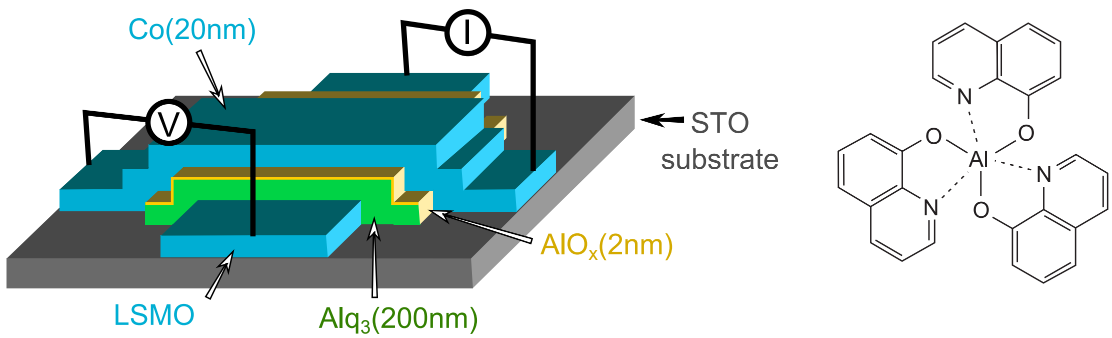

Figure 4. Sketch of the Alq_3 based OMTJ device and the Alq_3 molecule.

Details on the growth of the magnetic tunnel junctions with Alq_3 barriers could be found in Ref.[8] Fig. 5(a) presents the first (after zero bias zero field cooling) magnetoresistance (MR) curve measured, at T=92 K. It was found that the sample was in an intermediate (between low and high) resistance state, since high resistance proved to be around 30 kΩ. Figure 5(b) plots the first electrical hysteresis cycle tried on the sample in Fig. 5(a). As could be seen, the junction resistance is changed from the low (lower branch) to a higher resistance (upper branch) state. Note that such devices are characterized by resistive bistability (memristive behavior) and that the magnetoresistance across these devices varies for different non-volatile resistive states.[8]

In order to measure shot noise, the device was cooled down to 4 K. Low temperature helps to eliminate the contribution to noise from the charge traps (in form of random telegraph noise). We observed that the critical current values needed for switching the resistance of the spin valves have increased at low temperatures (see Figure 5(b)). The magnetoresistance response was also strongly suppressed below 4K, although the sample resistance hardly changed. This effect could be due to the MR contribution to the stray field discussed by Wang et al.[9] since: (*ii*) the resistance of the sample did not degrade, hence the loss of the MR response cannot be attributed to dielectrical breakdown; (*ii*) decreasing the temperature hardens the ferromagnetic electrode, changing the size and coercive field of the magnetic domains.

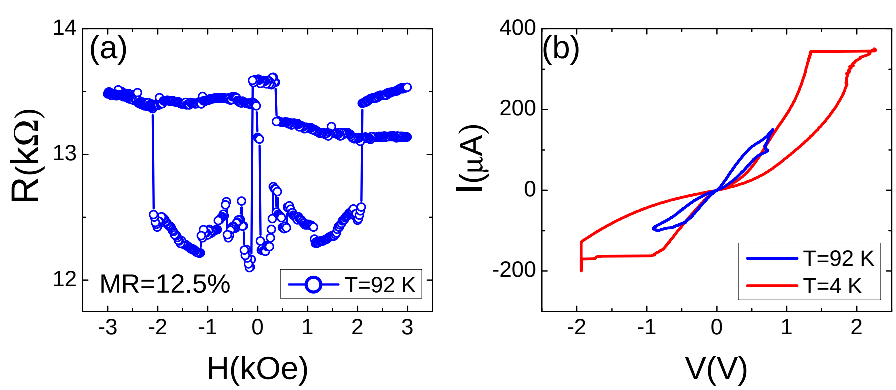

Figure 5. (a) Magnetoresistance of an organic junction with a 200 nm thick Alq_3 spacer. (b) $I - V$ curve at 92 K and 4 K showing the electrical hysteresis of the device in (a). The switch becomes increasingly difficult as the temperature is lowered below 10K.

4.2 Suppressed shot noise in the variable-range hopping regime

Let us finally discuss the shot noise for our Alq_3 based junctions. We have observed that junctions with thick molecular barriers show a different type of electronic transport than OMTJs with few nm thick PTCDA, as is apparent from the analysis of the Fano factor and conductance at different temperatures.

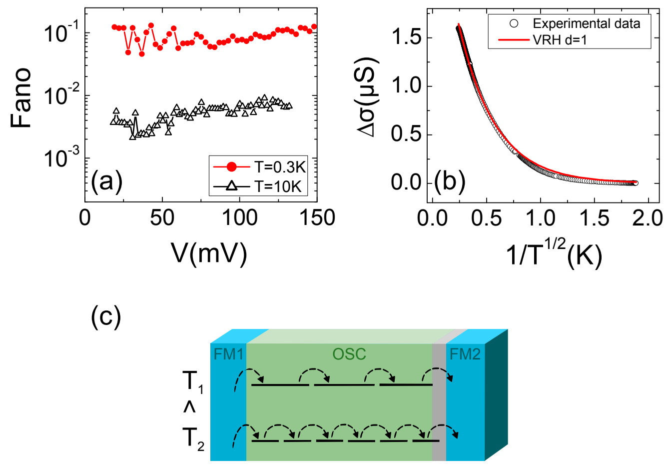

Figure 6. (a) The Fano factor is independent of the voltage but it decreases when the temperature is lowered. The noise is always subpoissonian ($F \ll 1$). (b) Dependence of the conductance with $1/\sqrt{T}$ of a sample with a 200nm thick Alq_3 barrier, fit by a variable range hopping law for d=1. (c) Schematic representation of temperature-dependent, multistep hopping through the organic barrier. T_1 and T_2 indicate low and high temperatures respectively.

Fig.6(a) summarizes our main findings on the shot noise in junctions with Alq_3. The shot noise is subpoissonian ($F \ll 1$) and nearly voltage independent, but strongly influenced by the temperature below 4K. A higher Fano factor at lower temperatures could mean electron transport dominated by variable range hopping. The fact that the shot noise is subpoissonian shows that multi-step tunneling takes place and the strong influence of the temperature agrees with the variable range hopping hypothesis, since a increase in Fano when the temperature is lowered points to an increase in the characteristic hopping length. As shown in Fig. 6(b), the dependence of the conductance (minus $\sigma_{T\to 0}$) with $1/\sqrt{T}$ of a sample with a 200nm thick Alq_3 barrier, seem to obey the variable range hopping dependence $\sigma = \sigma_0 exp(-(T_0/T)^{\frac{1}{d+1}})$ for d=1 (one dimension). Figure Fig. 6(c) also illustrates the temperature-dependent, multistep hopping. We conclude this part that the temperature dependence of the shot noise and conductance in O-MTJs with thick Alq_3 barriers (Fig.6) has indication of the Mott variable range hopping (VRH) regime over the thick molecular barrier.[10] Indeed, sequential tunneling is known to decrease the shot noise below poissonian values.[11] The Fano factor increases about 7-10 fold when the temperature decreases from 10 K to 0.3 K (Fig.6(a)), pointing out to a quasi one-dimensional VRH transport through the Alq_3 barrier at low temperatures.

5. CONCLUSIONS

The investigation of the conductance and shot noise in magnetic tunnel junctions with organic barriers has been studied in spin valve devices within the tunneling regime (PTCDA barriers) and with organic spacers of thickness well above it (Alq_3 barriers). ***(i)*** Our organic magnetic tunnel junctions with PTCDA barriers systematically exhibit superpoissonian tunneling statistics with Fano values between 1.5 and 2, likely due to localized states originated from interfacial bonds of the PTCDA molecules. ***(ii)*** These results are qualitatively accounted for within a model based on spin dependent electron tunneling with statistics controlled by an interacting two-level system.[1] ***(iii)*** The long-standing question regarding the type of transport taking place through thick, organic semiconductor spacers has also been addressed. The shot noise in magnetic junctions with thick Alq_3 barriers has been found to be subpoissonian and dependent on the temperature, consistent with variable range hopping.

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