Tunneling Magnetoresistance with Sign Inversion in Junctions Based on Iron Oxide Nanocrystal Superlattices

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1. Introduction

Pursuing spintronics with organic materials, molecular magnets and/or magnetic nanocrystals (NCs) is very promising [1-3]. In particular, integrating NCs with discrete energy levels [4, 5] into spin-nanodevices has attracted considerable interest due to expectation of novel properties resulting from the interplay between spin-dependent and single-electron transport [6-8]. Magnetotransport through NCs has been investigated in vertical structures within granular systems prepared by physical evaporation methods or within self-assembled superlattices of colloidal NCs. However, few superlattice layers of NCs were not investigated before in magnetic tunnel junctions (MTJ). This was done within the EU project SpiDME [9].

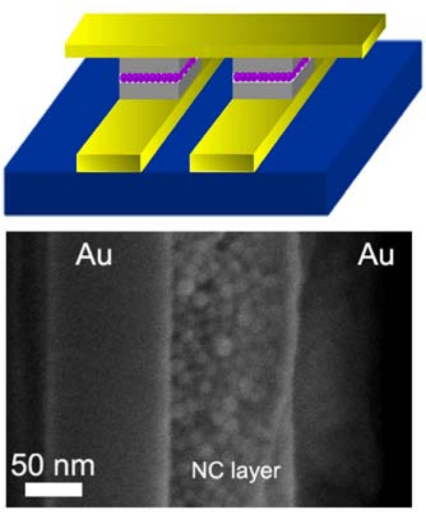

Figure 1. ***(top)*** *Cross-bar configuration of the magnetic tunnel junctions (MTJ).* ***(bottom)*** *Cross-sectional SEM image of a MTJ with NC superlattices.*

2. Experimental details

We employed iron oxide NCs synthesized by a modified two-step seeded-growth protocol [10]. They can be treated as core/shell objects individually made of an inner half-metallic Fe_3O_4 core domain embedded within a more oxidized γ-Fe_2O_3 shell. Due to their elevate monodispersity (size variance <5%), the NCs exhibited natural tendency to spontaneously organize into two-dimensional ordered superlattices. Devices were fabricated as cross-bar Au/SiO_2/NC layer/SiO_2/Au junctions having areas ranging from 150 to 2400 μm^2 (Figure 1top). The NC layer consisted of surperlattice thin films made of a few ordered NC layers and assembled starting from a concentrated NC solution by extremely slow solvent evaporation under external magnetic field. While Fe_3O_4 has fluctuating valence states of Fe^{2+} and Fe^{3+} providing electron hopping between them, γ-Fe_2O_3 has vacancies in the sites of minority carriers (Fe^{2+}) [11] and behaves as a disordered semiconductor.

3. Results and discussion

I–V curves of the fabricated MTJ exhibited similar sigmoidal shapes with higher resistances at small voltages, which can be fitted to a Simmons model for tunneling with similar values of barrier heights (around 0.30 ± 0.02 eV) and widths (1.3 ± 0.1 nm), which are plausible parameters. The current flow for positive bias was always about 1.4 times larger than for the negative polarity indicating asymmetric junctions. Moreover, current increased almost linearly with the area. For large area junctions, weak steps were observed at high voltages which were ascribed to single-electron tunneling (SET) through the NC array. However, when multiple conducting pathways are available within the junction, the conditions for observing Coulomb staircase are not easily fulfilled, as a large number of channels smear out SET effects.

Reducing the contact area led to the observation of quantum effects since few conducting channels are then available. In this case, Coulomb staircase can be better evidenced and, at room temperature, steps and discrete (charging) peaks were observed in the I-V curve and dI/dV spectrum, respectively (Figure 2top). Such patterns are typical of double-tunnel junction structures having dissimilar tunnel barriers. The large slope of the I-V curve around zero bias with the corresponding dI/dV peak around the Fermi level can be related to the metallic phase and the narrow conduction band of magnetite at room temperature [12]. Despite small variations, the voltage separation between adjacent steps was around 100 mV in small junctions. Roughly, we can assume NC with a diameter d = 13 nm and calculate $C = 2\pi\varepsilon_0\varepsilon_r d$, where ε_0 and ε_r ~ 2-3 are the dielectric constant of vacuum and tunnel barrier, respectively. This results in an estimated capacitance $C \approx 1.45$-2.17 aF corresponding to a Coulomb staircase period $e/C \approx 75$-110 mV, a value close to that measured experimentally.

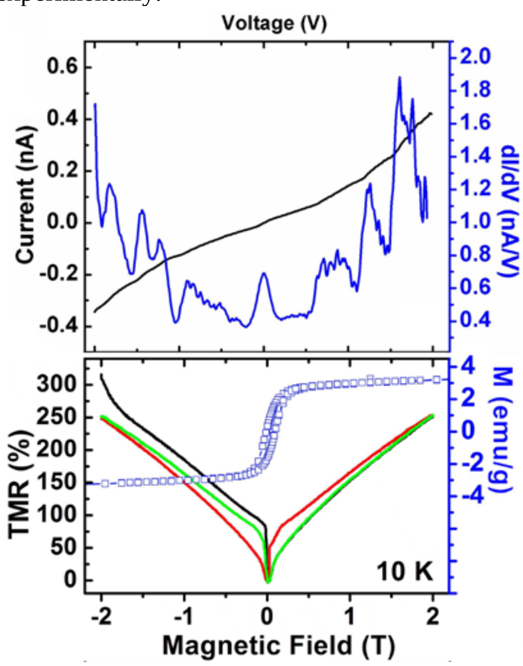

Figure 2. (top) *I-V curve and dI/dV spectrum for a small area MTJ (*150 µm^2*) with few conducting channels.* ***(bottom)*** *Positive MR at 10 K, along with the NC hysteresis loop (right axis).*

Further confirmation of transport in Coulomb Blockade (CB) regime comes from the observed $T^{-0.5}$ dependence of resistance on temperature (not shown) as expected for transport in granular systems typically described by Efros-Shklovskii variable range hopping (VRH) in case of mutual Coulomb interactions. The slope of lnR vs $T^{-0.5}$ plot is related to the Coulomb gap energy E_c. In our case, at higher temperatures E_c is ≈ 130 meV, while at low temperatures, E_c ≈ 75 meV. These values fit quite well with those evaluated earlier. At intermediate temperatures, a transition was observed starting at T_V~120-130 K, which roughly corresponds to Verwey transition in Fe_3O_4 associated with localization/delocalization of the extravalence electrons on Fe^{2+}/Fe^{3+} octahedral sites of the spinel crystal structure of magnetite [11]. As Fe_3O_4 is several orders of magnitude more conductive than γ-Fe_2O_3, the γ-Fe_2O_3 shell (boundary) resistances are the dominant contribution determining the ultimate resistance of NC superlattices above T_V. Below T_V, the extra electrons on Fe^{2+} sites involved in charge transport are frozen/localized and the Fe_3O_4 conductivity drops by two orders of magnitude. As a result, below T_V we expect the contribution of Fe_3O_4 cores to the overall junction resistance to increase. The change of relative core/shell contribution to conduction also influences the MR behaviour.

In our junctions, we found a noticeable correlation between the sign of MR and the regimes observed in the temperature dependence of the junction resistance. Specifically, a small MR was measured near 300 K, while ~5-6% negative MR was observed at 165 K in 2 T magnetic field. In this temperature range, the junction resistance is mainly determined by the more resistive γ-Fe_2O_3 shells. Thus, MR is not a bulk phenomenon of Fe_3O_4 cores, but is related to tunneling between Fe_3O_4 domains/cores on both sides of γ-Fe_2O_3 shells (boundaries), which leads to a negative MR, depending on the relative orientations of magnetic directions controlled by the magnetic field via a domain rotation process. For a granular system, the TMR ratio is often smaller than that calculated according to the Julliére model due to random orientation of the magnetic moments of the grains at zero field [6]. Here

$$TMR = \frac{m^2P^2}{1+m^2P^2}$$

where P is the spin polarization and m is the relative magnetization of the granular system. Once saturated (m = 1), the relation becomes $TMR = P^2/(1+P^2)$. Assuming $P \approx 0.5$-0.6 for iron oxide NCs [11], the resulting TMR is around 20-26%, which is higher than the measured value. However, we should take into account that transport in Fe_3O_4 cores is due to minority spin carriers and the γ-Fe_2O_3 shells act as spin-filter barriers on them (with a higher barrier for spin-down electrons). Moreover, we are still above the blocking temperature T_B ~ 90-100K and NC magnetization is thermally unstable. Thus, it is reasonable to expect a significant reduction of MR.

The MR then changes sign from negative to positive values across the Verwey transition. At

50 K, TMR is found to be 25-30% and as the magnetic field is ramped, a significant hysteresis is observed in MR curves for fields $\leq$ 80 mT. These field values are larger than those observed earlier in polycrystalline thin films and pressed powders [13] and can be associated to the NC magnetization since the MR reflects the NC ferromagnetism. Positive MR reported in granular systems are often related to various factors, such as curving of carrier trajectories in magnetic fields, shrinkage of localized electronic wavefunctions and suppression of hopping paths due to Zeeman splitting of the localized states, depending on the particular case of study [14]. In our junctions, below T_V, the extra electrons are frozen and localized, which is a first reason accounting for positive MR. Additionally, Zeeman splitting of the localized states contributing to carrier hopping can also contribute to positive MR in nanostructured arrays, leading to suppression of spin-dependent transport in the presence of external fields. The exchange coupling between different magnetic domains can enhance the Zeeman splitting of the localized states, leading to large positive MR [14].

On decreasing further the temperature down to 10K, a noteworthy increase in positive TMR is observed that drastically rises up to 300% (Figure 2bottom). Notably, we observed a good correlation of the low field features in the MR curves with the NC hysteresis loop (Figure 2bottom). The enhancement of positive MR cannot be explained simply by spin-polarization of discrete NCs alone, as the blocking temperature T_B and the tunneling dynamics between adjacent clusters have to be considered. Above T_B, the superparamagnetic moments are thermally unstable and the total magnetization decreases. Below T_B, the magnetization is seen blocked on the time scale of the measurement and the magnetic moments of the NCs are frozen along their easy axes. For $T > T_B$, the magnetic interactions among cluster domains in nanostructured materials are typically lower, while at low temperatures they become decisive. In particular, a magnetic exchange energy can arise when magnetic moments are not parallel and electron spin is conserved in tunneling. According to Inoue and Maekawa, these magnetic exchange interactions can lead to a large positive MR [15]. Moreover, at very low temperatures high-order processes of spin-dependent tunneling can play a dominant role in carrier conduction in the attempt of electrons to percolate the superlattice via NCs having parallel easy axis and thus preserve their spin. As a result, such processes involving successive tunneling of single electrons also produce MR enhancement, as reported for Co-Al-O granular systems [6]. Finally it should be mentioned that in other works, an enhancement of TMR was related to prominent co-tunneling effect in the Coulomb blockade regime, arising from uniform core size and shell thickness [16].

In conclusion, a switching from negative to positive TMR has been observed in MTJs sandwiching a superlattice thin film of iron oxide NCs. A good correlation has been found to hold between the magnetoresistance data, the expected magnetism of NC arrays, the charging energies evaluated from I-V curves, and the temperature dependence of their resistance. At low temperatures, a strong enhancement of TMR has also been observed.

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