

Growth of Self-Assembled Monolayers directly on a ferromagnetic metal surface

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Introduction

Spin-Electronics (spintronics), is a relatively new field of research based on the utilization in electronic transport of the spin of the electrons in addition to their charge. Traditionally, inorganic metals, insulators and semiconductors have been used as the main components in spintronic devices. However, this situation is currently evolving and a new field called Organic Spintronics is rapidly emerging. When compared to traditional inorganic materials, molecules not only have the traditional advantages inherited from organic electronics field: monodispersity, variability, low-density, flexibility, transparency, large scale processability and low-cost, but also the inherent weak spin-orbit coupling and hyperfine interactions found in organic systems that offers the possibility of preserving spin-coherence over times much longer than in conventional metals or semiconductors. Moreover, molecular materials should not be considered as a simple spin transmission media. In fact, as it has been very recently shown, they can also offer spintronics tailoring opportunities unachievable or unthinkable with inorganic materials. The molecular structure, the local geometry at the molecule/electrode interface and, more importantly, the ferromagnetic molecule/metal hybridization can strongly influence interfacial spin properties, for example, going from spin polarization enhancement to its sign control.[1]

Self-Assembled Monolayers (SAMs) are formed by molecules including functional groups (anchoring groups) displaying high affinities for a specific surface.[2] The directing force for the assembly is in most cases the formation of covalent bonds between the molecules and the solid surface; the assembly can be further stabilized by secondary intermolecular interactions within the monolayer being the final film thickness (some nanometers) determined by the size of the molecules.

SAMs as Spintronic Barriers

Recently we have developed the protocols for the grafting of SAMs over ferromagnetic oxide $\text{La}_{1/3}\text{Sr}_{2/3}\text{MnO}_3$ (LSMO) and has successfully integrated them into spintronics devices with the structure Co/SAM/LSMO.[3] Spin valves (SVs) and magnetic tunnel junctions (MTJs) are the simplest and most representative among the spintronics structures. A SV is a layered structure of two ferromagnetic (FM) electrodes separated by a nonmagnetic metallic or semiconducting spacer. The spacer allows spin polarized carriers to travel through it without much relaxation. In MTJs the two ferromagnetic-metallic electrodes sandwich a thin insulating layer that electrons must cross by tunnelling. Depending on their electronic structures SAMs can be used either in SVs or MTJs. As spacer SAMs MAIN ADVANTAGES are:

- i) Can be easily engineered: Are modular and their parts can be exchanged while keeping the others unchanged.
- ii) Are intrinsically nanometer thick: Film thickness will be determined by molecule size and SAM structure.
- iii) Have defined structures: SAM formation is a self-assembly process, structure is preprogrammed.
- iv) Can work at high bias voltage.[4]

However, as LSMO's surface Curie temperature (T_c) is close to room temperature, spintronics effects in LSMO-based devices are expected only at low temperature. So, in order to obtain spintronics effects at room temperature it will be desirable to substitute LSMO by a ferromagnet of higher T_c , as for example ferromagnetic metals or alloys, like cobalt (Co) or permalloy (Py).

Unlike LSMO, ferromagnetic metals readily oxidize and it is not surprising that SAM grafting protocols over FM electrodes are missing. The formation of SAMs on bare magnetic metals is a challenging task since surface oxidation (which suppresses surface ferromagnetic properties) during SAMs grafting has to be avoided. In this communication, we present our first results towards the integration of SAM into room temperature spintronics devices.

We have developed the grafting protocols necessary for the integration of SAMs on 3d ferromagnetic metals. We will present evidence that bare metal surface (Co, Py) remains un-oxidized under glove box conditions. Moreover, we have developed the methods to selective etch metal oxide under glove box environment in order to remove native oxide from oxidized surfaces (Figure 1).

Finally, we have tested SAMs grafting with thiols or phosphonic acids anchoring group on bare metal (Co, Py) and intentionally oxidized surfaces (Figure 2).

In fine, standard characterizations like contact angle measurements shows that only thiol group can be successfully grafted on ferromagnetic surfaces whereas phosphonic acids group works with oxidized metal surfaces.

References

- [1] C. Barraud, P. Seneor, R. Mattana, S. Fusil, K. Bouzehouane, C. Deranlot, P. Graziosi, L. Hueso, I. Bergenti, V. Dediu, F. Petroff, A. Fert, *Nat. Phys.* 6 (2010) 615.
- [2] A. Ulman, *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*, Academic Press, 1991.
- [3] S. Tatay, C. Barraud, M. Galbiati, P. Seneor, R. Mattana, K. Bouzehouane, C. Deranlot, E. Jacquet, A. Forment-Aliaga, P. Jégou, A. Fert, F. Petroff, *ACS Nano* 6 (2012) 8753.
- [4] M. Galbiati, C. Barraud, S. Tatay, K. Bouzehouane, C. Deranlot, E. Jacquet, A. Fert, P. Seneor, R. Mattana, F. Petroff, *Adv. Mater.* 24 (2012) 6429.

Figures

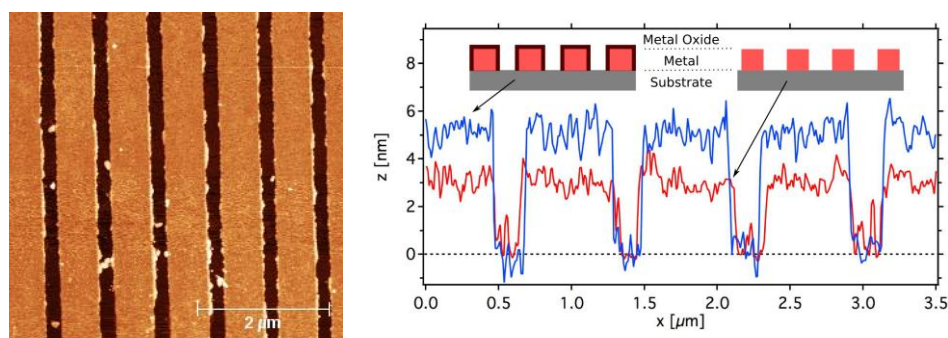


Figure 1 AFM image of a serie of Co lines made using the microcontact printing technique (left). Topographic profile of the lines before and after oxide etching (right). The difference in height corresponds to the oxide thickness.

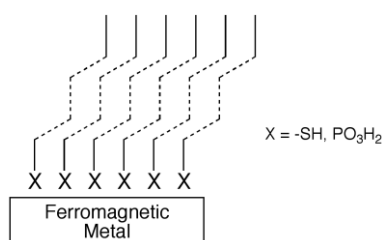


Figure 2