



IPCMS News

International Newsletter

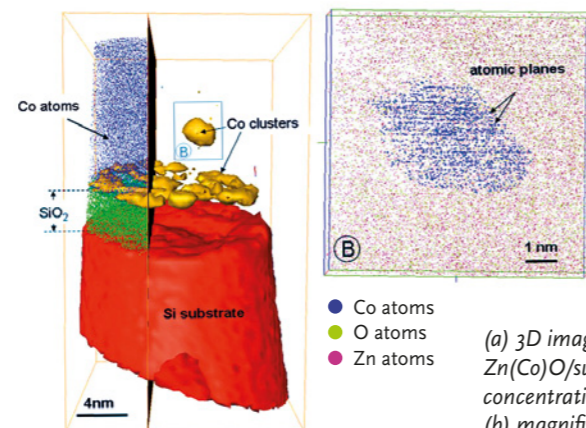
October 2011

No. 13

our results reinforce the assumption of a defect-induced ferromagnetism in Co-doped ZnO diluted magnetic semiconductors. ■

Evidence of Superparamagnetic Co Clusters in Pulsed Laser Deposition-Grown $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ Thin Films Using Atom Probe Tomography, R. Lardé, E. Talbot, P. Pareige, H. Bieber, G. Schmerber, S. Colis, V. Pierron-Bohnes, et A. Dinia, *J. Am. Chem. Soc.*, 2011, 133 (5), pp.1451-1458

Contact:
Aziz.Dinia@ipcms.u-strasbg.fr



(a) 3D image of the cluster decoration of the Zn(Co)O/substrate interface (in yellow, iso-concentration surface at 30 Co at.%).
(b) magnification of the Co cluster in region B.

♦ Giant magnetoresistance through a single molecule

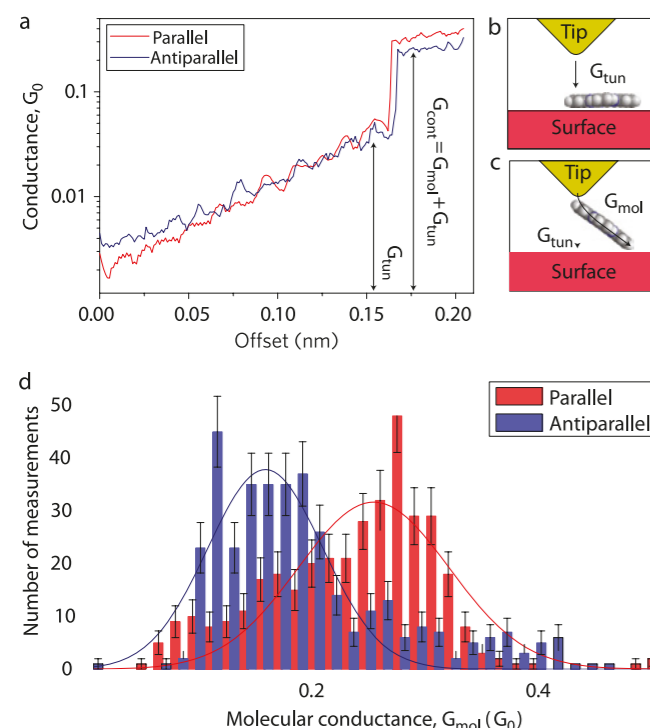
Giant magnetoresistance (GMR) occurs when ferromagnetic electrodes are contacted through a non-magnetic material. This phenomenon allows the detection of extremely small magnetic fields and

enables technological application eg in ultra-high density storage media. In this work performed in collaboration between the IPCMS and the Karlsruhe Institute of Technology, we used a scanning tunneling microscope in order to study GMR properties downsizing the device to its ultimate limits, namely realizing a well characterized junction including a Co nano-island with controlled magnetization, a phthalocyanine (H_2Pc) molecule and a Co tip. We measured for this system a GMR ratio of ~60% with a conductance that

amounts to a fraction of G_0 , the quantum of conductance ($G_0 \sim 77 \mu\text{S}$), a fact compatible with high sensitivity, high frequency device operation. To understand the origin of this large value of GMR, we performed transport calculations based on the density functional theory (DFT). The model correctly reproduces experimental values and identifies spin-dependent hybridization of molecular and electrode orbitals as the cause of the large magnetoresistance. ■

Giant magnetoresistance through a single molecule, S. Schmauss, A. Bagrets, Y. Nahas, T. K. Yamada, A. Bork, M. Bowen, E. Beaurepaire, F. Eves and W. Wulfhekel, *Nature Nanotechnology* 6, 185-189, (2011)

Contacts:
Martin.Bowen@ipcms.u-strasbg.fr
Eric.Beaurepaire@ipcms.u-strasbg.fr



Current-distance traces and magnetoresistance measured across single H_2Pc molecules between a Co tip and a Co nano-island.
a) Typical set of conductance-distance curves measured on top of a H_2Pc molecule.
b, c) Evolution of the contact geometry as the contact geometry decreases.
d) Histogram of corrected molecular conductances; the GMR ratio is obtained from a Gaussian fit to the data.

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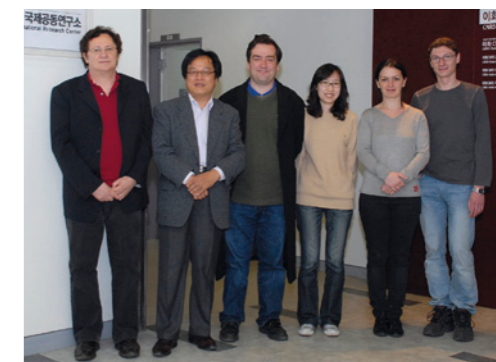
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Editorial

Since the inauguration of the « CNRS-EWHA International Research Center » (CERC) that took place last October 2010, at the EWHA womans university in Seoul, a femtosecond pump and probe laser experiment has been set up with the great help of Jean-Yves Bigot, Mirca Vomir and Marie Barthelemy from IPCMS. The first experiments performed using the brand new laser setup have exhibited highly interesting and promising results on conjugated organic molecules and meta-materials. Jean-Charles Ribierre, from EWHA, and Alberto Barsella, from IPCMS, are coordinating a STAR programme that is aimed at setting up a specific experiment set that will allow the testing of solid organic lasers that are optically pumped through one or two photon absorption.

From left to right: Jean-Yves Bigot, Jeong Weon Wu, Jean-Charles Ribierre, Jae Heum Woo, Marie Barthelemy, Mircea Vomir at « CNRS-Ewha International Research Center »



If graphene is to be sometimes in the future at the heart of new technological developments, the growth of large high quality layer is a must. Researchers at IPCMS have observed the growth of graphene layers from thin steel sheets paving the way in that direction. When molecules are placed on a substrate, they most of the time show very promising properties. A new mechanism is described here that decouples a molecule from a metal surface preserving its specific properties. Self-organization and metamaterials have raised the hope to perform breakthroughs in many fields but have also shown their ability to elude experiments. We have shown that one can take fully advantage of the self-organization of liquid-crystals to align gold nanoparticles that could be the scaffolding structure of a metamaterial. Pulsed laser deposition has the potential of permitting the mass-growing of new materials of interest, such as smaller and more sensitive devices to enhance the data storage density on surfaces. In Zn(Co)O thin films grown on silicon wafer, we have evidenced the decoration of the interface by nanosized clusters, reinforcing the assumption of a defect-induced ferromagnetism in the controversial Co-doped ZnO diluted magnetic semiconductor. Finally, we report here that a unique phthalocyanine can exhibit giant magneto-resistance therefore opening the way to a dramatic downscaling of future devices.

Marc Drillon, Director

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• **Publisher:** Marc Drillon - **Coordination:** Charles Hirlimann
• **Redaction committee:** Jean-Yves Bigot, Daniel Guillon, Stefan Haacke, Jean-Paul Kappler, Geneviève Pourroy, Wolfgang Weber
→ To subscribe, contact Charles.Hirlimann@ipcms.u-strasbg.fr

I.P.C.M.S

23 rue du Loess - B.P. 43
F- 67034 Strasbourg cedex 2, France
Tél: +33 38-810-7141
Fax: +33 38-810-7250

Design atelier.com

www-ipcms.u-strasbg.fr



♦ The growth of graphene layers observed in the electron microscope

The fabrication of graphene layers with reproducible structure and properties relies on our detailed understanding of the growth mechanisms. The nucleation and growth of graphene layers has not been accessible to direct observation until a recent *in-situ* experiment at the IPCMS showed the possibility of carrying out the growth of graphene in the specimen stage of an electron microscope. The study has been published in *ACS Nano* 5, 1529 (2011).

The most important technique to produce graphene for large-scale applications is the growth of carbon on catalytically active metal substrates. This is normally carried out in the vapour phase but is also feasible in a solid-state segregation process.

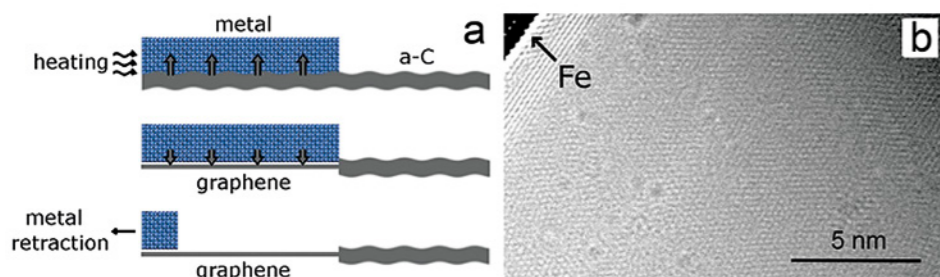
Such a solid-phase growth experiment was recently designed by the electron microscopy team at the IPCMS. Thin layers of Co, Ni, or Fe were deposited on an amorphous carbon film. Heating of this bilayer system in a dedicated high-temperature stage in an electron microscope induced the uptake of carbon by the metal. When a certain amount of carbon was in metallic solution, the nucleation of a graphene layer on the metal surface occurred. Subsequent heating or electron irradiation induced the retraction of the metal layer from the carbon film, leaving a clearly observable sheet of single- or multi-layer graphene behind. The ongoing nucleation and growth of graphene layers was directly observable at atomic resolution. The experiment allows

us to explain the growth of graphene by a bulk diffusion of carbon in the metal and segregation in certain areas, leading to the nucleation and subsequent growth of graphene layers. The dynamics of graphene growth was studied on different metals and in a wide range of temperatures. ■

Graphen growth by a metal-catalyzed solid-state transformations of amorphous carbon, J. A. Rodriguez-Manzo, C. Pham-Huu and F. Banhart, ACS Nano 5 (2), 1529-1534 (2011)

Contact:
Banhart@ipcms.u-strasbg.fr

A metal layer is deposited on an amorphous carbon film. Heating induces the uptake of carbon in the metal. Subsequently, a graphene layer nucleates on the metal surface. The retraction of the metal layer by heating uncovers the graphene layer (a). The electron microscopy image (b) shows a graphene layer that has grown from a Fe crystal (visible in the upper left corner).



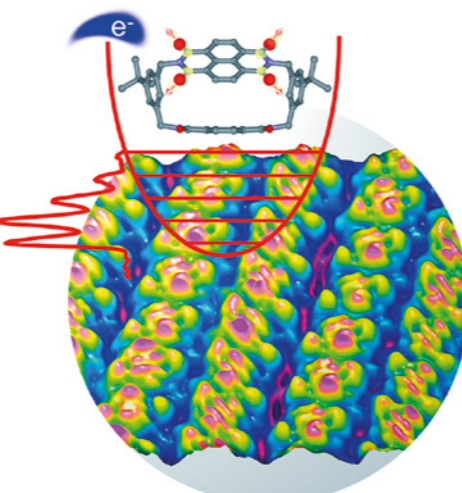
♦ Self-decoupling of a molecule from a metal surface

Our article focuses on the electronic coupling between molecules and a metal substrate. At the interface, charge transfer and hybridization affect the levels of an adsorbed molecule, which may significantly modify its properties. To recover and use the intrinsic molecular properties, which may be tailored over a wide range of values, a degree of decoupling from the metallic surface may be desirable. Effective molecular decoupling has been achieved using multilayers of molecules or ultrathin insulating layers. An alternative approach is to chemically modify a molecule using spacer groups in order to lift a particular subunit from the substrate. With this aim, for instance, bulky groups have been used to preserve switching capability of an azobenzene derivative. Previously, this approach was used to obtain an electrical insulation of a model molecular wire. However, these molecules turned out to be too flexible and thus deformed upon adsorption at metal substrates.

In our work, we use designed cyclophanes to achieve decoupling of one chromophore from a metal surface. These cyclophanes consist of two rigidly separated parallel-systems from which only one adsorbs to the surface, whereas the second one remains separated from the metal. We demonstrated that this organic molecule, with its height of a few hundred picometers on a metallic substrate, provides sufficient electronic decoupling of the top chromophore to enable detection of vibronic modes in scanning tunneling spectroscopy. These modes give rise to large signals that can be visualized with submolecular resolution in real space. ■

Electronic decoupling of a cyclophane from a metal surface, F. Matino, G. Schull, F. Köhler, S. Gabutti, M. Mayor and R. Berndt. Proc Natl Acad Sci USA, 108 (3), 961-964, (2011).

Contact:
Guillaume.Schull@ipcms.u-strasbg.fr



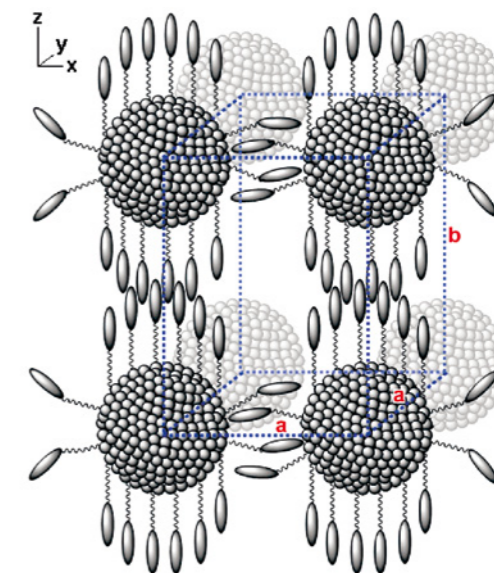
Chemical structure of a cyclophane molecule together with a measured vibrational spectrum corresponding to the stretching of the C=O bonds of the upper chromophore (in red) and a STM image of the self-organization of the molecule on Au(111).

♦ Liquid-crystalline gold metamaterials

Assembling spheroid metallic nanoparticles is of great interest for electronic, optical, and photonic applications. Metal nanoparticles derivatized with alkane thiols, acids, or amines can, if they are highly monodisperse, form body-centered cubic (bcc), hexagonal close-packed, or face-centered cubic (fcc) lattices with long-range order, as expected from arrangement of spheres. Derivatization of nanoparticles with liquid crystals may, in addition to enhancing the stability of the nanoparticles, considerably extends the possibility to generate all sort of ordered arrays of NPs, eg equidistant stripes, symmetrical 2D patterns, etc..., and not be restricted to the formation of such compact arrangements of spheres. In particular, devices with interesting optical properties could be generated from well-ordered arrays of nanoparticles, eg Au@NPs, whose sizes are much smaller than wavelength of light, offering thus the possibility of creating metamaterials.

In this context, several European teams joined efforts in the framework of an ESF EUROCORES SONS collaborative research project (coordinator, J.W. Goodby, University of York) in order to produce self-organized nanostructures by combining a variety of organic, inorganic and metal scaffolds with different mesogenic moieties. The self-organizing properties of the

liquid-crystalline coating is the driving force leading to the self-assembly of the nanoparticles in well defined hierarchical structures. In addition, the organic coating of the gold nanoparticles may influence the wavelength of the plasmon absorption, the structural organization of the nanoparticles and finally can induce an easier mixing of the nanoparticles with other media. Within such a collaborative project, the IPCMS team has been involved in the structure determination of mesophases exhibited by gold nanoparticles coated with 4-alkyl-4'-cyanobiphenyl groups. X-ray diffraction and neutron studies indicate the presence of a lamellar structure with a periodic alternation between gold-containing sublayers and the liquid crystal matrix. Moreover, molecular modeling shows that two types of interaction occur in the condensed phase: intramolecular π - π stacking of the biphenyl units and intermolecular π - π stacking by interpenetration of the biphenyl units of adjacent nanoparticles. The effect of the competition between these two types of interactions results in a topological distortion of the spherical nanoparticle into, presumably, a more tactoidal shape.



Schematic representation of the local arrangement of the functionalized nanoparticles

Self-assembly and shape morphology of liquid-crystalline gold metamaterials, M. Draper, I. M. Saez, S. J. Cowling, P. Gai, B. Heinrich, B. Donnio, D. Guillon, and John W. Goodby, Adv. Funct. Mater. 2011, 21, 1260-1278

Contacts:
bdonnio@ipcms.u-strasbg.fr
daniel.guillon@ipcms.u-strasbg.fr

♦ Evidence of superparamagnetic Co clusters in pulsed laser deposition-grown $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ thin films using atom probe tomography

Since the first observation of stable ferromagnetic properties of Co doped ZnO in 2001 many research works have been realized on this material, a large amount of experimental data have been accumulated and different mechanisms aiming at explaining the ferromagnetic properties in Dilute Magnetic Semiconductors (DMS) have been proposed. However the origin of the ferromagnetic behavior is still a matter of debate. In many reports the ferromagnetic properties are attributed to the dilute phase, whereas others suggest that ferromagnetism originates from the formation of cobalt clusters.

In this controversial context, highly sensitive characterization techniques are required for elucidating the ferromagnetism origins.

In collaboration with R. Lardé from Rouen University, atom probe tomography (APT) was used in order to characterize at the atomic scale the Co spatial distribution in $\text{Zn}(\text{Co})\text{O}$ thin films grown by pulsed laser deposition on silicon wafer. The APT analyses have evidenced the presence of nanosized Co clusters close to the interfaces with the Si substrate and revealed the decoration of the $\text{Zn}(\text{Co})\text{O}/\text{SiO}_2$

interface by a Co cluster assembly. This observation is consistent with the superparamagnetic relaxation evidenced by the zero field cooled (ZFC)/ field cooled (FC) magnetization curves. Indeed, the size of the Co clusters (3-4 nm) observed by APT shows unambiguously that all Co clusters exhibit a superparamagnetic behavior at room temperature. These analyses provide strong evidence that the room-temperature ferromagnetism observed in the magnetization curves cannot be attributed to the observed Co clusters. Because there is no experimental evidence of the presence of other secondary phases, ■■■