IPCMS News
International Newsletter
June 2008
No. 7

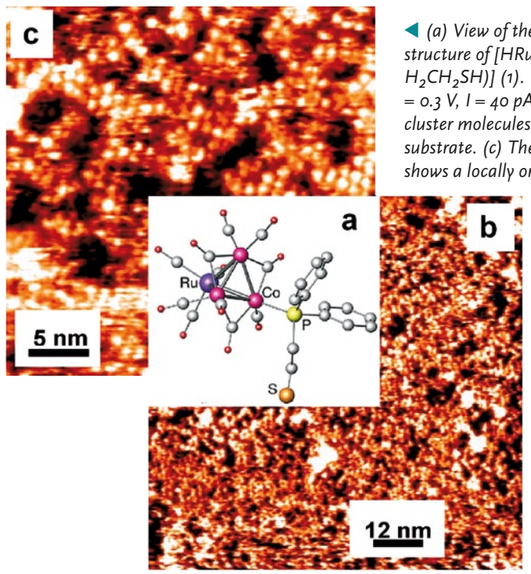
• Grafting and thermal stripping of organo-bimetallic clusters on surfaces: towards controlled Co/Ru aggregates

One of the main objectives in the field of high-density recording media is the development of microscopically-controlled nanoparticles and nanostructured magnetic materials involving heterobimetallic or binary cluster-substrate interfaces. This approach is based on the combination of 3d element and 4d element (strong spin-orbit coupling) which is a promising way to achieve both a large magnetic moment and high anisotropy.
These clusters should allow storage of bits on an always smaller number of particles until the ultimate goal of bit storage on a single cluster with the smallest possible size is achieved at room temperature.

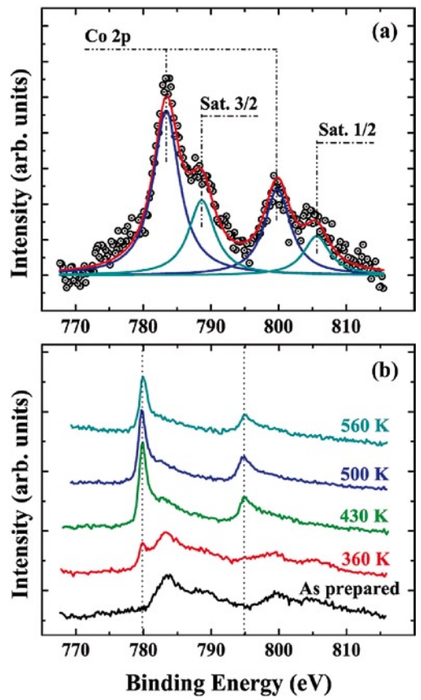
The approach described here takes advantage of the ability of molecular chemistry to provide mixed-metal organometallic clusters with a perfectly known proportion of the transition metal atoms A and B they contain. Tetrahedral A_xB_{4-x} carbonyl clusters, where x = 0-4, form an interesting family of precursors. We focus here on Co_3Ru because of the potentially excellent magnetic anisotropy properties of this alloy. For this purpose, we achieved the self-assembling of $[HRuCo_3(CO)_{11}(PPh_2C_2H_4SH)]$ clusters on Au(111) surface. Subsequently, the thermal annealing was performed in UHV so as to recuperate the $RuCo_3$ metallic monolayer. X-ray photoelectron spectroscopic measurements performed as a function of annealing temperature show that the cobalt and ruthenium centers converge towards metallic character and that the stoichiometry of the alloy is retained during the annealing process. ■

A. Naitabdi, O. Toulemonde, J.P. Bucher, J. Rosé, P. Braunstein, R. Welter and M. Drillon, Chem. Eur. **J. 14**, 2355 (2008).

Contact : bucher@ipcms.u-strasbg.fr



◀ *(a) View of the molecular structure of $[HRuCo_3(CO)_{11}(Ph_2PCH_2CH_2SH)]$ (1). (b) STM image (U = 0.3 V, I = 40 pA) of self-assembled cluster molecules on Au(111)/mica substrate. (c) The close up view shows a locally ordered-structure.*



▶ *Co_{2p} XPS spectra: (a) just after self assembly with corresponding fits. (b) Co_{2p} peaks for increasing annealing temperatures. A new peak for $Co_{3/2}$ appears at 779.8 eV as a result of annealing, corresponding to the binding energy of elemental Co. This behavior expresses the evolution of the Co center in the Co_3Ru unit toward a metallic behavior and points toward the onset of the loss of the carbonyl moieties.*

Summary

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Editorial

The first French-Korean school on «***Nanomaterials for Magnetism and Spintronics***» took place at IPCMS during the third week of February 2008. This meeting aimed at strengthening the scientific interactions between IPCMS, Nancy University and the Ewha University, jointly organizing the school. This was an opportunity for around 20 graduate students from Korean Universities to meet around 30 participating students from France, to visit our Institute, present their results and have scientific exchanges with IPCMS researchers.

A series of courses were dedicated to current topics in magnetism, essentially devoted to applications related to spin electronics.
Speakers came from the organizing institutions, with invited guests from France, Switzerland and the United States. The talks introduced magnetism at the nanoscale, presenting physical and chemical methods for creating samples down to the molecular size scale for which new magnetic properties and new applications are envisioned.
Specific applications for spin electronics were detailed, as well as new areas of research, as for example those involving graphitic structures. New mesoscopic effects and high-frequency investigations completed the survey of current topics in the exploding field combining electrical and magnetic properties of materials at the nanoscale.

Marc Drillon
Director

IPCMS News
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• **Redaction committee:** Jean-Yves Bigot, Alain Fort, Jean-Paul Kappler, Geneviève Pourroy, Wolfgang Weber
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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

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◆ Versatile surface functionalisation of dendronised polymers

The dendronisation of linear polymer chains by dendrons wedges on each monomer repeat unit leads to a new class of macromolecules, called linear dendronised polymers (or denpols). The growing interest for dendronised polymers arises from their ability to adopt a wormlike morphology and from their large number of terminal groups accessible to functionalisation.
Recently, we reported the synthesis of denpols by using the unconventional living anionic polymerisation technique. The macromonomers were carrying allyl end branches, leading to denpols covered by allylic branches. The presence of the reactive allylic groups made possible a subsequent surface functionalisation of the denpols. By using hydrosilylation, hydroboration or radical addition of mercaptans, the surface of the denpols can be covered by a large variety of functional groups such as siloxane moeities, perfluorinated chains, oligo(ethylene glycol) chains or hydroxyle groups. Despite the high steric hindrance, the grafting efficiency was excellent, leading in some cases, to a quasi-complete conversion of the allyl groups. In the case of the most sterically demanding siloxane chains, a surface congestion effect is expected to be reached, as sketched below. Covering the surface of the denpols with such a high density of functional groups (up to 9 per monomer repeat unit) naturally provides the polymer with remarkable properties. For instance, covering the denpols with siloxane or perfluorinated chains induces a liquid-crystalline organisation of the polymers. ■

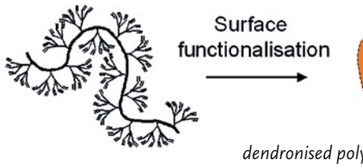


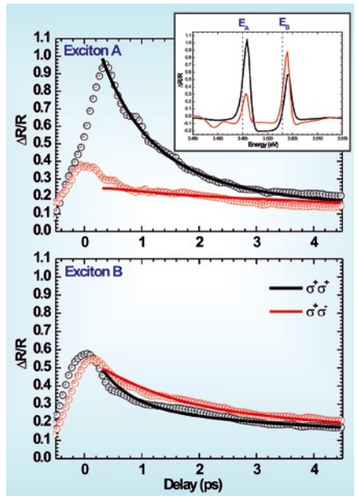
Illustration of a surface congestion of a dendronised polymer induced by the grafting of bulky groups (e.g. siloxane chains) onto the lateral allyl branches.

F. Moingeon, J. Roeser, P. Masson, F. Arnaud, S. Méry. *Chem. Commun.*, 1341-1342 (2008)

Contact:
stephane.mery@ipcms.u-strasbg.fr

◆ Spin relaxation in wurtzite GaN

Gallium nitride (GaN) and its related alloys have been extensively studied in the last ten years for their light emitting properties and are now intensively used in optoelectronic devices like green and blue LEDs, blue laser diodes and UV-photodetectors. The Blu-ray™ disc technology, for example, uses GaN-based blue laser diodes operating at a wavelength of 405 nm. But light emission is not the only application area where GaN is expected to shine.
Because of their wide bandgap (~ 3.5 eV for GaN), nitride based nanostructures show large carrier-confinement energies. Quantum dots are expected to operate at room temperature and are promising for applications, such as single-photon sources for quantum cryptography or in spintronics. However, few experimental data can be found on the spin dynamics in nitride compounds and the processes, responsible for the spin relaxation, are not clearly identified. Therefore, we use circularly polarized ultrashort (~ 100 fs) laser pulses to achieve optical orientation of exciton populations and study their temporal evolution, and to discriminate among the different possible spin relaxation processes.
We demonstrate that spin relaxation is dominated by a dislocation assisted Elliott-Yafet mechanism. In semiconductors, because of the spin-orbit interaction, a certain fraction of momentum scattering events result in spin flips. Threading dislocations are the main structural defects in GaN. They are generated during its heteroepitaxy on substrates with unmatched lattice parameters and are already known to be responsible for non radiative recombination of excitons. We show that, because of the strain and Coulomb fields they engender around them, they can also efficiently scatter charged carriers and thus enhance the spin relaxation rate through the Elliott-Yafet mechanism.
Therefore, to slow down the spin dynamics implies to avoid dislocations, which are always present in GaN, due to the lack of lattice matched substrates. Our work shows that, by localizing the excitons on a size scale smaller than the mean distance between dislocations, scattering can be avoided and spin relaxation inhibited. In this context, GaN/AlN quantum dots are very promising for spin manipulation on long time scales. ■



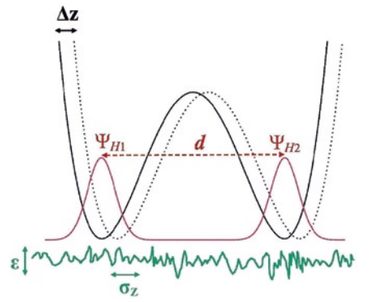
Spectrally integrated ΔR/R decays, for co- and counterpolarized configurations of pump and probe pulses, of the A and B excitons in wurtzite GaN. Inset: Corresponding spectra for a delay of 1 ps.

C. Brimont, M. Gallart, O. Crégut, B. Hönerlage et P. Gilliot
Excitonic Spin Relaxation Dynamics in GaN
Phys. Rev. B **77**, 125201 (2008)
Virtual Journal of Nanoscale Science and Technology **17** (11) (March, 17, 2008)
Virtual Journal of Ultrafast Science **7** (4) (April, 2008)
doi : 10.1103/PhysRev**B**.77.125201

Contact:
pierre.gilliot@ipcms.u-strasbg.fr

◆ Quantum coherence in a trapped Bose-Einstein condensate

Recent experiments have highlighted the coherence properties of atomic Bose-Einstein condensates, by measuring the interference fringes obtained when two condensates come into contact [M. A. Kasevich, Science **298**, 1363 (2002)]. If one of the condensates is slightly perturbed, we expect a gradual deterioration of the quantum coherence, leading to a lower visibility of the interference fringes. In order to quantify this effect, we have used the concept of *quantum fidelity*, defined as the square of the scalar product of the wave functions of two condensates evolving in slightly different Hamiltonians. Numerical simulations showed that the quantum fidelity stays constant until a critical time that depends on the logarithm of the perturbation, and then falls sharply.



Schematic representation of the proposed experiment.

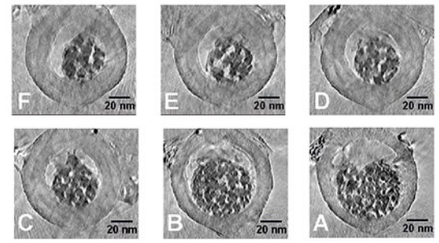
To test this behavior, we proposed an experiment where two identical condensates are created in a double trap. The trap is suddenly shifted by a small distance Δz, and a random potential, with amplitude ε and correlation length $\sigma_z << d$, is switched on. The condensates evolve in each trap for some time, after which the confinement is removed, so that they can expand freely and eventually overlap. The visibility of the observed interference fringes should display a behavior similar to that of the quantum fidelity, characterized by a rapid drop after a critical time. ■

G. Manfredi and P.-A. Hervieux, Phys. Rev. Lett. **100**, 050405 (2008).

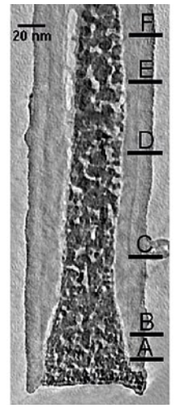
Contact :
Giovanni.Manfredi@ipcms.u-strasbg.fr

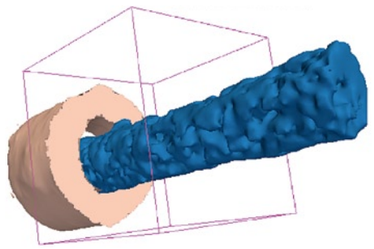
Electron tomography of magnetic $CoFe_2O_4$ nanowires inside carbon nanotubes

During the past few years, a significant scientific interest has been devoted to the study of confined (0D or 1D) nanomaterials, i.e. nanoparticles and/or nanowires due to their unusual physical properties. In this general framework, a particular attention was focused on the study of $CoFe_2O_4$ nanowires casted inside carbon nanotubes, obtained by mild chemical synthesis at relatively low temperature, in order to avoid the excessive formation of carbide-like phases. However, up to now, no microstructural investigation of these porous nanowires has been reported, even if their magnetic behaviour is strongly dependent on their structural characteristics and organization. For such investigation, electron tomography (or 3D TEM) is the most appropriate technique, because it allows to visualize directly the 3D structure, and in particular to deduce physical parameters of interest for application in magnetic devices.
A detailed investigation of $CoFe_2O_4$ nanowires, performed using the electron tomography technique showed that the size of the $CoFe_2O_4$ monocrystalline particles is closely dependant on their location within the nanotube, i.e. small particles close to the tube tip (5 nm) and bigger particles inside the tube channel (15 nm). As the theoretical critical size for superparamagnetic relaxation in $CoFe_2O_4$ is between 4 and 9 nm, the size distribution obtained by 3D-TEM agrees with the Mössbauer study that suggests the presence of two different magnetic components inside the nanowire. As regards to the spatial arrangement, TEM tomography revealed also that the nanowire is formed by several chain-like assemblies of nanoparticles almost parallel to the longitudinal axis. Finally, we have shown that, using this preparation method and for this internal diameter of nanotube, CoFe2O4 nanowires exhibit a continuous structure along the tube, with a residual porosity of 38%.
This study is a part of an exemplary collaboration between IPCMS and LMSPC *(Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse)*. ■



Successive transverse sections through the reconstructed volume showing the dependence of the size of $CoFe_2O_4$ nanoparticles on their position along the nanotube axis





Example of longitudinal section through the reconstructed volume and view of the 3D reconstruction model.

O. Ersen, S. Bégin, M. Houllé, J. Amadou, I. Janowska, J.-M. Grenèche, C. Crucifix, and C. Pham-Huu,
Nano Letters **8,** 1033-1040 (2008).

Contact:
ovidiu.ersen@ipcms.u-strasbg.fr