Program

9h45-10h30  Jérôme Lagoute (CNRS - University Paris Diderot) « Scanning Tunnelling Microscopy studies of graphene doping and graphene-molecule interactions »

10h30-10h45  Coffee break

10h45-11h10  Amjaad Abou Latif (GPM Rouen) « Atom probe analysis of Sm-Co-Cu-Fe magnetic alloys »

11h10-11h50  Paul Koenraad (Eindhoven University of Technology) « Atomic scale analysis of semiconductor nanostructures and doping atoms by scanning tunnel microscopy and atom probe tomography »

12h00-13h30  Lunch

13h30-14h00  Williams Lefebvre (GPM Rouen) « Correlative investigations by HAADF-STEM and Atom Probe Tomography »

14h00-14h40  Lorenzo Rigutti (GPM Rouen) « Optically active nanostructures in the Atom Probe : from the multi-microscopy to the in-situ approach »

14h40-15h30  Guillaume Schull (CNRS - University of Strasbourg) « STM-induced light emission: from molecular LED to subnanometric optical microscopy »

15h30- ...  Visit of the GPM Laboratory

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Nitrogen doping of graphene: an atomic scale view from scanning tunneling microscopy experiments

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Due to its bidimensional character, graphene is a rich playground to study electronic phenomena in low dimension, and is full of promises for applications in many areas. Beyond the basic properties of the pure material, tailoring the properties of graphene has become an active research field as it can reveal particular physical properties and open new opportunities for graphene based applications. In that context, chemical doping and the interaction with organic molecules have focused a particular attention in order to tune and exploit the properties of graphene.

Nitrogen doping, obtained by the insertion of nitrogen atoms in the carbon lattice, is particularly interesting as it allows to perform a n-doping with minor structural perturbations. The study of nitrogen doped graphene by scanning tunnelling microscopy (STM) has allowed to reveal the structure of nitrogen doped graphene and the electronic effect induced by the insertion of nitrogen that turns out to more complex than a rigid band model of doping.

Beyond the effect on the atomic and electronic structure of the material, nitrogen doping can also modify the interaction of graphene with external material such as molecules that can be exploited for sensing or catalysis. In order to gain more understanding of the basic phenomena occuring in the interaction of graphene with molecules, we have studied the interaction of porphyrin with graphene (see figure), as a model system for molecule-graphene interaction. Local spectroscopy, combined with imaging and manipulation, allows to reveal the local modification of molecule-graphene interaction at the doping sites.

The STM studies provide more understanding on the effect of doping on the properties of the graphene material, and on its interaction with other objects such as molecules.
Atom probe analysis of Sm-Co-Cu-Fe magnetic alloys

Amjaad Abou Latif

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The microstructure of mechanically milled SmCo3Cu2/α-Fe alloys has been investigated by Mössbauer spectrometry and atom probe tomography. The structural changes that occur upon milling and subsequent annealing were related to the previously reported magnetic data obtained on the same samples. Milling SmCo3Cu2 and α-Fe powders leads to the formation of α-Fe(Co) regions and Sm-(Co,Fe)-Cu regions, due to the Co/Fe interdiffusion. The deterioration of the microstructure during milling induces a drastic reduction in the coercivity, while the increase of the Co content in the α-Fe(Co) regions can be related to the increase of the saturation magnetisation. Upon annealing, a partial oxidation of the hard magnetic regions occurs, leading to the decrease, which could be responsible for the very low coercivity of the corresponding samples. The release of the Co atoms from the oxidised hard magnetic phase leads to an increase of the proportion of Co atoms in the Fe-rich regions, leading to a further increase of the saturation magnetisation.
Atomic scale analysis of semiconductor nanostructures and doping atoms by scanning tunnel microscopy and atom probe tomography

Paul Koenraad
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Present day semiconductor nanoscience depends heavily on the precise construction of nanostructures in which atomic scale details determine their opto-electronic properties. It is thus of key importance to have techniques that allow such details to be assessed by novel microscopy techniques that can obtain atomic resolution, preferable in 3D. In this presentation I will show recent results that we have obtained by two exciting microscopy techniques that allow for an atomic scale resolution. We have used cross-sectional Scanning Tunneling Microscopy (X-STM) and Atom Probe Tomography (APT) on a range of semiconductor nanostructures such as quantum dots and rings. The XSTM technique offers a superb 2D true atomic resolution in a single atomic plane intersecting the nanostructure. Atom Probe Tomography is a technique that only recently has become available for the analysis of semiconductor nanostructures. Laser induced field emission is used to get a full, atomically resolved, 3D map of the composition of the semiconductor nanostructure. In the presentation I will apply and compare these techniques on quantum dots and rings that have been obtained by various growth procedures such as the traditional Stransky-Krastonow process, droplet epitaxy or by applying Sb during the dot formation process. I will also show a few examples of the study and manipulation of (individual) doping atoms in a semiconductor.
Correlative investigations by HAADF-STEM and Atom Probe Tomography

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The ultimate capabilities achieved by electron microscopies and their associated techniques inevitably raise the following question: is there room for conceiving new ways of investigating materials at the nano-scale? Indeed, most recent TEMs and STEMs easily achieve sub-Angström spatial resolution, while allowing elemental mapping at the same scale. Meanwhile, electron tomography has unambiguously demonstrated the possibility to image atomic positions and defects. In these instruments, some physical properties (e.g. optical, magnetic) are now accessible, again with increased resolution. However, as far as an ultimate machine would allow correlating physical properties with a “perfect” determination of atomic species and atomic positions in 3D, one must recognize that such a tool is not yet available. Aside from electron microscopes, Atom Probe Tomography (APT), which is intrinsically a 3D technique, has received increased attention owing to drastic developments during the last decade. This tool enables reconstructing volumes of matter by determining atom positions in 3D, which nature is determined by time of flight mass spectrometry. Thanks to the improvement of specimen preparation protocols, APT can be applied to much broader areas of materials science (semi-conductors, bio-materials, geo-materials, soft mater and even liquids). Nowadays, intrinsic limitations of this tool reside in its limited detection efficiency (roughly 50% of atoms are detected) and in its anisotropic spatial resolution (though sub-Angström resolution is currently accessible along the direction of analysis, sub-nanometer resolution is achieved along transverse directions).

Strong advantages of APT rely in its possibility to detect all types of atoms, independently of their atomic number, in its excellent detection limit (few ppm in favorable cases but rarely more than 100 ppm), and in its intrinsic 3D nature. In order to collect a significant amount of information on a same nano-object, it is relevant to consider a correlative approach combining a TEM/STEM and APT. Motivations for such an approach are numerous. A non-exhaustive list would evoke: i) the possibility to associate structural defects (in TEM) with segregations (in APT); ii) associating the morphology of a particle (in electron tomography) with a 3D field of composition (in APT); iii) improving the quality of APT reconstructions by accessing additional information about the specimen morphology in TEM/STEM.

This presentation will begin with a rapid overview of the efforts made by the APT users community to promote this approach. Then, some illustrations will be given which relate the correlative investigation on alloys and quantum wells. The possibility to image APT specimens in STEM in high resolution mode (cf. Figure), while enabling atom counting will be discussed on the basis of HAADF-STEM image simulations.
Figure: Al-1.7at% Ag alloy sample containing Ag-rich nano-scale precipitates investigated in APT and STEM. (a) Schematic superposition of the APT reconstruction (top) and of the APT specimen observed in BF-STEM once the APT analysis has been stopped. (b,c) Views in APT (b) and HAADF-STEM (c) of the same Ag precipitates.
Optically active nanostructures in the Atom Probe: from the multi-microscopy to the in-situ approach


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Correlating two or more microscopy and spectroscopy techniques on the same nanoscale object may yield a relevant amount of information, which is difficult to achieve by other means. In this contribution, we present several results of correlated studies of microphotoluminescence (μ-PL), high-resolution scanning transmission electron microscopy (HR-STEM) and laser-assisted atom probe tomography (APT) on single nano-objects containing quantum confined systems based on III-N and II-O materials. This approach can be applied to the study of heterostructure interface definition, presence of extended defects such as stacking faults or dislocations, carrier localization and optical emission in quantum confined systems [1-4]. Furthermore, the use of complementary techniques may be extremely helpful for a correct interpretation of atom probe results and for understanding the limitations of the applied techniques [3,5]. Finally, we will show that the study of PL in situ in an atom probe allows for fine structure spectroscopy of color centers in diamond field-emission tips under electric field-induced strain.

Correlative analysis of QDs from an APT specimen tip containing several tens of GaN/AlN QDs
(a) PL spectrum of the tip, revealing multi-excitonic features (b) Effective mass model of the electronic properties of one QD based on the data extracted from (c) the APT volume reconstruction of the structure (only Ga atoms reported) [5]

STM-induced light emission: from molecular LED to subnanometric optical microscopy.

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The electric current traversing the junction of a scanning tunneling microscope (STM) may generate a local emission of light. During the last years, we have used this method to study the intrinsic luminescence properties of individual molecules. This work has progressed in two directions. On one side we have used the ability of the STM to manipulate matter with atomic-scale precision to form single-molecule light emitting devices [1]. Composed by individual molecular wires suspended between the tip and the sample of the STM (see figure), these devices generate an emission of light whose color, intensity and bandwidth can be controlled with high precision [2,3]. On the other side, we used the intrinsic resolution of the STM to performed sub-molecularly resolved vibronic spectroscopy of molecules separated from a metallic surfaces by a thin insulating layers [4]. These results constitute an important step towards photonic measurements with atoms-scale resolution.


Figure: Artistic view of a single-molecule optoelectronic device operated with a scanning tunnelling microscope.