IMAGING AND NANO-ARPES

An innovative and powerful tool for the nanosciences

In recent decades we have witnessed exponential advances in the different areas of the new nanotechnologies. These advances, seen particularly in nanoelectronics, nanomagnetism and nanochemistry, among others, affect almost every aspect of our lives and are major players in our evolution towards the "information and automation age".

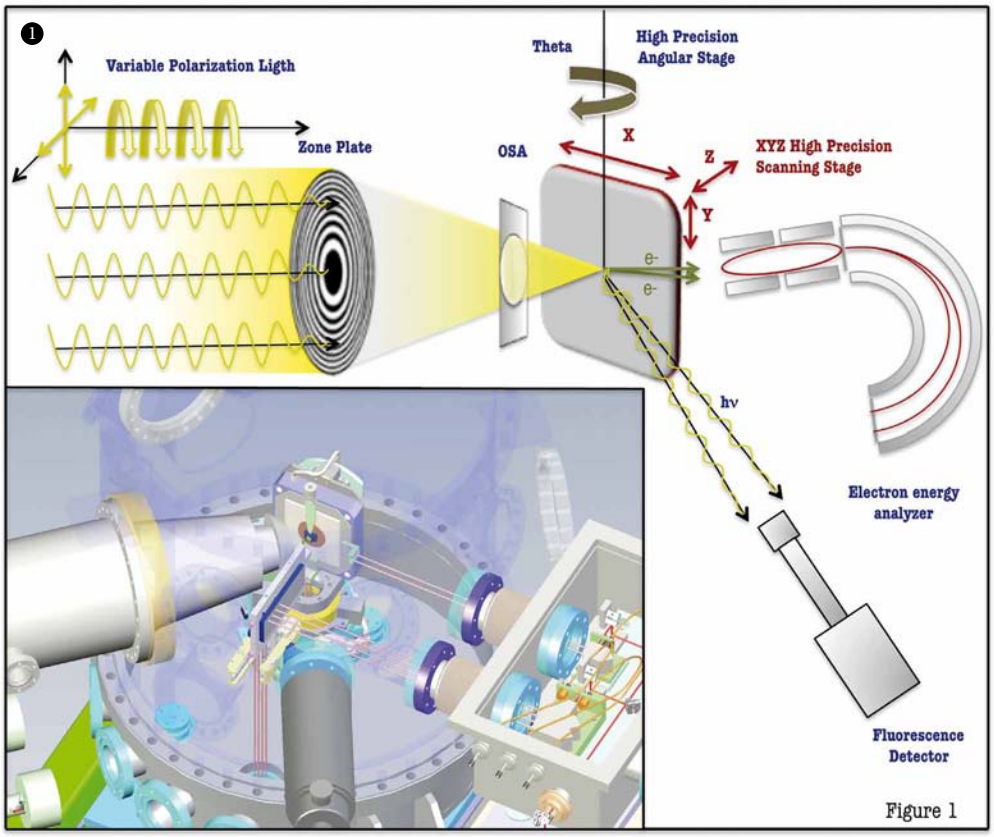

Figure 1

Following the fundamental step in the creation of nano-objects and even if these "building blocks" have shown remarkable properties, they would have remained unexploited if, at the same time, we had not developed new tools capable of viewing and scrutinizing objects on a wide range of scales, from a few microns to a few tens of nanometers.

Recently, great progress has been made as a result of the rapid expansion of modern microscopies. However, even if they have achieved nanometer spatial resolution, the challenge still remains to provide powerful high-energy-resolution spectroscopic tools for probing nano and micro-areas.

Electronic properties at nanometer resolution

The challenge is to quantify and analyze the electronic properties of advanced materials on a nano and micrometer scale. For such a result, analysis of the electronic structure must be comprehensive, not only with regard to detection of core levels, but also to study the structure of delocalized valence bands, directly responsible for chemical bonds, electrical transport and the thermal and mechanical properties.

Traditionally, angle-resolved photoemission spectroscopy (ARPES) is the only technique capable of making sufficiently precise measurements of the dispersion of the band structure of materials in reciprocal space. The state of the art ARPES equipments installed at synchrotron radiation sources is such that it can offer energy and angular resolution of better than 5 meV and 0.1°, respectively. Yet, until now, no instrument has been capable of performing spatially resolved ARPES experiments on the nanometer scale.

This paper presents the first results of the Nano-ARPES microscope recently installed on the ANTARES beamline at SOLEIL. This sophisticated instrument is able, with a spatial resolution of several tens of nanometers, of carrying out the direct imaging of core levels and their chemical shifts, band electronic structures in reciprocal space and constant

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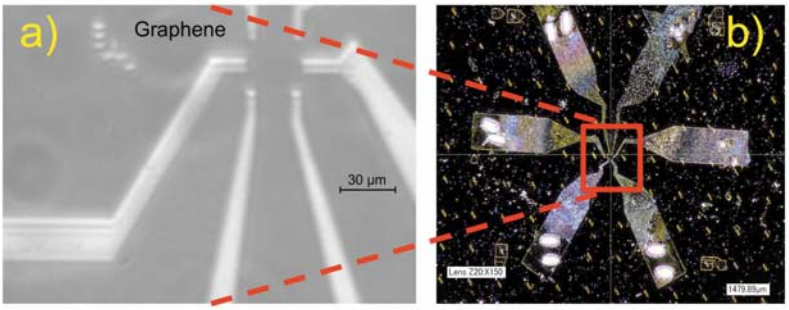

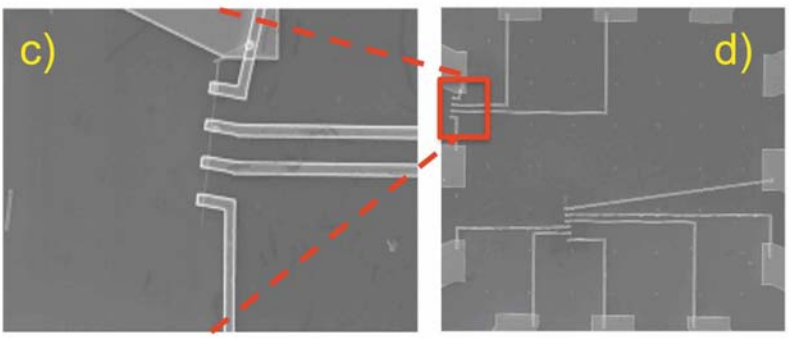

Figure 1: Diagram of the Nano-ARPES instrument. The ZP's central stop and the order sorting aperture (OSA) intersect the zero and higher diffraction orders and lets through only the first order. The microscope is equipped with a fluorescence detector to carry out in situ X-rays adsorption experiments.

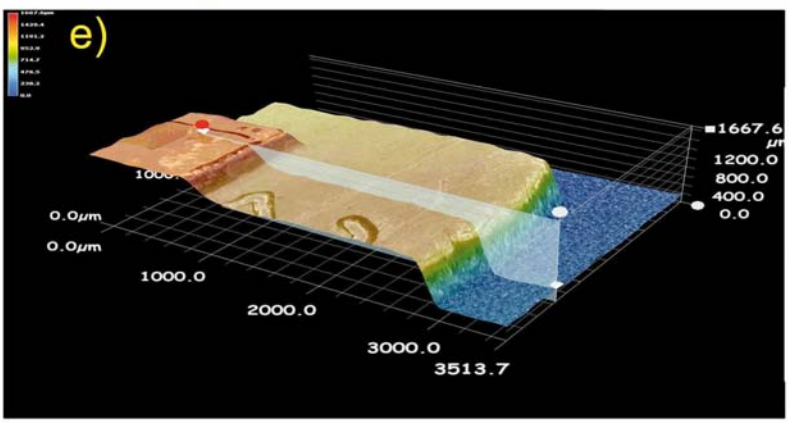

Figure 2: Exfoliated graphene film visualized by optical microscopy (a) and SEM (b). Parts (c) and (d) show SEM images of isolated silicon nanowires. Finally, visualization of a HOPG crystal by optical microscopy is shown in (e).

energy surfaces in reciprocal space, especially the Fermi surfaces.

First results on ANTARES

Figure 1 shows a diagram of the ANTARES microscope. It differs from conventional ARPES instruments mainly in that the sample can be mounted on a high-precision plate that ensures nanoscale scanning of samples in the x, y and z directions. The polar angle (θ) and the azimuth angle (φ) can also be automatically scanned over a 90° range. Finally, the soft X-ray beam (from 20 to 900 eV) with a controlled linear or circular polarization can be focused to about 80 nm (or better), using Fresnel Zone Plate lenses ("flat area", ZP). The ANTARES microscope has two operating modes, spectroscopy with nano-spot and spectroscopic imaging.

Figure 2 shows some examples that, far from being an exhaustive list, were selected to illustrate the types of the most representative specimens currently studied by the ANTARES Nano-ARPES microscope. Several samples of exfoliated graphene less than 30 µ m wide and one atom thick (the thinnest material ever isolated) were oriented and largely characterized using this Nano-ARPES microscope with excellent reproducibility of results (Ref. 1). The ANTARES microscope has also measured the valence states and core levels of isolated nano-objects such as boron-doped silicon nanowires (Figure 2, ref 2). Finally, Figure 2 shows the visualization of a crystal of highly oriented pyrolytic graphite (HOPG), which, despite its apparent homogeneity, is composed of micrometric grains.

To demonstrate the capabilities of the new microscope, we present the HOPG imaging and spectroscopy study. The sample is a polycrystal composed of grains of micrometer-sized single-crystals of graphite randomly oriented in the basal plane of the crystal. The basic unit of the HOPG is graphite, which has a planar structure, where in each layer, carbon atoms are arranged in a hexagonal lattice. The sp^2 electrons in the carbon atoms in each plane are bonded by strong covalent σ bonds and covalent π bonds for their other p electrons. These π links are delocalized conjugated bonds which are perpendicular to the atomic planes, and are responsible of the high electrical and thermal conductivity of graphite.

Figure 3 shows a 7 µm x 7 µm map of the photoemission intensity of a reduced energy window around the Fermi level, which is the energy that separates the occupied from the unoccupied bands. The microscope's detection geometry was fixed so that it can only detect the intensity from the grains oriented in the ΓK direction, where only the π bands approach the Fermi level. The thermal and mechanical stability of the microscope makes it possible to obtain high contrast and highly reproducible images. The visualization of each grain, each measuring 1-2 microns, is direct and fast. The Nano-spot mode of the microscope allows performing a full spectroscopic and electronic band

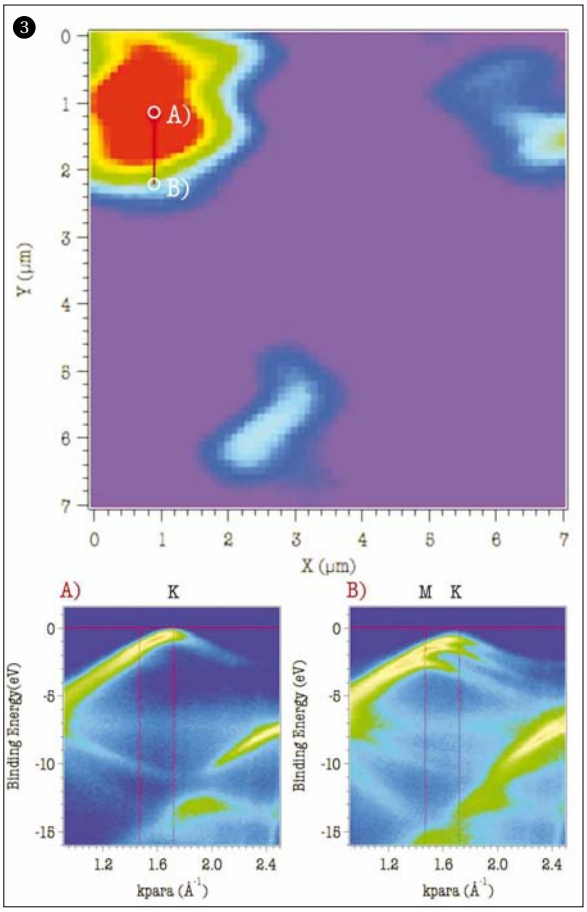

Figure 3: Spatially and angularly resolved photoelectron intensity maps of an HOPG crystal.

dispersion determination not only inside the grain but also in its surroundings (Figs. 3A and 3B).

Another way of studying the electronic band dispersion is to analyze photoelectron intensity maps at constant energy. However, for this, very precise angular scanning is necessary that requires almost perfect coincidence of the light source (or ZP), the Scienta analyzer focus and the mechanical axis of rotation of the microscope in the region of the sample to be measured, which in this case is the surface area of a grain only 2 µm wide.

Figure 4a shows the dominant features of the Fermi surface mapping of a single grain of the HOPG crystal. It reveals small pockets of electronic states concentrated in the six corners of the Brillouin zone of graphite. Figure 4b shows the same Fermi surface map detected without ZP, in traditional ARPES mode. The Fermi surface is now characterized by a ring with a ΓK radius, which includes the six points of all individual grains randomly oriented in the HOPG crystal.

Thus, the new Nano-ARPES microscope recently installed on ANTARES, is already capable of providing spectroscopic images with a spatial resolution of several tens of nanometers, while preserving angular and energy resolutions comparable to the best performing ARPES instruments installed on synchrotron radiation sources.

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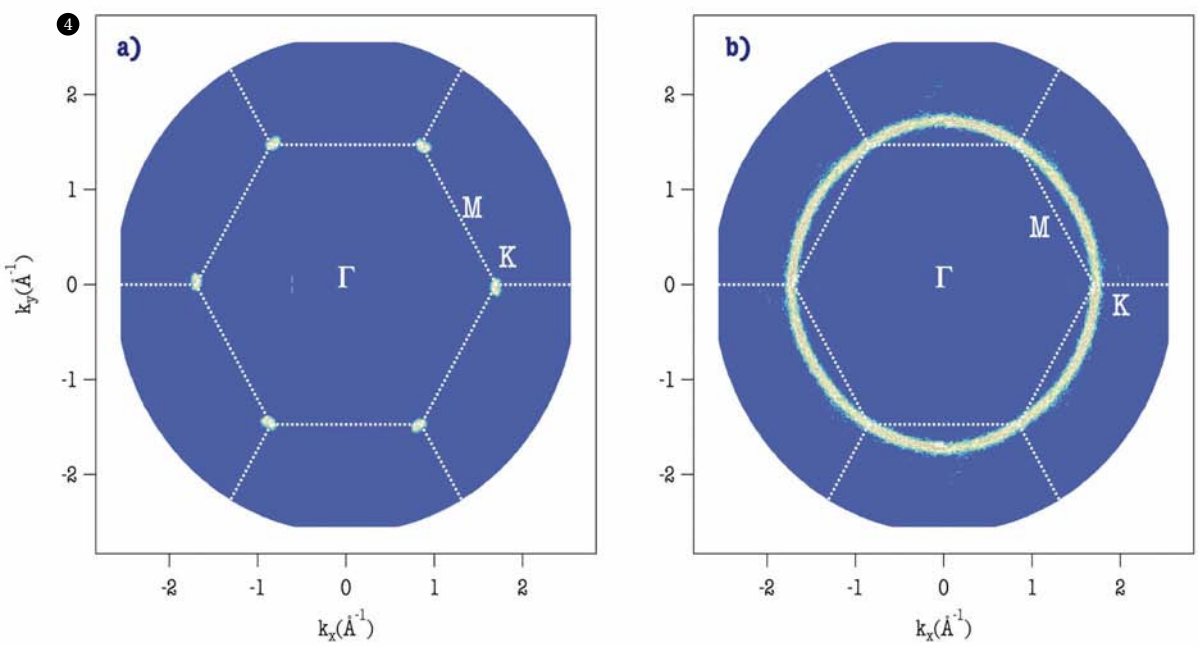

Figure 4: Fermi surface of a single grain of graphite in a HOPG crystal by Nano-ARPES (a) and Fermi surface of a HOPG crystal by conventional ARPES (b).