

Understanding nano-materials using chemical and electronic imaging

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ABSTRACT

Research and development of atomically thin, 2D materials as well as nano-objects and composites have sparked enormous scientific interest. The main goal in this field is to disclose the implication of heterogeneities from a chemical and electronic point of view. In this context, the description of the electronic structure of the material as well as its chemical composition and distribution must be complete. This objective is rather pertinent because the chemical bonds, reactivity, electrical transport as well as the thermal, magnetic and mechanical properties of matter are driven by its electronic structure. In order to fill this need, we have recently developed a novel microscope, particularly well-suited to provide valuable spectroscopic and electronic information in the real and reciprocal space of mesoscopic samples. In the present report, the more relevant results of the recently built ANTARES microscope will be disclosed.

Keywords: electronic and chemical imaging, nano-materials, nano-ARPES, band structure, photoemission

1 INTRODUCTION

During the last decades many scientific research areas have experienced remarkable progress in diverse fields of nanosciences and nanotechnologies. In an even rather wider field, complex and smart materials are also often isolated in small crystallites and they present serious difficulties to be synthesized without fluctuations in their compositions or crystalline orientation.

Overcoming the critical step of the manufacture of nano-objects or complex materials and even if these "smart-units" have remarkable properties, they would have remained unexploited if new tools have not been developed for analyzing and measuring those objects on a wide range of scales, from a few microns to tens of nanometers. Hence, the precise and fine electronic and compositional characterization is revealed rather intricate if the novel materials are affected by phase separation or magnetic domains, composites with nano- or micro-crystallites embedded in isolating and flexible host materials as well as nano- or micro- patterned objects, among others.

Recently, a tremendous and fast expansion in modern microscopic methods has been realized. However, beyond

the achievement of the *angstrom* spatial resolution, the challenge still remains in order to consolidate energy resolved spectroscopic methods with lateral nanometric resolution. A fine chemical and electronic analysis with submicron spatial discrimination has been revealed to be indispensable for many scientific problems.

The main goal then is to follow the implication of heterogeneities and confinement on the delocalized or partially localized electronic states. For such aim, the description of the electronic structure must be complete, not only with regard to the core level detection provided by conventional techniques (like XPS, Raman, etc., etc.), but also taking into account those states of the valence band as those electronic states are directly responsible for the chemical bonds, reactivity, electrical transport as well as the thermal and mechanical properties of matter.

Bearing these objectives in mind, we present here the new ANTARES microscope offering a spectroscopic non-destructive nano-probe to study advanced materials. This innovative tool combines a ultramodern technology able to perform precise electronic valence band determination and chemical imaging [1,2] .

2 RESULTS

Taking advantage of this innovative facility, a wide variety of experiments have been already carried out on many interesting materials since the beginning of the user operation a few years ago. Here we present some examples that, far from being an exhaustive list, they will give a flavour of the type of problems that can be successfully tackled by ANTARES microscope.

Semiconductor nano-wires have shown promising properties for many device applications, but controlled doping with electronic impurities remains an important challenge. Limitations on dopant incorporation have been identified in nano-crystals, raising concerns about the prospects for doping other nanostructures. In addition, progress has been hindered by the lack of methods to quantify the dopant distribution in single nanostructures. Nano-photoemission can in principle allow performing non-destructive microscopic analysis of the chemical composition and electronic structure of single nano-wires. Such quantified information could have important implications on controlling the incorporation of impurities

in semiconductor nano-wires and on turning them into electrically active dopants.

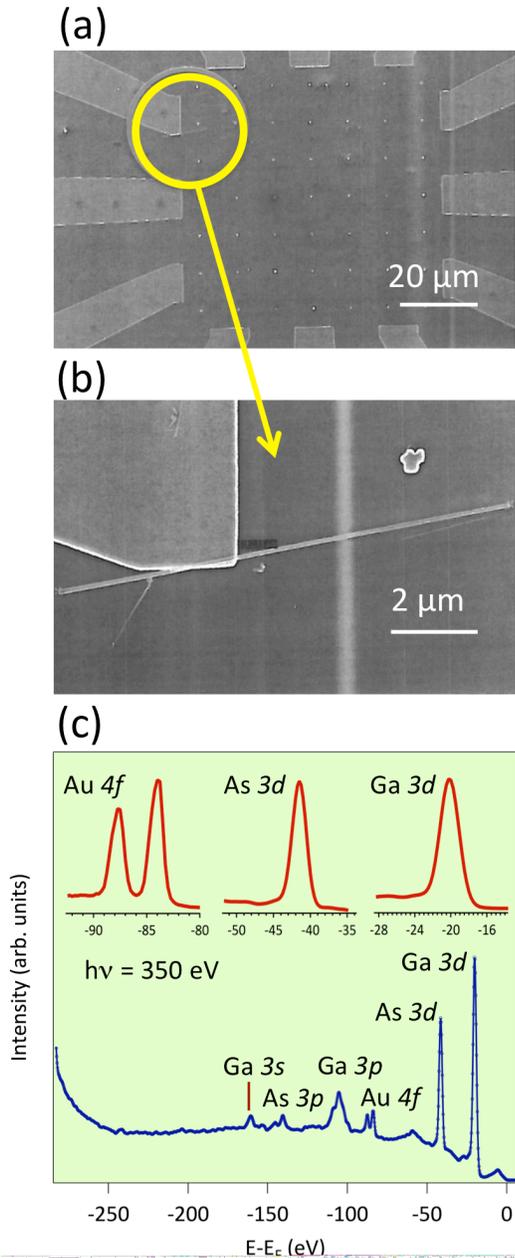


Figure 1 Panel a-c: Characterization by micro- and nano-core level of silicon nano-wires on GaAs substrate patterned with gold. Panel (a) and (b) show SEM images of the sample and the silicon nano-wire connected by gold legs. Panel (c) displays a micro-XPS overview spectrum with significant signal of Au (4f), As (3d) and Ga (3d) core levels. Top insets of the panel show individual core level spectra measured using nano-XPS. The spectra have been all recorded using incident photon energy of 350 eV. Panels (d) and (e) show real-space two-dimensional images of the elemental distribution of the patterned sample by monitoring the area of the As (3d) core level spectrum indicated in the inset of panel (c).

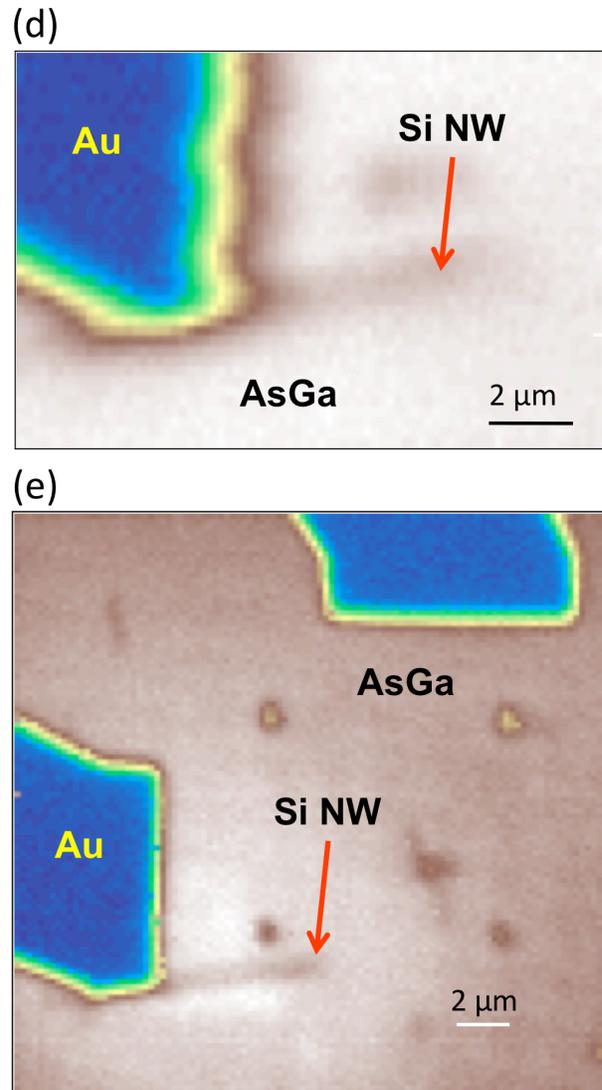


Figure 1 Panel d-e

Valence band and core levels measurements of isolated nano-objects such as boron-doped silicon nano-wires have been carried out recently using Antares microscope, with a spatial resolution better than 100 nm. Figure 1 shows one of these silicon nano-wires connected to gold legs on a GaAs patterned substrate.

In panel (a) a secondary electron microscopy (SEM) image of this sample depicts its characteristic pattern with twelve gold legs and small gold dots that act as markers of different areas of the sample. Panel (b) illustrates a zoom of panel (a) where a single nano-wire can be identified. A survey photoemission spectra recorded using a large photon spot of ~ 90 μm (micro-XPS) of this patterned sample comprehensively indicates the presence of gallium, arsenic and gold, revealed by significant signal of Au (3d), As (3d) and Au (4f) core levels. However, this spectroscopic

information is totally insensible to the patterning of the sample and it is not even able to detect the small signal due to the presence of little concentration of nano-wires in the investigated sample (see panel (c)).

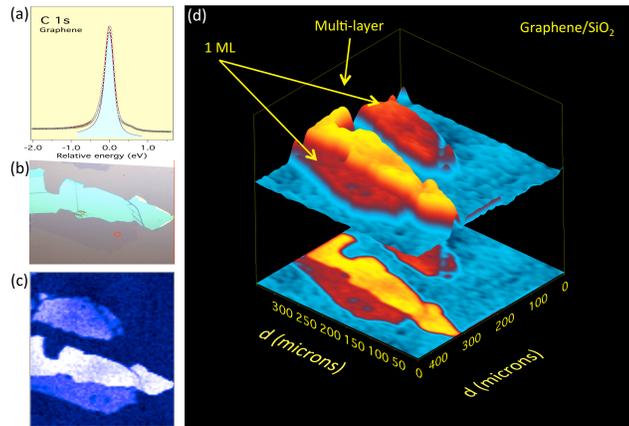


Figure 2 Nano-core level results on exfoliated graphene samples on SiO_2 substrates recorded at ANTARES beamline. Panel (a) shows C 1s core level recorded with a nano-spot of ≈ 100 nm size using incident photon energy of 350 eV in the area of the sample that correspond to one-atom thick graphene film. The reference binding energy is $284.5 (\pm 5)$ eV. Panel (b) displays an optical micrograph of the high-quality exfoliated graphene single crystal transferred on an isolated SiO_2 substrate. Panel (c) and (d) show two- and three-dimensional nano-core level imaging x - y mapping the intensity, respectively, of the C 1s intensity displayed in panel (a).

Top and bottom right panels show the same type of spectroscopic information displayed in Fig. 1c but as two-dimensional images, taking advantage of the precise sample scanning and focalized nano-spot performance of the ANTARES microscope. The nano-core level image of panel (d) shows one of the gold legs connected to the silicon nano-wire, using a spot size of ~ 100 nm. Despite the image is clear due to the lack of interferometer control during this measurements, the contrast of the image is rather poor and spurious distortions are observed particularly evident in the straight areas of the patterned sample, for example the front part of the main gold leg. As soon as the real time interferometric feedback closed-loop is included in the measurements, the obtained images are free of thermal drifts and mechanical vibrations as can be seen in Fig. 1e.

Bottom right panel of fig. 1e shows then the same area of the sample of panel (d) but with much better contrast and spatial resolution recorded and free of thermal drift distortions. The resulting nano-XPS image plots the intensity of the selected core level (in this case As 3d) as a function of the x and y position of the nano-spot on the sample. As it is displayed on the inset of panel of Fig. 1c,

the Scienta spectrometer is able of recording almost simultaneously the intensity of all characteristic core levels present in the sample investigated, i.e. in this case Au (4f), As (3d), Ga(3d) and Si (2p). Thus, from one unique sample scanning, independent images can be generated plotting the intensity of each recorded core level as a function of the sample position, describing thus the quantitative distribution of each element present in the investigated specimen.

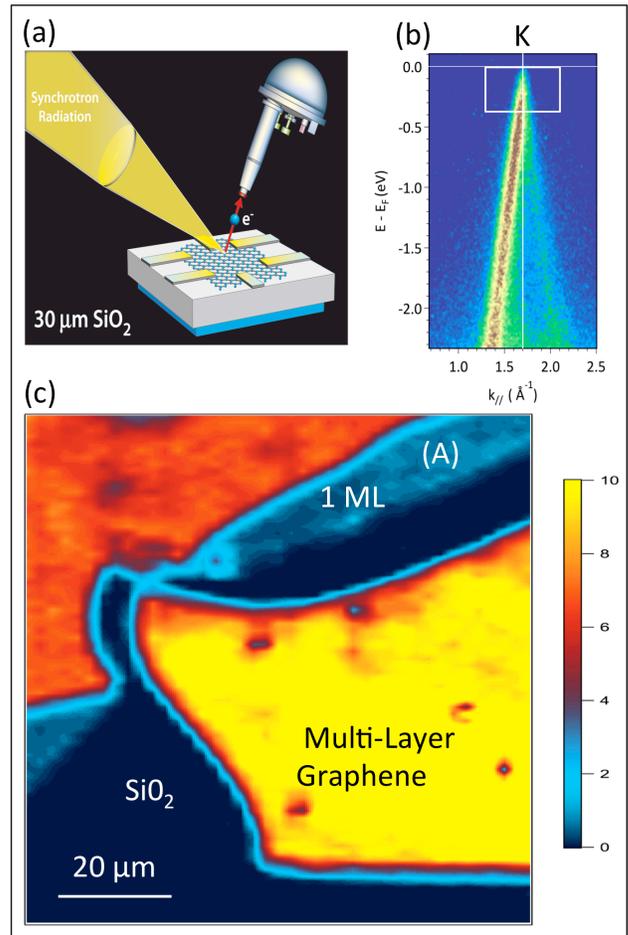


Figure 3 Real-space image and nano-ARPES electronic band dispersion close the Dirac point of the single- and multi-layer graphene films on SiO_2 substrate. (a) scheme of the nanoARPES apparatus describing the set up to manipulate micro samples together with the detector set-up (the scale are not respected). (b) nanoARPES data at the labelled "A" position indicated in the image of panel (c). NanoARPES mapping is presented on a linear scale as a false-colour image in panel (c). This real-space image represents the intensity variation of the graphene states with a selected $k_{//}$ and binding energy values (states confined in the white box of panel (b)), close to K symmetry point of the graphene Brillouin zone.

Figure 2 shows the same type of nano-core level results monitoring this time the intensity of carbon 1s core level of an exfoliated graphene sample deposited on SiO₂ substrate. The real-space image displaying the intensity of the C1s core level is shown in Fig. 2d. The two-dimensional distribution of the graphene C 1s core level (Fig. 2a) allows the localization and determination with high precision of the extension of one-atom thick layer, bilayer and multilayer graphene areas after the exfoliation and transfer of the graphene to the isolated SiO₂ substrate. The three-dimensional representation of the C 1s core level intensity in panel (d) displays clearly the extension and different thicknesses of the exfoliated graphene, showing the shape of the sample fully concordant with its optical micrograph depicted in panel (b).

Even if element specific images like the ones presented in Fig. 1 and Fig. 2 are quite advantageous providing useful chemical and compositional information of the rather small samples, the information of the valence band electronic states are uncovered by this type of data. On the other hand, as soon as the photon energy is lowered allowing working in the energy range where the cross section of the valence band states is high (i.e., close to the Fermi level), the instrumental requirements become much more challenging. Figure 3 shows an example where one exfoliated graphene sample transferred to a SiO₂ substrate has been investigated using the nano-angle resolved photoelectron spectroscopy (nanoARPES) facilities of the ANTARES microscope. The study is very similar to the one recently carried out on one-atom thick graphene films grown on copper foils by chemical vapour deposition [3,4], where our interest has been centred on the characterization of the robustness of the Dirac relativistic-like electronic spectrum as a function of the size, shape and orientation of the single-crystal pristine grains (of $\approx 2\text{-}4\ \mu\text{m}$) in the graphene films investigated.

Also, graphene multilayer samples grown by sublimation on silicon- and carbon-terminated SiC substrates (5) have been investigated in ANTARES in order to unravel the problem associated to the eventual different stacking order of individual carbon layers. Particularly, epitaxial graphene grown on C-face SiC has for quite some time been claimed to be fundamentally different compared to graphene grown on Si-face SiC. A rotational disorder between adjacent layers has been reported and suggested to explain why classical ARPES results from multilayer C-face graphene exhibited a single π -band cone, the characteristic of monolayer graphene. Here also, by nanoARPES mapping of individual μm -sized grains we could clearly unravel the conical band dispersions close to the Dirac point of single and multilayer graphene as well as the verification of the characteristic Bernal (AB) stacking within grains [6].

Similarly, nano-ARPES mapping and E vs k_{\parallel} data close to the Fermi level on exfoliated graphene transferred to an isolated SiO₂ substrate is shown on Figure 3. Bearing in mind that the description of collective electronic excitations are essential for many open issues in graphene physics, the ability to perform nanoARPES experiments with high energy, momentum and lateral resolution on micro- and nano-sized samples allows us to determine the lateral dependence of relevant features like gap-size, doping, effective mass, Fermi velocity and phonon coupling among other relevant properties. These fine electronic structure description are essential to resolve important fundamental and applied problems related to layer, bilayer and multilayer as well as boundary grain issues of low-dimensional nano- micro-sized samples.

3 CONCLUSIONS AND PERSPECTIVES

In summary, we have presented some relevant examples describing the current performance of the new ANTARES microscope. Indicating that it offers a spectroscopic nano-probe to study complex materials able to imaging selected electronic states with precise binding energy and momentum in the reciprocal space. Micro- and nano-spot punctual and mapping experiments can be easily combined in order to obtain in situ an averaged and nano-lateral discriminated information of the samples investigated¹.

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