EELS spectroscopy in a TEM : new possibilities, new measurements, new applications

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Summary- This abstract reports recent trends in the development and use of Electron Energy Loss Spectroscopy (EELS) in a TEM environment. It points out how new fields of investigations are being opened as a consequence of advances in instrumentation, methodology and associated theory.

1. Introduction

Measuring the energy lost by the primary electron beam in an electron microscope, when travelling through the specimen, has been recognized as a powerful source of information since its early days. Electron Energy-Loss Spectroscopy (EELS) has now reached a mature role and it constitutes a major component of any new electron microscope, in particular for materials science studies. When dealing with characteristic core-loss signals, it is commonly used for elemental mapping, in which case atomic resolution and single atom sensitivity have been demonstrated [1, 2], and it has found wide areas of applications in many scientific domains. In the low-energy loss domain, it detects individual (interband transitions) or collective (plasmons) responses of the electron gas of the material and it provides novel routes, yet often unexplored, to map electronic or optical properties with an unprecedented resolution. In all cases, the optimized extraction of an useful information relies on the parallel development of theoretical tools for simulating the experimentally recorded data, in particular on an advanced understanding of the physics of excited states which is involved in typical spectroscopies under the primary beam of particles.

2. New possibilities

Progress in instrumentation, data processing and simulation have been performed in parallel to fully offer and exploit new possibilities. Among the wide diversity of recent developments, major increments in spatial and energy resolution have been obtained by the introduction in (S)TEM columns, of new electron optics devices such as C_s correctors or monochromators, which make available a simultaneous intrinsic performance of respectively 0.1 nm in microscopy and 0.1 eV in spectroscopy. The present overview focuses onto new aspects of spectrum acquisition (dual detection, multi-dimensional spectrum-imaging modes) and processing (deconvolution) introduced on our own equipment.

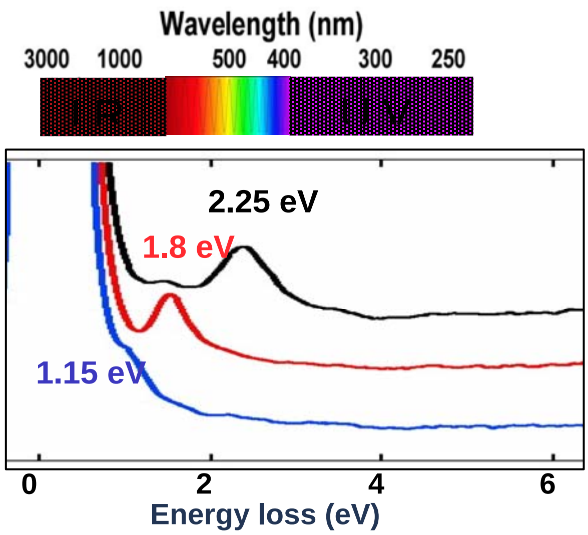

Figure 1 : Examples of spectra recorded for different probe positions on the surface of a single Ag triangular thin prism (on apex in blue, on edges in red, on centre in black) deposited on a mica substrate. After deconvolution and subtraction of a deconvoluted zero-loss peak, after realignment of multiple spectra acquired with very short times (typically 50 spectra with <5ms per spectrum), they clearly exhibit signals with satisfactory signal-to-noise ratio in a spectral domain encompassing the visible optical range and extending down to about 1 eV, see [3].

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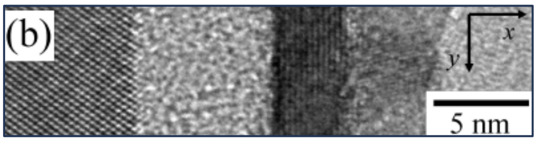
3. New measurements

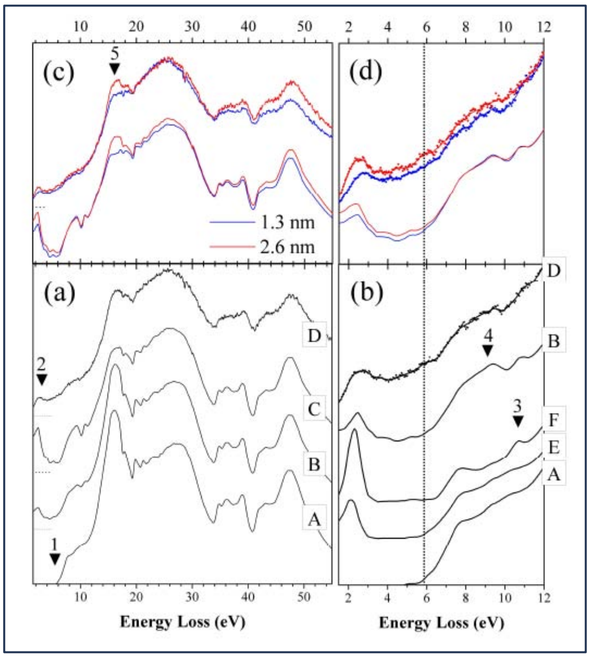
With these advanced tools in hand, a large varsity of new problems can be investigated and new measurements be realized. The spectrum-imaging approach [4] allows to raster the probe over a given specimen area and to collect spectra for every successively addressed position. For instance, in the case of core-loss signals, refined ELNES measurements, close and at the apex of interfaces between different materials, have to be compared with simulated spectra, including as intermediate steps *ab initio* modelling of the local atomic structures and calculations of the electron density of states (DOS).

In the low energy-loss part of the spectrum, new routes are now opened to disentangle the local electronic response of the material in terms of band structure (band gap, interband transitions, excitons) from the long-range response of the neighbouring architecture, encompassing the electromagnetic fields generated by surface and interface plasmons (see fig. 2). A satisfactory understanding of the recorded data then requires extensive modelling, relying on a well suited adaptation of classical models and formulae.

Figure 2 : EELS spectra (top curves in figs (c) and (d) left, and D in (a) and (b)) acquired for different positions of the incident electron beam travelling through the HfO_2 layer incorporated within the cross-sectioned multicomponent stack shown below. They must be compared with simulated spectra corresponding to the relevant experimental conditions, derived in a dielectric continuum description. In these conditions only, one can disentangle the local response from long-range effects (coupled interface plasmons, in particular), which are generated in such a complex case, see [5] for full discussion.

Si SiO$_2$ HfO$_2$ TiN Si





4. New applications

Using the new ultimate performance, bond mapping deduced from the spatial variations of the fine EELS structures on characteristic core-edges (ELNES), constitutes a key to relate the transport properties to the interfacial electronic structure and atomic scale chemistry in microelectronics devices or in spin tunnel junctions (see abstract by K. March et al., this conference). When studying the mechanical behaviour of crystalline materials, a similar approach can be followed to evaluate bond strength at clean interfaces (or grain boundaries) or in the presence of segregated impurities. In both cases, only the use of angström size probes delivered by aberration corrected illumination optics will reveal its full power (see abstract by R.F. Klie at this conference)..

As for low-loss signals, their impact to map electronic or optical properties is evident. When applied to isolated metallic nanoparticles, we have recently demonstrated that the measured EELS signal is closely related to the electromagnetic density of states (EMDOS) determined by the nanostructure shape and dimensions, thus opening new access to the comprehension of plasmon physics and to the mastering of plasmon engineering, both of direct relevance for future progress in nanophotonics (see [3] and abstract by J. Nelayah, this conference).

[1] K. Suenaga et al., *Science* **290** (2000) 2280

[2]M. Varela et al., *Phys. Rev. Lett*. **92** (2004) 095502

[3] J. Nelayah et al., *Nature Physics* **3** (2007) on line 1st April 2007

[4] C. Jeanguillaume and C. Colliex, *Ultramicroscopy* **28** (1989) 252

[5] M. Couillard et al., submitted (2007)