High-Resolution Scanning Transmission Electron Microscopy (HRSTEM) Techniques: High-Resolution Imaging and Spectroscopy Side by Side

Daniel G. Stroppa,[a, b] Luiz F. Zagonel,[a] Luciano A. Montoro,[a] Edson R. Leite,[c] and Antonio J. Ramirez*[a, b]

1. Introduction

Nanoscience is becoming increasingly relevant for the development of novel technologies as the assessment of the nanoscale configuration and properties of systems becomes more accessible. Developments in both theory and experiments provide improved understanding of the underlying phenomena and their role on the properties of nanomaterials.[1] A significant part of this advance and the further use of distinguished properties obtained at the nanoscale are due to progress in characterization techniques.

Quantitative analysis of nanostructured systems requires remarkable efforts due to the inherent restrictions of high-resolution characterization techniques.[2] In this scenario, the combination of theoretical and experimental tools is effective for a comprehensive description of the features of nanomaterials.[3]

Transmission electron microscopy (TEM) techniques can be highlighted among the characterization techniques due to their versatility for quantitative data retrieval from nanostructured samples. More specifically, high-resolution scanning transmission electron microscopy (HRSTEM) techniques have shown unprecedented characterization possibilities due to the combination of high-resolution imaging, diffraction, and spectroscopy in a single experiment.[4] This characteristic allows the mapping of different electron-interaction events on the sample, which implies the possibility of probing features with accurate localization. In this sense, HRSTEM techniques point towards the quantitative characterization of the properties of materials with atomic resolution.[5]

Scanning transmission electron microscopy (STEM) is based on electron scattering analysis as a focused beam scans over a thin sample. Although STEM is approximately as old as TEM and SEM techniques,[6] some recent instrumental developments have greatly enhanced its performance and supported a reasonable number of breakthrough results. Among these advances are the spherical aberration (Cs) and chromatic aberration (Cc) corrections,[7–9] monochromator implementation,[9] and improved synchronous systems for data acquisition.[10]

In addition to instrumental enhancements, several theoretical tools were developed and implemented to improve the characterization possibilities and to provide more reliable quantitative analysis, among them are more accurate image simulation and spectrum analysis procedures,[11, 12] the implementation of deconvolution models,[13, 14] and multivariate statistical analysis (MSA)[15] for improved information extraction from raw data.

The aforementioned improvements to STEM techniques are mostly related to two fundamental criteria that define characterization efficiency: spatial and energy resolution. Spatial resolution is related to beam size and delocalization of interaction events, which dictate how fine the details of the sample assessed could be. State-of-the-art STEM microscopes are currently near 50 pm spatial resolution.[9] Energy resolution for...
spectroscopic techniques is related to the possibility of distinguishing different inelastic interactions between the electron beam and the sample by their inherent energy losses. The most advanced STEM microscopes have energy resolution better than 0.1 eV. The role of spatial and energy resolution on STEM can be better understood by analyzing how information is extracted by each related technique and how the experimental configuration affects data acquisition.

The use of STEMs as versatile electron-scattering experimental setups with high-resolution imaging capability enhances the quantitative analysis possibilities of nanostructured systems. The following sections present an overview of state-of-the-art HRSTEM techniques and their application to the quantitative analysis of nanocrystalline materials.

2. Imaging Modes and Image Simulation

Figure 1 presents a schematic illustration of a STEM microscope, including the most relevant detectors for imaging and spectroscopic techniques. STEM techniques can be generally described as sequential scans of a focused electron beam over a selected region of the sample and the simultaneous use of annular detectors, which select electrons with different scattering angles with respect to the original beam propagation. Pixel-by-pixel data acquisition provided by these detectors is used to reconstruct STEM images.

The major advantage of the experimental setup of STEM techniques is that it allows images to be acquired by using electrons that have undergone different interactions, such as diffraction and Rutherford scattering, and provide information related to the physical phenomena that occur during electron-sample interactions.

The high-angle annular dark field (HAADF) imaging mode in STEM is based on the detection of incoherent quasi-elastic electron scattering by the nuclei of atoms, which is usually the predominant contribution for scattering angles higher than 80 mrad. A first approximation of these scattering events by the Rutherford model indicates that their cross-section is dependent on the squared atomic weight (Z^2). However, the occurrence of a channeling effect as electrons travel through the sample requires a much more complex analysis for reliable quantitative analysis of the HAADF signal.

The combination of optimized HRSTEM instrumental configuration and enhanced models for the evaluation of incoherent electron scattering allow novel approaches for the determination of chemical species on single-layered materials and thin films, the detection of heavy atom impurities on nanowires, and the assessment of the 3D morphology of nanocrystals.

An application of HAADF imaging for the characterization of CeO₂ nanocrystals is presented on Figure 2. The depicted analysis approach uses the intensity dependence of the HAADF signal on the weight of atomic columns to retrieve nanocrystals dimensions along the zone axis. The major advantage from this methodology is the possibility of characterizing the 3D morphology from a single HAADF-HRSTEM image.

State-of-the-art HAADF-HRSTEM allows a 3D reconstruction of the nanocrystals from either a set of images or from single images in particular cases where the crystallographic symmetry of the nanostructures can be effectively used in combination with the HAADF intensities profile. In this scenario, enhanced analysis and simulation procedures applied to HAADF imaging...
and improvements to the HAADF tomography spatial resolution are likely to merge into an effective tool for the characterization of nanocrystals at the atomic scale. One of the main advantages of the HAADF imaging mode in tomography is diffraction contrast suppression at oriented zone axes.

The combination of HAADF characterization and electron-scattering analysis from other angular ranges has been increasingly applied to the extraction of additional features from crystalline samples. One example is the designed use of specific angle ranges for selecting high-order Laue zones (HOLZ), which can provide information about the ordering of atomic species along the electron beam direction. In addition, the medium-angle annular dark field (MAADF) has been applied to 3D defect analysis in STEM tomography.

Information extraction from low-angle scattering analysis also presents novel possibilities, especially for lighter atomic species. The combination of HAADF and annular bright field (ABF) allowed the direct imaging of atomic columns of oxygen and hydrogen on Al$_2$O$_3$ and VH$_2$, respectively, and provided unambiguous identification of chemical species on single-layered BN.

Image simulation procedures are an essential tool for the evaluation of the images obtained and for the extraction of quantitative information from them. State-of-the-art multislice image simulation procedures provide the identification of a single high-Z dopant atom, the evaluation of the relative chemical composition, and the location of dopant atoms inside an oriented atomic column.

3. High Spatial Resolution Spectroscopy

HRSTEM spectroscopy techniques focus on the direct acquisition of quantitative information from a number of signals generated during scanning of the incident electron beam over the sample. After proper collection, these signals can be used for the construction of maps of properties that are presented together with HRSTEM imaging results. The simultaneous acquisition of high-resolution images and spectroscopic signals allows the attainment of quantitative data with accurate localization, which is the main advantage of HRSTEM and represents a unique feature among characterization techniques.

Of the signals generated during the interaction of an electron beam with matter, characteristic X-rays and low-angle scattered electrons are most commonly used in spectroscopy analysis by HRSTEM. Characteristic X-ray detection is performed by an additional detector placed as close as possible to the sample to maximize the collection angle, as illustrated in Figure 1. The acquisition of low-angle scattered electrons and the practice of electron energy-loss spectroscopy (EELS) require a spectrometer with dispersive optics to sort the collected electrons according to their energy loss due to inelastic interactions with the sample.

3.1. XEDS

Although the X-ray energy-dispersive spectroscopy (XEDS) technique for STEM already presented the possibility of atomic resolution spectroscopy by using an optimized experimental setup, the combined use of high brightness electron guns, Cs-corrected STEM microscopes, and enhanced X-ray detectors have recently increased the possibilities of atomic resolution characterization. In addition to the above-mentioned collection angle optimization, these enhancements are mainly related to two other features that determine the efficiency of XEDS analysis.

The first one is the compromise between probe size and the effective beam current, which defines the spectroscopy spatial resolution and X-ray signal output, respectively. The use of Cs correction hardware for improvement of the probe formation allowed more efficient beam focusing and the use of larger apertures due to reduced aberration influence, thus resulting in a larger effective electron density.

The second one is the relationship between the signal-to-noise ratio (SNR) and the dwell time for each collected spectrum, which plays a major role on the quantification accuracy/precision and on the required data acquisition time. The use of MSA on XEDS datasets containing numerous spectra with poor SNR allowed quantitative analysis with enhanced accuracy and precision. Successful analysis from low SNR XEDS spectra points toward reducing the dwell time, thus providing faster data acquisition and reduced sample degradation.

Figure 3 presents successful atomic resolution chemical mapping of a SrTiO$_3$ sample by XEDS-HRSTEM spectroscopy. The combined use of a high brightness field emission gun (FEG) and an optimized XEDS detection system are key aspects of such measurements.

In addition to the aforementioned advances that supported atomic resolution spectroscopy, XEDS-related techniques were
substantially enhanced by an improved model, which allowed accurate absolute quantification of the spectra by the use of more general standard samples. Finally, current characterization possibilities indicate that high-resolution XEDS analysis may be applicable to almost all elements of the periodic table.

3.2. EELS

The analysis of low-angle scattered electrons in HRSTEM experiments provides a variety of information about localized interaction phenomena associated with inelastic electron scattering events. Although analogous spectroscopy techniques based on synchrotron radiation, such as X-ray absorption fine structure (XAFS), are able to extract similar information, HRSTEM-EELS presents the possibility of probing such features with enhanced spatial resolution.

The identification and quantification of inelastic scattering events require thin samples to minimize effects from multiple scattering. The optimum sample thickness is determined by the interaction cross-section for the inelastic scattering event that is going to be analyzed and is usually in the range of a few nanometers. In addition to adequate sample conditions, the use of adequate instrumental configurations is mandatory to attain reliable HRSTEM-EELS results. Spatial resolution is not only determined by the probe size, but also by the stability of the electron probe and its propagation through the sample and by the localization of inelastic scattering and multiple scattering effects. In addition, similar to XEDS, HRSTEM-EELS analysis requires beam current maximization to improve the SNR.

Regarding the EELS spectra, the low-angle scattered electrons can be classified in three general groups according to their energy loss: the zero-loss peak (ZLP) comprises the electrons with no or negligible energy losses, the low-loss (LLR) region includes electrons with energy losses up to 50 eV, and the core-loss (CLR) region contains electrons with energy losses higher than 50 eV. As the inelastic scattering signal intensity decreases as a function of energy loss, the different above-cited groups have distinct magnitudes. For thin samples, reduction factors of $10^{-1}$ and $10^{-3}$ are expected for the discrimination of the valence configuration, assessment of the optical properties and band gap, and measurement of the interface properties. A combination of ZLP deconvolution and monochromator hardware have been successfully used to map surface plasmons in metallic nanoparticles. In addition, LLR analysis is applicable to cryo-microscopy for water measurements on biological materials and gas-phase analysis for the quantitative analysis of gas mixtures.

The CLR comprises the transmitted beam component that has undergone interactions with core electrons. Because these interactions are much more localized than LLR (typically a few Å), analysis of atomic resolution chemical maps is feasible by CLR scattering signal analysis. However, an optimized experimental setup is required to obtain atomic resolution imaging and spectroscopy simultaneously.

Spectral imaging by using selected energy intervals has been successfully applied to identify the composition of atomic columns on interfaces and crystalline defects with atomic resolution. This methodology has also been used to deal with challenging problems in materials chemistry, such as mapping of the chemical composition of individual Ce–Zr pyrochlore catalytic nanocrystals with atomic resolution. The combined results from HAADF–HRSTEM imaging and HREELS spectroscopy for the chemical mapping of individual Ce$_2$Zr$_2$O$_8$ nanocrystals is depicted in Figure 4.

Although atomic resolution chemical mapping is still a developing field, few CLR analysis approaches have presented great perspectives on the characterization of materials. Some examples are bond-type mapping on a BN complex and valence mapping on Co-doped ZnO nanostructures.
4. Novel Approaches on HRSTEM

In addition to advances to more usual imaging and spectroscopy techniques, some methodologies associated with HRSTEM have evolved towards the characterization of nanomaterials with atomic resolution.

4.1. Cathodoluminescence

In recent years, the growing importance of nanostructured semiconductors, such as III-V nanowires, is renewing interest in cathodoluminescence (CL). Instrumentation advances increased the achievable spatial and spectral resolution to about 1 nm and 5 meV, respectively. In addition, improvements can be expected in the near future due to advantages of low-voltage STEM featuring spherical and chromatic aberration corrections. Moreover, the development of efficient CL detectors has pushed the current measurement limits to a new level.

The effective spatial and spectral resolutions of CL measurements associated with STEM are greatly dependent on and limited by sample features. This is due to the secondary effect of the recombination of electron–hole pairs excited by the electron beam, which results in CL signal delocalization. Additionally, CL peaks can also be arbitrarily broad, depending on the sample band structures, as seen in standard photoluminescence experiments.

Figure 5 shows a characterization of GaN quantum disks (QDisk) and AlN barriers as stacks grown in a nanowire by the combined use of HAADF-STEM imaging and CL spectroscopy. Similar to EELS, the CL spectrum is obtained by scanning the electron probe and simultaneously acquiring the HAADF signal and CL spectrum for each pixel. Single QDisks can be readily distinguished on the HAADF images and, by selecting different wavelengths in the spectrum image, light emission from single QDisks can be resolved. A correlation between the size and emission energy of the QDisks can be extracted for each QDisk.

4.2. Scanning Confocal Electron Microscopy

Reconstruction of the 3D morphology of the nanostructures is a current challenge for materials characterization, especially when high-resolution information on segregation of chemical species is required. Apart from HRSTEM tomography and reconstruction of the HAADF-HRSTEM images based on the recorded intensities, scanning confocal electron microscopy (SCEM) on STEM mode is a suitable technique for extracting structural information along the imaging zone axis.

The SCEM technique is based on the analysis of electron microscopy images acquired under different defocus conditions, either by changing excitation of the condenser lens or by controlling the sample position. Theoretical studies supported by image simulation procedures and experiments using different imaging modes, on STEM regime indicate that the SCEM technique can provide spatial resolution up to 1 nm along the zone axis and can unveil depth localization of heavy atoms (Bi) on a lighter matrix (Si). State-of-the-art SCEM presents high-resolution depth profile analysis for nanocrystals by the use of STEM-optimized optical systems, including Cs correction. Further advances are expected by the use of novel Cc correction hardware and improved analysis methods.

4.3. Diffraction Mapping

In addition to imaging and spectroscopy approaches, the STEM experimental configuration can be applied to mapping of the crystalline structure with high spatial resolution by analyzing local diffraction patterns. Although it is analogous to the TEM selected-area diffraction technique, the STEM mode with a parallel electron beam provides the mapping possibility during the scanning procedure and a higher spatial resolution can be achieved. Similarly, convergent-beam electron diffraction (CBED) mapping can be performed on STEM by altering the optical system to attain a small and convergent probe. High-resolution applications of diffraction mapping techniques include local Ge concentration determination in Si/SiGe nanostructures, the evaluation of lattice distortions on InP nanowires containing an axial screw dislocation, and strain mapping in metal oxide semiconductor field-effect transistors (MOSFET) devices. In addition, improved grain orientation mapping on polycrystalline materials has been demonstrated by the use of precession-enhanced electron diffraction. Moreover, diffraction analysis on STEM mode currently provides new information on electron-scattering processes of crystalline materials.
5. Outlook

Recent advances in HRSTEM present a number of unique possibilities for the characterization of materials. This is easily seen as the combination of high-resolution imaging and spectroscopy becomes more usual for the extraction of chemical and structural information of a wide range of nanostructured systems.

In this scenario, support provided by HRSTEM tools is invaluable for solving questions in various fields within materials science, chemistry, and physics. At the same time, perspectives are drawn by current progress on related hardware and analysis techniques, which indicate that HRSTEM will consolidate its position as an essential tool for nanoscience and nanotechnology.

Acknowledgements

We acknowledge the financial support of the Brazilian research funding agencies FAPESP, CNPq and FineP; the German research funding agency DAAD. We would also like to thank the Ernst Ruska Centre staff at Forschungszentrum Jülich and the STEM group staff at Université Paris-Sud for fruitful discussions and scientific support.

Keywords: atomic resolution imaging • high-resolution scanning transmission electron microscopy • materials science • nanostructures

[11] The Dr. Probe software was developed by Dr. Juri Barthel, ER-C Forschungszentrum Jülich, ju.barthel@fz-juelich.de.
High-Resolution Scanning Transmission Electron Microscopy

MINIREVIEWS


Received: September 22, 2011
Published online on January 13, 2012