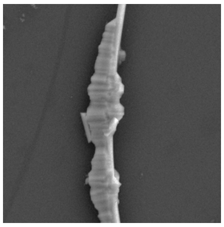
Correlative Spectroscopy

Multimodal spectroscopy techniques for nanostructured materials characterization



Application Note

Advanced Materials RA90

Raghda MAKAREM[1], João-Lucas RANGEL[2], Praveena MANIMUNDA[3], Emilio Nogales DIAZ[4], Francis NDI[3], Didier HOCRELLE[2], Jérémy BRITES[2]

[1]HORIBA FRANCE SAS, 455 Avenue Eugène Avinée, 59120 Loos, France
[2]HORIBA FRANCE SAS, 14 Boulevard Thomas Gobert - Passage Jobin Yvon, CS45002 - 91120 Palaiseau, France
[3]HORIBA Scientific, 20 Knightsbridge Rd, Piscataway, NJ 08854, United States
[4]Universidad Complutense de Madrid, Departamento de Física de Materiales, Plaza de Ciencias 1, Ciudad Universitaria, 28040 Madrid

Abstract: In this article, we present the combination of Raman spectroscopy, Photoluminescence and SEM-CL techniques, where the instruments weren't physically connected. Smart nanostructured materials require a comprehensive understanding of their morphology, elemental and chemical composition. nanoGPS Suite solution allows a colocalized combination of a variety of microscopy techniques, providing a full characterization of nanostructured materials and a precise superimposition of the results obtained.

Keywords: Raman, Photoluminescence, SEM, Cathodoluminescence, nanostructure, Ga_2O_3 nanowires.

Introduction

Smart nanostructured materials involve an extensive understanding of their morphology and chemical composition to develop novel designs. Optical and transport properties could be strongly dependent on the morphology of such nanomaterial. Additionally, one can broadly increase the capabilities of such nanostructure by mixing several chemical elements or compounds. Semiconducting oxides like nanowires, nanobelts or nanorods are part of the smart materials' family which shows a wide range of applications, such as lasers, sensors, photocatalysts, solar cells, optical and mechanical resonators, biomedical and healthcare devices. In the past years, scientific studies were mainly published on synthesis, characterization, and applications of semiconducting oxide nanowires. A paper from Alonso-Ortis, M., et al., 2017, highlighted that the high aspect ratio and the surface of nanowires and nanoparticles influences both the physical- and chemical properties and their growth mechanism. Varley, J. B., et al., 2012, described that considering the physical properties of theses nanomaterials, it is a challenge to get efficient doping of oxide nanowires with controllable conductivity.

Spectroscopy techniques such as Raman, Photoluminescence and SEM-CL, play a key role for a comprehensive characterization of such complex and novel nanomaterial. Thanks to the high specificity combined with a good spatial resolution, these techniques can bring crucial information for nanostructures' investigations. The combination of these spectroscopic techniques can bring a lot of information about the studied sample. While Raman spectroscopy provides molecular composition and phase information, SEM-CL provides optical properties and doping, and SEM gives insights about the structure, elemental composition, and morphology of oxides. Further, Photoluminescence spectroscopy can be used to identify the band gap, homogeneity, impurity levels and defects.

However, a critical point on this type of study is the ability to measure a specific area or artefact at the same location through all the techniques available. Being colocalized, allows a comprehensive characterization of the sample and a precise superimposition of the images. HORIBA Scientific developed a new relocalization solution, called nanoGPS navYX™. Based on the nanoGPS technology (Acher, O., *et al*., 2021).

nanoGPS navYX™ can precisely relocalizes the specific areas in the sample from one instrument to the another with a high degree of accuracy, rapidly and easily.

In this application note, we present the key role of nanoGPS navYX™ as a relocalization tool for colocalized characterization of nanostructured materials and the advantages of Raman, Photoluminescence and SEM-CL correlated measurements.

Instrument and methods

Sample Preparation

In this work, a skewer-like heterostructure formed of a main longitudinal Ga_2O_3 nanowire decorated with SnO_2 nanoparticles, was analysed in depth. This architecture consists of a Ga-containing trunk with thicknesses between 50–150 nm for different skewers, surrounded by Sn-containing rhombohedral-shaped particles. The source materials, pure Ga and tin oxide powders, were placed on the top of a gallium oxide pellet, which acted as the substrate, into an open tubular furnace. Skewer-like structures were extensively produced after 15 h of thermal treatment under an argon gas flux of 0.8 l/min. All samples were supplied for our experiments by Dr. Emilio Nogales Díaz from Universidad Complutense de Madrid.

nanoGPS navYX™ relocalization technology

nanoGPS navYX™ is a relocalization method based on machine readable small-patterned tags fixed on the samples or their substrates. The patterns include an imaged-based position sensing technology, for which an image of a small part of the tag can automatically be interpreted into absolute coordinates and angular orientation. Taking a single snapshot on the tag with an imaging instrument provides the correspondence between sample and moving stage coordinates. This correspondence is a crucial information to guarantee the colocalization of the images by using different objectives or different instruments, bringing a huge benefit for the user, a full characterization of their sample at the same location (Figure 1).

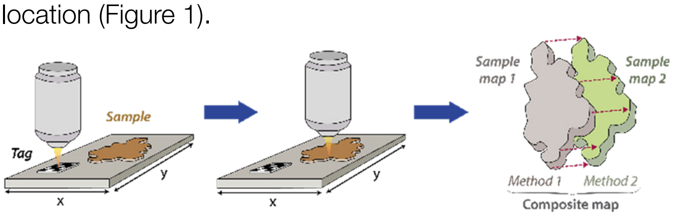


Figure 1: HORIBA nanoGPS navYX™ relocalization technology. 1st step: Start the session on the tag; 2nd step: generate the POIs and 3rd step: Superimpose all generated images.

Raman Spectroscopy

Raman spectroscopy is a powerful and non-destructive characterization tool to study nanomaterials. It has the capability of characterizing the structural properties of nanomaterials, as well as detecting the layer thickness, band structures, strain effects, doping type, concentration, electron–phonon coupling, and interlayer coupling.

HORIBA LabRAM Soleil™ is a Raman multimode microscope offering the highest throughput with no compromise on resolution, thanks to the high efficiency dielectric mirrors, coupled with high quality gratings. The instrument comes with specially designed edge filters and a motorized kinematic filter holder to guarantee 30 cm^{-1} cut-off, becoming the perfect instrument for molecular analysis of complex samples. Mapping in 100 times faster than a conventional Raman, thanks to the innovative SmartSampling™ technology. The patented QScan™ feature offers lightsheet confocal Raman imaging (Figure 2).

HORIBA LabSpec6, is the complete software solution starting from the instrument control/data acquisition, going through the data pre-processing and data analysis, thanks to the software module MVA+ and xSTaiN™ developed by HORIBA and ending on a powerful spectra identification, thanks to the comprehensive database, called KnowItAll™, powered by Wiley.

Figure 2: LabRAM Soleil Raman microscope

Photoluminescence Spectroscopy

Photoluminescence (PL) measurements on oxide nanostructures were performed using HORIBA Standard Microscope Spectroscopy (SMS) systems. SMS microscope platform brings unique flexibility and multimodality. It can easily be configured to measure Photoluminescence, Time-resolved Photoluminescence, Raman, Absorbance and Reflectance. In this study a 375 nm laser, with a maximum power of 40 mW was used as a source of excitation (Figure 3). HORIBA LabSpec6 and nanoGPS navYX™ was used for data acquisition and sample relocalization.

Figure 3: Multi-modal HORIBA SMS system, equipped with motorized X,Y stage for PL mapping, and iHR320.

SEM-CL Spectroscopy

Scanning Electron Microscopy (SEM) is an imaging system that allows morphological and structural analysis of solid samples at micron or even nanometric scale. It is mainly based on the detection of secondary electrons emerging from the surface under the impact of a very fine primary electron beam which scans the observed surface and makes it possible to obtain images with a resolving power often less than 5 nm and great depth of field. The FEG-SEM is equipped with HORIBA H-CLUE (Figure 4) hyperspectral Cathodoluminescence add-on detector which provides optical properties such like bandgap and doping at the nanoscale. Using the scanning electron beam as an excitation source, the attainable resolution is on the order of a few tens of nanometers, when a multimodal confocal microscope like LabRAM Soleil can only provide those properties at the micron scale.

In addition, SEM-CL analysis offers the advantage of a high sensitivity to variations in chemical composition on a lower detection limit than techniques based on X-ray fluorescence analysis. Therefore, it is advantageous over conventional SEM-EDS and SEM-WDS analyses for detecting trace elements.

Figure 4: HORIBA H-CLUE Cathodoluminescence system

Results

In this section, the complementary information of the SEM images, Cathodoluminescence, Photoluminescence and Raman analysis can be investigated. Thanks to the nanoGPS navYX™, innovative relocalization technique, the results of the Ga_2O_3/SnO_2 nanowires were taken at the same position by changing the sample through different instruments and using the immediate relocalization.

Figure 5 shows a Secondary Electron SEM image of the growth of a Ga_2O_3/SnO_2 nanowire at 10KV on a magnification of 2000x.

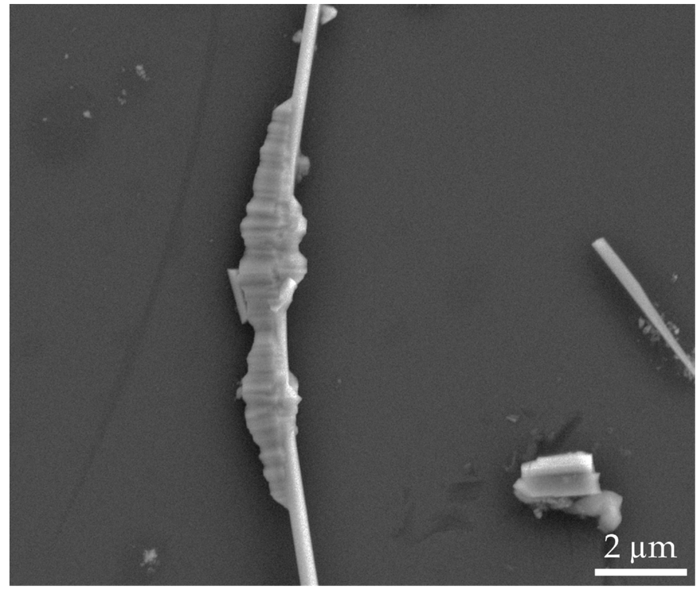


Figure 5: SEM image of a Ga_2O_3/SnO_2 nanowire

Figure 6 shows a Panchromatic CL (PCL) image. It is considered as the first step in CL study because it helps to quickly know with high definition where the sample is luminescent, but with no information of the precise wavelength. In this case, no information about the material composition.

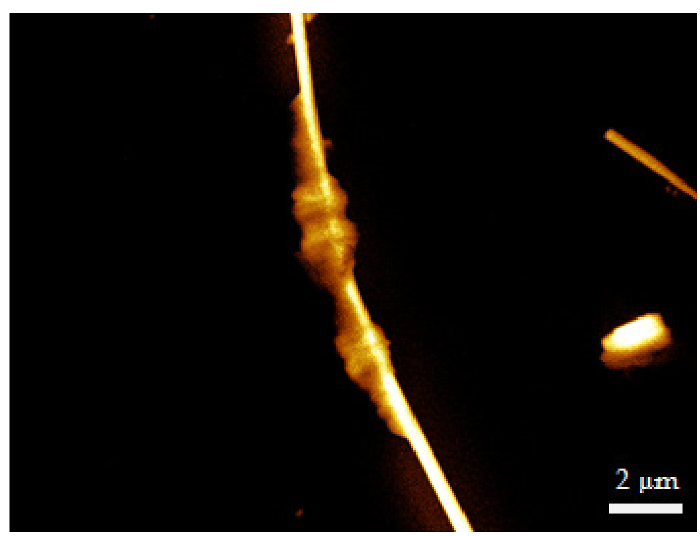


Figure 6: PCL image of a Ga_2O_3/SnO_2 nanowire

To complete the imaging study, a spectral analysis has been carried out on a wide spectral range, in order to identify the precise emitted wavelength. For this purpose, Monochromatic (MCL) and Hyperspectral CL images have been acquired to differentiate the single elements. As we can see on Figures 7. a, b, c the main axis of the structure is made of Ga_2O_3 nanowire, surrounded by SnO_2 nanostructures. The CL emission from Ga_2O_3 is composed of two components

(~ 370 nm and 410 nm). The SnO_2 patches showed emission at 640 nm. The obtained spectra corroborate the results published by Alonso-Ortis, M. et al., 2017, confirm that the Ga_2O_3 is located in the wire (Figure 7. a - blue) and the SnO_2 is forming rhombohedral particles around the wire (Figure 7. b – red).

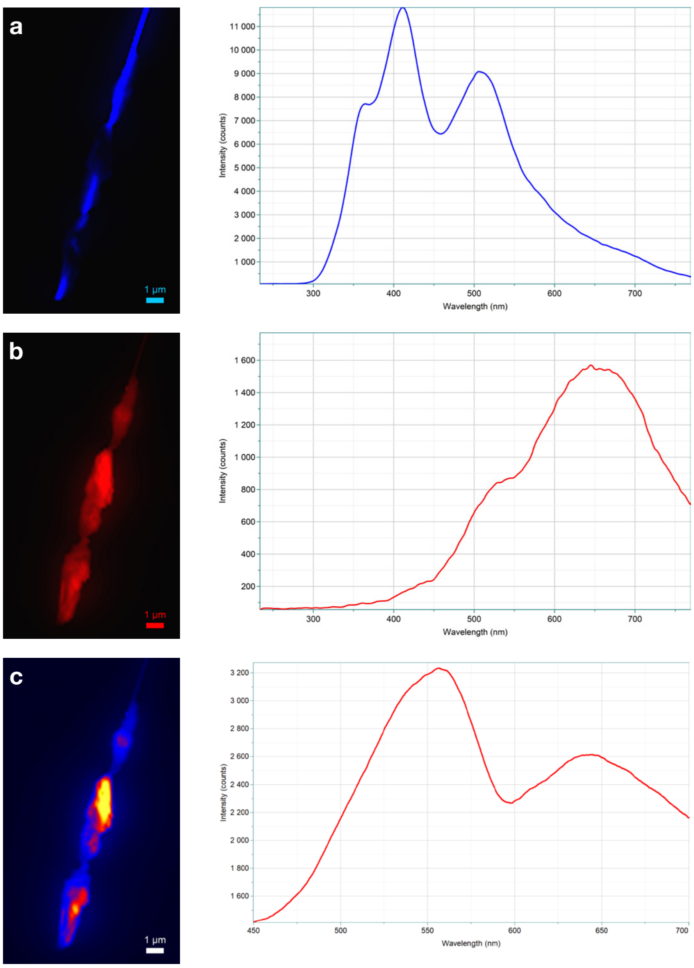


Figure 7: Monochromatic CL (MCL) images and its corresponding spectrum. (a) Ga_2O_3 (b) SnO_2 (c) Photoluminescence map (640 nm) and spectra from Ga_2O_3 nanowire with SnO_2 clusters.

After CL characterization, the coordinates were registered from each sample Point of Interest (POI), thanks to the nanoGPS navYX™ solution. Then, the sample was transferred to the HORIBA SMS laboratory in USA for PL measurements. Using nanoGPS navYX™, and the prerecorded POIs, the Ga_2O_3/SnO_2 was precisely relocalized under SMS microscope. The PL map generated from the Ga_2O_3/SnO_2 nanostructure is shown in Figure 7c. In the PL map, the PL spectrum showed a convoluted Ga_2O_3 and SnO_2 peaks. The PL map a higher 640 nm band intensity is seen on the regions where SnO_2 patches are deposited. It is believed that the native defects on SnO_2 is responsible for the enhanced emission (Varley, J. B., et al., 2012).

To understand the chemical composition variation across the nanostructures, and to supplement the CL and PL measurements, a detailed Raman mapping was carried out. For that, the sample was shipped back to HORIBA France Raman laboratory. Thanks to nanoGPS navYX™ relocalization technology, a Raman study was successfully carried out on the sample at the exact same position, where CL and PL analysis were performed.

Finding such nanostructure on a multimodal optical microscope is a challenge indeed, especially at low magnifications. Compared to shuttle solutions or fiducial marks, nanoGPS navYX™ technology is very convenient to use, and saves a lot of time for scientists. The calibration procedure is very quick, and it records both the XY positions and the angle. The points of interest can be found in seconds even in remote laboratories, on multiple instruments.

Figures 8. a and 8. b below can demonstrate the importance of the relocalization solution. The relocalization mechanism has been used and in a single mouse click arrived at the same point of interest observed on the previous instrument.

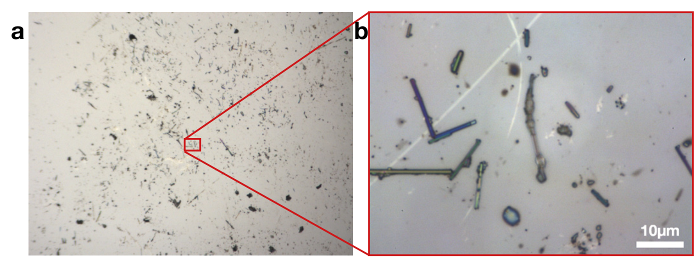


Figure 8: Reflected white light image taken on the HORIBA LabRAM Soleil™ at (a) low magnification and (b) high magnification

In addition, hyperspectral analysis has been done with Raman Spectroscopy as reported in Figure 9.

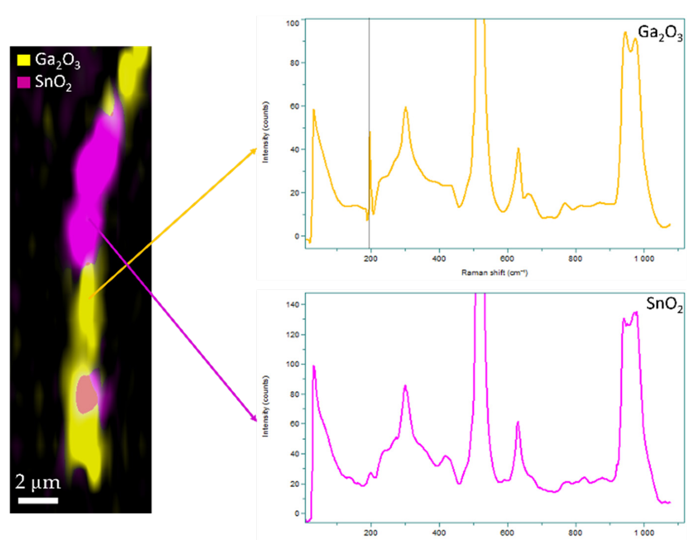


Figure 9: Raman Map of the Ga_2O_3/SnO_2 nanowire and its corresponding spectrum

The correlative microscopy results described in this application note can be displayed by superimposing all data measurements thanks to graphYX software powered by Mountains Digital Surf. graphYX helps the user to enhance and overlay multivariate analysis images from several modalities (Raman, CL, SEM, PL), adjust their position and orientation, highlight sample features, smooth artifacts, play with palettes and transparencies, add 3D views, and much more.

Figure 10 shows an superimposition of the video white light image and CL Map.

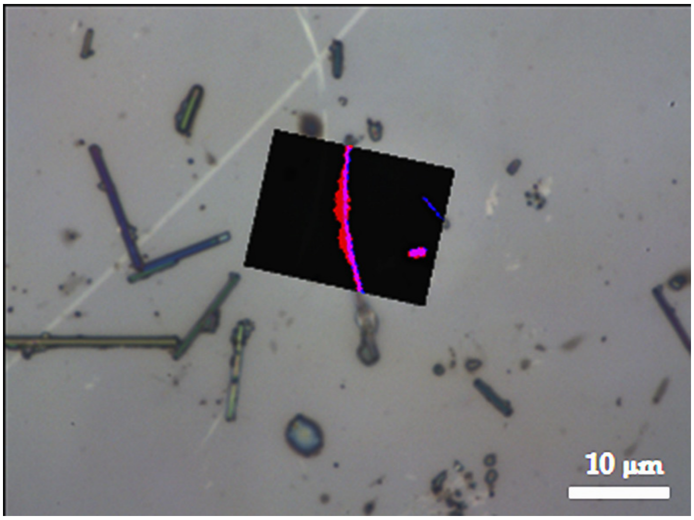


Figure 10: Superimpose of video white light image and CL Map

Conclusion

A new approach to carry out correlative observations has been presented. The so-called nanoGPS navYX™ tags can be imaged with different microscopes, over a wide range of magnification.

A relocalization accuracy of a few µm up to 10 µm is routinely observed, and the orientation error is negligible to the human eye. This is sufficient to remove any ambiguity in colocalized observations.

nanoGPS navYX™ is expected to save time and to open new opportunities to researchers. Spotting the same areas of interest without waste of time means more time for the research.

According to nanoGPS navYX™ approach, SEM-CL and Raman microscopy had been deployed showing complementary information of the same sample that leads to a complete knowledge of the specimen in question.

References

Alonso-Orts, M., *et al*., Nano Lett., 2017, 17, 515–522.

Olivier, A., *et al*., Meas. Sci. Technol., 2021, 32, 045402.

Varley, J. B., *et al*., Phys. Rev. B: Condens. Matter Mater. Phys., 2012, 85, 081109.

Manuel Alonso-Orts, Ana M. Sánchez, Steven A. Hindmarsh, Iñaki López, Emilio Nogales, Javier Piqueras, and Bianchi Méndez, Nano Lett. 2017, 17, 515–522

info.sci@horiba.com

www.horiba.com/scientific

USA: +1 732 494 8660
UK: +44 (0)1604 542 500
China: +86 (0)21 6289 6060
Taiwan: +886 3 5600606
France: +33 (0)1 69 74 72 00
Italy: +39 06 51 59 22 1
India: +91 (80) 4127 3637
Brazil: +55 (0)11 2923 5400
Germany: +49 (0) 6251 8475 0
Japan: +81(75)313-8121
Singapore: +65 (6) 745-8300
Other: +33 (0)1 69 74 72 00