MATERIALS SCIENCE AND MATERIALS ENGINEERING – CONTRIBUTORS' INSTRUCTIONS

CHECKING YOUR PROOFS

The text content for your contribution is in final form when you receive your proof. Please read your proof for accuracy and clarity, as well as for typographical errors. DO NOT REWRITE.

Please ensure you answer all Author Queries. While it is appreciated that some proofs may require updating/revising, please try to keep any alterations to a minimum.

Titles and headings should be checked carefully for spelling and capitalization. Please be sure that the correct typeface and size have been used to indicate the proper level of heading. Review numbered items for proper order – e.g., tables, figures, footnotes, and lists. Proofread the captions and credit lines of illustrations and tables. Ensure that any material requiring permissions has the required credit line, and that the corresponding documentation has been sent to Elsevier.

Note that these proofs may not resemble the image quality of the final version of the work, and are for content checking only. Artwork will have been redrawn or relabelled as necessary, and is represented at the final size.

PLEASE KEEP A COPY OF ANY CORRECTIONS YOU MAKE.

RETURNING YOUR CORRECTIONS

Proof corrections should be returned in one communication to MRW-MATSproofs@elsevier.com by 25 August 2015.

Corrections should preferably be annotated on the pdf of your proof, and sent by e-mail to: MRW-MATSproofs@elsevier.com. The e-mail should state the Module title and article code number in the subject line, e.g. Materials Science and Materials Engineering 02028

Note that a delay in the return of proofs could mean a delay in publication. Should we not receive your corrected proofs within 7 days, Elsevier may have to proceed without your corrections.

CHECKLIST

Author queries addressed/answered? ☐

Affiliations, names and addresses checked and verified? ☐

Figures and tables checked? ☐

Updated articles

Permissions (for new figures/tables etc as appropriate) details checked and completed? ☐

Outstanding permissions letters (for new figures/tables etc as appropriate) attached/enclosed? ☐

New Articles

Permissions (for all figures/tables as appropriate) details checked and completed? ☐

Outstanding permissions letters (for all figures/tables as appropriate) attached/enclosed? ☐

If you have any questions regarding your proof please contact the Elsevier MRW Production Department at: MRW-MATSproofs@elsevier.com.

MATS 02591

Author Query Form

ELSEVIER

Title: Reference Module in Materials Science and Materials Engineering (MATS)

Article Title/Article ID: Nanostructured Materials: Metrology/02591

Dear Author,

During the preparation of your manuscript for typesetting some questions have arisen. These are listed below. Please check your typeset proof carefully and mark any corrections on the proof or compile them as a separate list. Your responses should then be returned with your marked proof/list of corrections to Mike Nicholls and Sam Mahfoudh at Elsevier via **MRW-MATSProofs@elsevier.com**

Queries and/or remarks

	Please consult the first page of this pdf containing the instructions before you start reviewing the proof.
Q1	Please note that cross references to other articles within this Encyclopedia are not allowed as per style, hence 'see Scanning Probe Microscopy' has been deleted.

MATS 02591

Non Print Items

Abstract

Metrology is the science of measurement, applicable to any field of science and technology. The growing interest in applying nanomaterials to societal needs is now urging that increasing attention be given to the development of scientific and applied nanometrology. As it is impossible to give a broad coverage of all classes of nanomaterials, here we use sp^2 carbon nanostructures as an illustrative system for the development of nanometrology, with focus on carbon nanotubes and graphene, as prototypes for one- and two-dimensional nanostructures.

Keywords

MATS02591
c0010

Nanostructured Materials: Metrology ☆

A Jorio, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil
MS Dresselhaus, Massachusetts Institute of Technology, Cambridge, MA, USA

s0010

1 Definitions for Metrology and Nanometrology

p0010

Metrology is "the science of measurement, embracing both experimental and theoretical determinations at any level of uncertainty in any field of science and technology," as defined by the International Bureau of Weights and Measures (BIPM, 2004). Metrology can be divided into three subfields: scientific metrology, applied metrology, and legal metrology. Legal metrology is the end of the line, concerning regulatory requirements of well established measurements and measuring instruments for the protection of consumers and fair trade. In applied metrology, the measurement science is developed toward manufacturing and other processes, ensuring the suitability of measurement instruments, their calibration, and quality control. Scientific metrology is the basis of all subfields, and concerns the development of new measurement methods, the realization of measurement standards, and the transfer of these standards to users. The metrology is coordinated by national laboratories, such as the National Institute of Standards and Technology (NIST, USA) and the National Institute of Metrology, Quality and Technology (Inmetro, Brazil), which are internationally coordinated by the BIPM. In parallel, standardization is coordinated by the International Organization for Standardization (ISO), together with other organizations like the Versailles Project on Advanced Materials and Standards (VAMAS), whose main objective is to support trade in high-technology products, through international collaborative projects aimed at providing the technical basis for drafting codes of practice and specifications for advanced materials.

p0015

The growing interest in applying nanomaterials to societal needs is now urging that increasing attention be given to the development of scientific and applied metrology to address nanomaterials as the newly developing field of nanometrology. This multidisciplinary field spans many disciplinary fields, such as chemistry, physics, materials science, biology, engineering, and nanoscience. Nanomaterials embrace the full range of traditional materials classes. The distinction between metrology in general and metrology on the nanoscale stems from the different properties of materials on the nanoscale as compared to their bulk counterparts. The Technical Committee for Nanotechnologies Standardization (TC-229) of ISO defines the field of nano-technologies as the application of scientific knowledge to (1) understanding and control of matter and processes at the nanoscale, typically, but not exclusively, below 100 nanometers in one or more dimensions where the onset of size-dependent phenomena usually enables novel applications; (2) utilizing the properties of nanoscale materials that differ from the properties of individual atoms, molecules, and bulk matter, to create improved materials, devices, and systems that exploit these new properties (ISO, 2005). Specific tasks include developing standards for terminology and nomenclature; metrology and instrumentation, including specifications for standard reference materials; test methodologies; modeling and simulations; and science-based health, safety, and environmental practices. However, the fundamental aspects for the development of protocols and standards in nanomaterials, i.e., for building the basis for nanometrology, are still under construction.

p0020

The International System of Units (SI from the French *Système International*) is an evolving system, related to the physical understanding of nature, changing in accordance with advances in science and technology (Valdez, 2005). Today's SI is based on seven units: length (m), mass (kg), time (s), electric current (A), thermodynamic temperature (K), amount of substance (mol), and luminous intensity (cd), all the other units being derived from these. A fundamental goal of metrology is that different institutions should be able to calibrate these basic units, obtaining the same values within the same uncertainty. The historical way of doing that has been by using standard materials. The methodology today is trying to define the SI units based on fundamental constants. The meter convention was signed in 1875 as the distance between two lines made on a platinum–iridium prototype. The present definition dates from 1983: "The meter is the length of the path traveled by light in vacuum during a time interval of 1/299,792,458 of a second." This definition actually fixes the speed of light in vacuum. The ampere is defined as "the constant

☆*Change History*: Figures 2 and 3 were modified. Figure 6 was added. A new table was added. The text was revised accordingly.

MATS 02591

current, which, if maintained in two straight parallel conductors of infinite length, of negligible circular cross-section, and placed 1 meter apart in vacuum, would produce between these conductors a force equal to 2×10^{-7} N." This definition sets the permeability of vacuum at $4\pi \times 10^{-7}$ Hm^{-1}. The definition of mass, however, still remains as the one adopted in 1901: "The kilogram is the unit of mass; it is equal to the mass of the international prototype of the kilogram." The platinum–iridium international prototype is maintained at the BIPM (Paris). Considerable efforts are being made to define the kilogram in terms of fundamental constants, linking the kilogram to the Planck constant, the Avogadro constant, or the mass of an atom of ^{12}C. The definition of the mole dates from 1971: "The mole is the amount of substance of a system that contains as many elementary entities as there are atoms in 0.012 kilogram of ^{12}C." This definition refers to unbound atoms. As a consequence of the differences in binding energy, 0.012 kg of graphite has about 4×10^{14} more ^{12}C atoms than the same mass in the gas phase. A given mass of diamond at room temperature contains about 10^{12} fewer atoms than the same mass of graphite (Valdez, 2005).

p0025   New ideas need new measurements and this is where the novel class of materials, the nanomaterials, is playing an important role. From the International Vocabulary of Basic and General Terms in Metrology (ISO 1993): "Measurement is the set of operations having the object of determining a value of a quantity." 'To measure' means 'to compare,' by experiment, the unknown value of a quantity with an appropriate unit, adopted by convention. The problem does not end with the definition of the meter. Length standards at different levels (from atomic to macroscopic distances) are needed to ensure traceability along all scales. The measurement accuracy is limited by instrumental uncertainty, such as counting electrons and missing one count by co-tunneling, and by the Heisenberg uncertainty principle. Nanotechnology opens new paths for achieving quantum limited sensitivity.

p0030   In this article we focus on scientific metrology to indicate some conceptual pathways for constructing the basis for applied and legal metrologies. Being impossible to give a broad coverage of all classes of nanomaterials, which include metals, ceramics, polymers, etc., here we use sp^2 carbon nanostructures as an illustrative system for the development of nanometrology, with focus on carbon nanotubes and graphene, as prototypes for one- and two-dimensional nanostructures. This is not the personal choice of the authors, but a generalized concept, and is the one adopted by the ISO-TC229. The sp^2 carbon nanostructures are stable enough for manipulation, simple enough (just sp^2 bonded carbons) for modeling, and have been at the forefront of nanoscience and nanotechnology (Jorio *et al.*, 2008; Novoselov *et al.*, 2012). Since the properties of nanomaterials are strongly size dependent and are largely still in the discovery stage, the development of the science of nanometrology is especially challenging and rapidly evolving. Both the measurement process and the environment of a nanomaterial often perturb the properties of the nanosystem, and therefore establishing robust measurement protocols is also very challenging.

s0015   ## 2   Tools for the Development of Nanometrology

p0035   This section focuses on tools for the development of nanometrology, while the discussion of the problems and challenges of nanometrology is made in the following section. Nanometrology covers a broad range of measurements, addressing chemical and structural characterization, electronic, thermal, and mechanical properties, fabrication and monitoring of nanodevices, as well as theoretical modeling of nanomaterials properties. The bare-bones nanometrology programs focus on the evaluation of the purity and the uniformity of the dispersion of typical nanomaterials, with a view toward standardizing the specifications provided with materials purchased from suppliers In this context, typical commercial samples have been measured from a metrological standpoint by a variety of techniques and at various size scales. At the macroscopic scale, thermo-gravimetric analysis (TGA), UV–visible–near infrared (NIR) absorption, and NIR fluorescence measurements are investigated comparatively. Spanning macroscopic and microscopic scales, optical techniques, such as X-ray photoemission spectroscopy (XPS), optical transmission, ellipsometry, reflection microscopy and Raman spectroscopy are used. Fluorescence quenching microscopy (FQM) and low-energy electron microscopy (LEEM) are two novel techniques that are useful for layer characterization in two-dimensional systems (Kyle *et al.*, 2012). Electronic techniques, such as scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), and Auger electron spectroscopy (AES) are used for microscopic characterization. Finally, at the nanoscopic scale, scanning probe microscopy (SPM) and transmission electron microscopy (TEM) characterization can be employed, as well as near-field optical techniques, which couple SPM and optical spectroscopy.

Q1

p0040   Statistical comparisons made between TGA analysis working at the milligram scale and quartz crystal microbalance studies working at the microgram scale can give very different kinds of information regarding nanomaterials, relative to impurity content and distribution. Multistep manipulation processes during measurement protocols seem likely to introduce sample inhomogeneity and other changes affecting performance at the nanoscale. For example, using single wall carbon nanotubes (SWNTs) as a nanometrology prototype, Raman characterization based on the D-band/G-band intensity ratio (see **Figure 1**) showed a large scatter from one region to another in samples purified by a 'standard procedure' and indicated that the purification process which is used commercially for the removal of amorphous carbon and catalytic particles also modifies the SWNT properties themselves. A near IR absorption protocol has been developed for measuring the amount of carbon material that is indeed forming carbon nanotubes, as compared to other carbonaceous structures. This analysis is based on the relative area below the absorption peaks related to carbon nanotubes and the rest of the absorption spectra (Itkis *et al.*, 2003). Such a kind of analysis has indicated that the percentage of nanotubes to other carbon material in typical commercial samples tended to be significantly overestimated by

MATS 02591
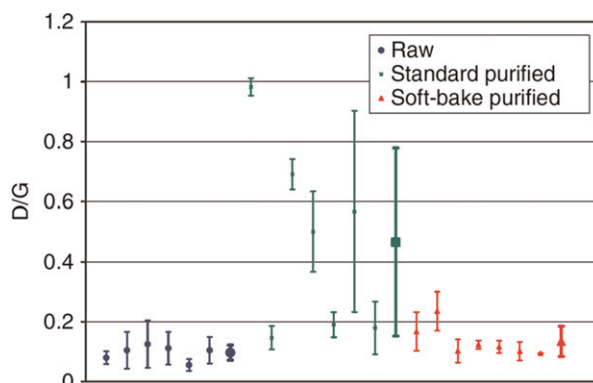
f0010   **Figure 1** Analysis of the intensity ratio between the two peaks in the Raman spectra of carbon nanotubes, named the G band (at 1582 cm^{-1}), the spectroscopic signature of sp^2 carbon, and the D band (at about 1350 cm^{-1}), the usual signature used to specify the presence of disordered sp^2 or amorphous carbon (typical Raman spectra of nanotubes are shown in **Figure 3**). The D/G intensity ratio is here plotted for a set of 20 measurements on three different samples, named raw SWNTs, standard purified and softbake purified samples. For each series of samples, the last (bold) data point represents the running average of all samples with an error bar indicating one standard deviation, while the preceding data points represent an average and one standard deviation for the individual samples in the series. The X-axis only spans each of the various measurements. The spacial inhomogeneity for the D/G intensity ratio introduced by the 'standard purification' method shows that the multi-step processing of samples introduces a large uncertainty in the definition of the resulting standard purified material (Nikolaev *et al.*, 2007).

producers (perhaps by a factor of 2). However, this procedure has some simplifications, like assuming the absorption efficiency for carbon nanotubes and other types of carbons is the same, which is not the case, since nanotubes are seamless and other types of carbons have edges. This is a clear situation where a reference material is needed for the calibration of this protocol. To promote utilization of the on-going standards work at an early stage and as it continues to evolve, a Recommended Practice Guide has been made available on a NIST website. The metrology work done to date indicates the need for significant improvement in the purification of commercial nanotubes, in the uniform dispersion of nanotubes throughout commercial samples, and in the specification used to characterize products offered for purchase. The engagement of other metrology institutes worldwide on developing practice guides, measurement protocols, and standard reference materials will certainly help the development of nanotechnology.

p0045   Nanometrology in the two-dimensional (2D) graphene systems started later than in the one-dimensional (1D) carbon nanotubes, but the advances have been fast (Kyle *et al.*, 2012), first because the advances are based on the previous developments in the field of nanotubes, second because developing nanometrology in the hexagonally structured surface has been much simpler than to work on the quasi-molecular 1D carbon nanotube, a system where length, diameter and chiral angles are intrinsic parameters that make standardization more complex. The current graphene metrology techniques are summarized in **Table 1**.

p0050   For more in-depth scientific metrology, related to materials properties at the nanoscale, measurement tools, such as TEM and SPM, with nanoscale resolution are required. Being able to image a nanomaterial with atomic resolution by TEM is very important and has had a large impact on understanding nanomaterials properties. Not only does SPM provide a complementary tool to TEM for structural characterization, but SPM can also be used to characterize both electrons and phonons. The increasing emphasis on electron microscopy in the nanoworld is related to the major advance that has occurred in the very recent past in greatly increasing the resolution of TEM instruments by the introduction of aberration-corrected optics in the latest TEM instruments. Present instruments can deliver atomic resolution images with enhanced contrast and image stability (see **Figure 2**). It is now possible to image individual atomic defects, dynamic dislocations, and linear chains of carbon atoms growing inside the cores of carbon nanotubes, just to give a few examples. While the achievements of TEM instruments are impressive and keep evolving, interestingly there is no protocol yet available for calibrating length measurements in a TEM instrument, over the full range of sample lengths seen in state-of-the-art TEM instruments, ranging from atomic lengths to the largest sample sizes of interest.

p0055   Optics also offers a very important set of tools for nanomaterials characterization since light provides a sensitive and versatile chargeless and massless probe. In particular, resonance Raman spectroscopy (RRS) at the nanoscale becomes an unusually powerful tool because of the strong size-dependent effects exhibited by nanomaterials. For example, RRS can be used to distinguish metallic from semiconducting carbon nanotubes, to evaluate the diameter distribution of SWNTs in a given sample, to determine the structural indices (n,m) for individual nanotubes, the number of layers and stacking order in graphene and the difference in properties from highly ordered pyrolytic graphite (HOPG), the presence of defects in damaged graphene and damaged nanotubes, and the difference between these nanocarbons and single-walled carbon nanohorns (SWNH) or amorphous carbons (see **Figure 3(a)**) (Dresselhaus *et al.*, 2010, Jorio *et al.*, 2011). Photoluminescence (PL) and Rayleigh scattering usually share the advantage of providing a much stronger signal than RRS (Jorio *et al.*, 2008). Brillouin light scattering can also measure particle sizes from the study of acoustic waves.

MATS 02591

t0010   **Table 1**   Standard characterization techniques can deliver information about graphene structure and properties, such as number of layers, edge structure, number of defects, changes in the Fermi level, and thermal conductivity. The industrial metrics measured by graphene characterization techniques, according to Kyle *et al.* (2012) are listed here.

	Layers	*Edge structure*	*Defects*	*Fermi level*	*Thermal conductivity*
Transmission electron microscopy	Cross-section of cut or fold. Depends on how cut of fold is made.	Atomic edge structure imaged directly	Variations in lattice structure imaged directly	–	–
Scanning electron microscopy	–	Identified in extended edges of high-quality exfoliated flake	–	–	–
Low energy electron microscopy	Oscillations in the electron reflection spectrum	–	Reciprocal lattice structure determined from diffraction pattern	–	–
Auger electron spectroscopy	Ratio of element peak intensities	–	Relative peak height/positions	–	–
AFM atomic force microscopy	Sharp height variations at edges	–	–	–	–
Scanning tunneling microscopy	–	Scanning bias voltage	Density of states measurements	Scanning bias voltage	–
Raman spectroscopy	Relative peak height (G and G') and comparative lineshape. Polarization matters	D peak height using polarization parallel to the edge	D/G relative peak height and G band linewidth	G peak frequency and linewidth	Relationship between G peak frequency and dissipated power
X-ray photoemission spectroscopy	–	–	Relative peak height/frequency	Determined from dopant type and concentration	–
Optical transmission	2.3% attenuation per layer. Depends on the wavelength	–	–	–	–
Ellipsometry	Amplitude of polarization angle shift	–	–	–	–
Reflection microscopy	Color contrast. Depends on substrate	–	–	–	–
Fluorescence quenching microscopy	Intensity contrast, customized by dye layer thickness	–	–	–	–
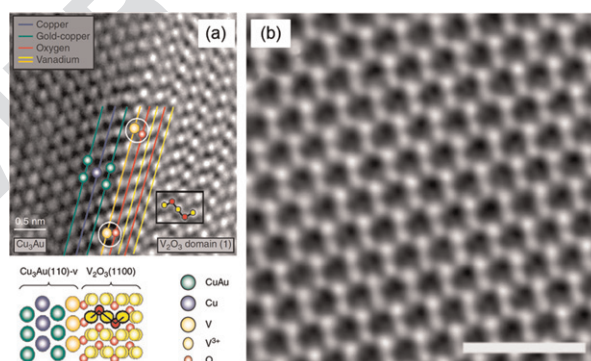
f0015   **Figure 2**   (a) Aberration corrected high-resolution transmission electron microscopy (AC-HRTEM) image of the interface structure of a thin two-dimensional monocrystalline film of V_2O_3 grown on a Cu_3Au crystal. The image was obtained using a TEM instrument with spherical aberration (Cs) image correction. The difference in brightness indicates the brightness of different atomic species. At the interface, an extra vanadium monolayer is introduced between the part of the Cu_3Au substrate and the oxide layer. The vanadium sites are not related to the V2O3 crystallography but instead are connected to the metal side ($Cu_3Au(001)$-V), as illustrated in the model shown below the TEM image (Niehus *et al.*, 2007). (b) AC-HRTEM image for graphene, with a scale bar of 0.8 nm (Rasool *et al.*, 2013). The simplicity based on the presence of a single atomic layer made of a single atom, combined with the strength of the carbon-carbon bonds, makes graphene a prototype material for the development of nanometrology.

MATS 02591
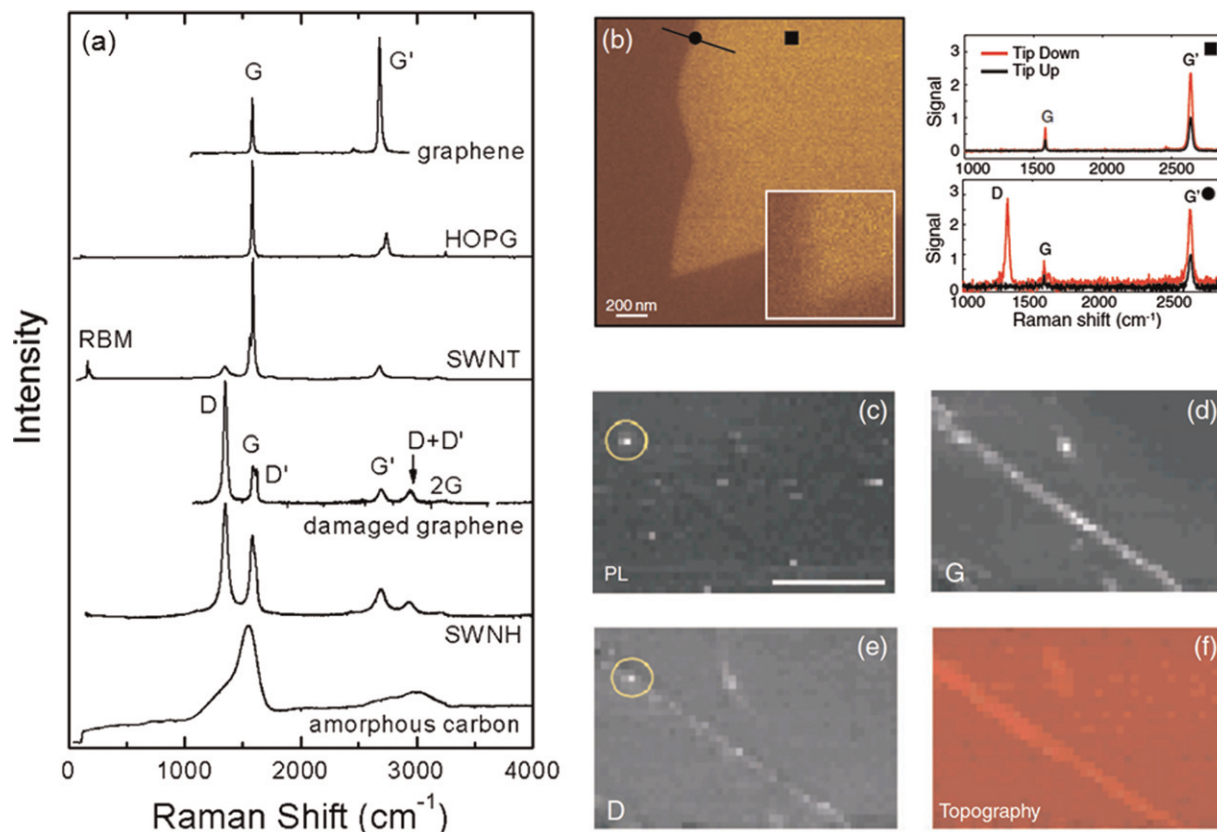
<u>f0020</u> **Figure 3** (a) Raman spectra from different types of sp^2 nanocarbons. The graphene-related structures are labeled next to their respective spectra. The main features (RBM and disorder-induced D, D′ and D + D′ bands; first-order Raman-allowed G band; and second-order Raman overtones G′ (2iTO) and 2G) are labeled in some of the spectra, but the assignment applies to all of them. The detailed analysis of the frequency, line shape, and intensity for these features gives a great deal of information about each respective sp^2 carbon structure (Dresselhaus *et al.*, 2010). (b) TERS image of the G band of a single graphene flake. Inset: confocal image of the same area with the color contrast scaled by $\times 3$. Raman spectra, with (red) and without (black) the tip, acquired in the center (top panel) and at the edge (bottom panel) of the flake. The locations are indicated by the black square and circle in the image, respectively (Beams *et al.*, 2014). (c–f) Near-field photoluminescence image of a SWNT revealing localized excitonic emission. The scale bar denotes 250 nm. (d) and (e) Near-field Raman imaging of the same SWNT shown in (c), where the image contrast is provided by spectrally integrating over the tangential G and defect-induced D Raman bands, respectively. (f) Corresponding topography (atomic force microscopy) image (Maciel *et al.*, 2008).

<u>p0060</u>   The major limitation for optics in nanometrology is the diffraction phenomena, which restricts spatial resolution to the range of the light wavelength λ, typically above hundreds of nanometers. However, this limit has been overcome using two different classes of phenomena. In the far-field limit (propagating electromagnetic waves), the super-resolved fluorescence microscopy has been implemented, for example, with the stimulated emission depletion (STED) of fluorescence from all molecules in a sample, except from those in a small region of the studied sample. With saturating stimulated emission, the remaining active region can almost be made arbitrarily smaller. By scanning the light spot defining the fluorescing region across the studied sample and monitoring the fluorescence emission continuously, a computer reconstruction of the object can be obtained. The Nobel Prize in Chemistry 2014 was awarded jointly to Eric Betzig, Stefan W. Hell, and William E. Moerner "for the development of super-resolved fluorescence microscopy" (Ehrenberg, 2014). The other phenomenon relies on the near-field (non-propagating wave) optical regime. Scanning near-field optical microscopy (SNOM) has been used to show at the same time the topography, the Raman spectra, and the photoluminescence spectra from one single nanostructure, thus providing, at the same time, information about the morphology, as well as the electronic and vibrational properties of nanomaterials (see **Figures 3(b)** and **3(c)**). This technique can be used to locate individual defects spatially in a single nanotube or a graphene flake by looking for an abrupt change in the spectral signature as the spectrum is scanned along the system. Historically, near-field optics has been applied to single-molecule experiments. The tip-enhanced Raman spectroscopy (TERS) has developed substantially in the last five years, achieving sub-nanometer scale resolution in single molecule spectroscopy (Zhang *et al.*, 2013), and being theoretically and experimentally resolved for 1D and 2D systems, using carbon nanotubes (Cancado *et al,.* 2009) and graphene (Maximiano *et al.*, 2012; Beams *et al.*, 2014) as prototype materials.

p0065   For fabrication and performance evaluation, different techniques have been developed. Focused ion beams (FIBs) can contribute to nanofabrication by cutting any material with an energetic Ga ion beam, with a resolution going down to about 10 nm (Archanjo et al., 2011), while the most recent use of a beam of He ions offers at least a twofold improvement in resolution (Archanjo et al., 2014). The parameters for current, milling time and angle are strongly material dependent, and the resolution is limited by the problem of materials redepositing while ion milling. Research on the development of the ion milling technique is at an early stage, and substrate might play a role in the experimental results. Mechanical properties at the nanoscale can be measured by nanoindentation for hardness and the elastic constants, and by nanotribology, for adhesion and friction. These techniques are the basis for the development of nanolubricants, which are likely to improve the performance of rotors and moving parts through local rather than global dissipation of their excess thermal energy.

s0020   ## 3   Challenges for the Development of Nanometrology

p0070   A big concern for nanomaterials characterization is the effect of the probes on the measurements, i.e., the electron probes, the scanning tips, the electrical contacts for transport measurements and the presence/absence of a substrate. Nanotransport can, in principle, distinguish metallic from semiconducting nanotubes, in a current versus voltage (I–V) plot. It is, however, difficult to make an ohmic contact to a nanosystem, since most contacts have a Schottky barrier that must be overcome in order for current to flow. Thermal contacts exhibit a Kapitsa resistance. Besides the difficulties of the measurements, the presence of contacts can change the intrinsic properties of the nanostructure (see **Figure 4**). Thus, nanotransport measurements offer serious metrological challenges in developing reliable and reproducible measurement procedures. Achieving high quality electric contact to graphene is easier than to carbon nanotubes, due to the larger available contact surface area, but still, reliable contacts remain a challenge for the development of reproducible devices produced on a large scale. Most interesting, graphene has emerged as a new quantum standard for resistance. Resistors can be calibrated directly using single-electron pumps in graphene to a much higher precision than what would be possible using conventional methods (Janssen et al., 2013).
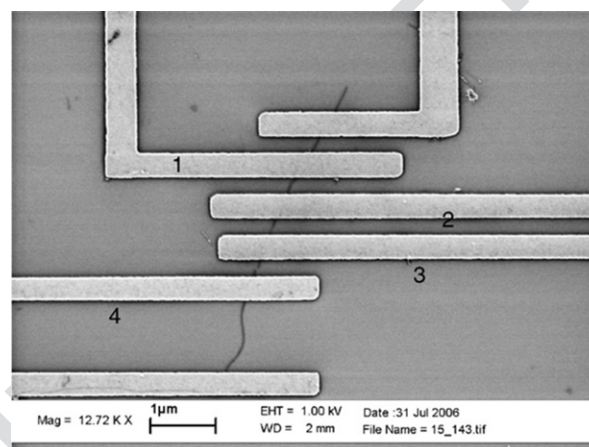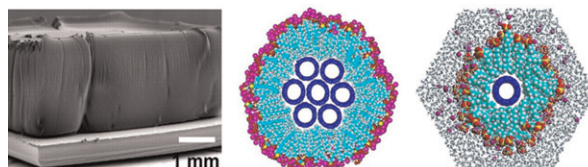

f0025   **Figure 4**   How can we extract information from a material that is extremely small and delicate, and will certainly be perturbed by the probes used for the measurements? For resistance measurements of macromaterials, the four-contact geometry is used to avoid the interference of the resistance from the measurement system. However, experiments show that if four contacts, as shown above, are applied along the length of a nanotube, the resistance R12 + R23 + R34 is not equal to R14, because nanoscale transport measurements of this type themselves are perturbed by the leads or contacts (Jorio and Dresselhaus, 2007; Purewal et al., 2007).

p0075   There are three major problems concerning the applicability of optics as an accurate metrological tool:

(i)   although analysis of frequencies ω and intensities I can deliver quantitative information, both ω and I measurements usually rely on comparative analysis and standard materials. For example, although it is possible to assign, when using the RRS or PL techniques, the amount of light coming from a specific (n,m) carbon nanotube in a sample, the quantitative determination of the (n,m) population within a nanotube sample is hindered at present by the absence of an independent experimental method for the determination of the magnitude of the matrix element governing the excitonic absorption and emission intensity from SWNTs. While a direct counting procedure of metallic and semiconducting tubes has been done, their optical properties are still expected to be strongly dependent on both tube diameter – because of the excitonic nature of the excited states and the energy dependence of the broadening factor – and chiral angle – due to the strong chirality dependence of the electron–phonon coupling. Calculations of the (n,m) dependence of the Raman frequencies, RRS matrix elements and excited state lifetimes have been developed for SWNTs (Saito et al., 2011), but further studies like twisting,

MATS 02591

folding and substrate effects have since advanced our understanding. A similar problem appears for counting the number N of graphene layers. While differentiating a single layer from a bilayer with AB stacking is possible through the lineshape of the second order G' band (~ 2700 cm^{-1}), the presence of larger values for N locally and the presence of different stacking orders locally are harder to establish, and require sample-dependent comparative analysis.

(ii) Environmental effects due to substrates, wrapping agents, functionalization, strain, or other mechanisms are expected to strongly influence the optical response (see **Figure 5**). This is especially important for nanotubes, where the excitonic nature of the excited states makes them especially sensitive to their dielectric environment (Miyauchi et al., 2007), and for graphene, where charge transfer and strain are usually significant due to the large contact surface (Lee et al. 2012). Another example of environmental effects are those that can be studied using the radial breathing mode (RBM), whose frequency (ω_{RBM}) provides a simple spectroscopic signature of the SWNT diameter (d_t). The experimental results in the literature have been fitted with the relation $\omega_{RBM} = A/d_t + B$, but the values for A and B vary from one publication to another, while only one SWNT sample has shown the relation expected from theory, that is, $\omega_{RBM} = 227/d_t$ (Araujo et al., 2008). Even 'isolated' single-wall carbon nanotubes suspended over trenches exhibit a ω_{RBM} dependence on d_t that is not in accordance with the expected dependence, i.e., $\omega_{RBM} = A/d_v$ but includes a non-zero value for the constant B accounting for the environmental effects on ω_{RBM}, thus preventing the graphene limit from being achieved, i.e., $\omega_{RBM} \rightarrow 0$ when $d_t \rightarrow \infty$ (Paillet et al., 2006). Controlling environmental effects is vital for a variety of applications of functionalized nanostructures for sensors and biomedical applications.

f0030 **Figure 5**   How do we extract information from a material that is extremely small and delicate, and will certainly be perturbed by its environment? On the left are ultra-long vertically aligned SWNTs grown from a Si/SiO2 substrate by the water-assisted chemical vapor deposition method. Here the tubes are enclosed in a forest of carbon nanotubes and may be shielded from the external environment (Hata et al., 2004). Sonicating single wall carbon nanotubes (SWNTs) in an SDS-aqueous solution were shown to disperse SWNT bundles (middle) into isolated single-wall carbon nanotubes (right) (O'Connell et al., 2002). This dispersion procedure has been largely used by the research community to do experiments on unbundled individual tubes (Jorio and Dresselhaus, 2007). Procedures, such as sonication and HCl purification, are being used, but protocols that leave the tube unperturbed have not been clearly developed nor have present protocols been properly evaluated for the perturbations they produce.

(iii) The presence of defects is also expected to strongly influence their optical properties, since defects change the local SWNT structure and act as trap states for excitons. It is important to note that defects also introduce localization, influencing transport. While AC-HRTEM can image defects with unprecedented clarity, other accurate and accessible measurement techniques are not yet available for detailed defect characterization at the nanoscale, suitable to be applied on materials that will be incorporated into devices. Graphene enabled a big step forward in the use of Raman spectroscopy to quantify defects, since the perfect 2D surface enabled the use of STM to count defects, thus calibrating the Raman response fiducially (see **Figure 6**).

4   The Future of Nanometrology

s0025

p0095   It is clear that, when working on the nanoscale, we face unprecedented problems to perform reliable measurements. The development of nanometrology is today an urgent requirement for making possible the transformation of nanoscience into nanotechnology. From what the metrology community has learned from the example of nanotubes and graphene, to address present industrial needs, protocols are required for characterizing basic concepts like: (1) tube diameter and length distributions, (2) metallic to semiconducting nanotube ratios in a mixed sample, (3) the presence of structural defects and doping, (4) surface area, (5) optical efficiency. The uncertainty behind all measurements in the nanocarbon field is certainly decreasing the speed of both scientific advance and technological development. However, despite the progress that has been made thus far, research is needed to establish a simple and reliable protocol (or measurement standard) for the specification of the content, purity, and dispersion characterization within a given sample that is offered for sale.

p0100   For metrology techniques to be adopted by industry, they must offer high-throughput, be scalable, and be insensitive to environmental factors. These are aspects required for automated robotic decision making. While the techniques that have been thus far developed do address industrial interests, they are still far from meeting the criteria for industrial application. Most of the work that has been done by the academic community addresses single-walled carbon nanotubes, generally with diameters in the range of 0.7–1.5 nm, with a clear lack of knowledge on how to address MWNTs (multi-wall carbon nanotubes), which is where many of

MATS 02591
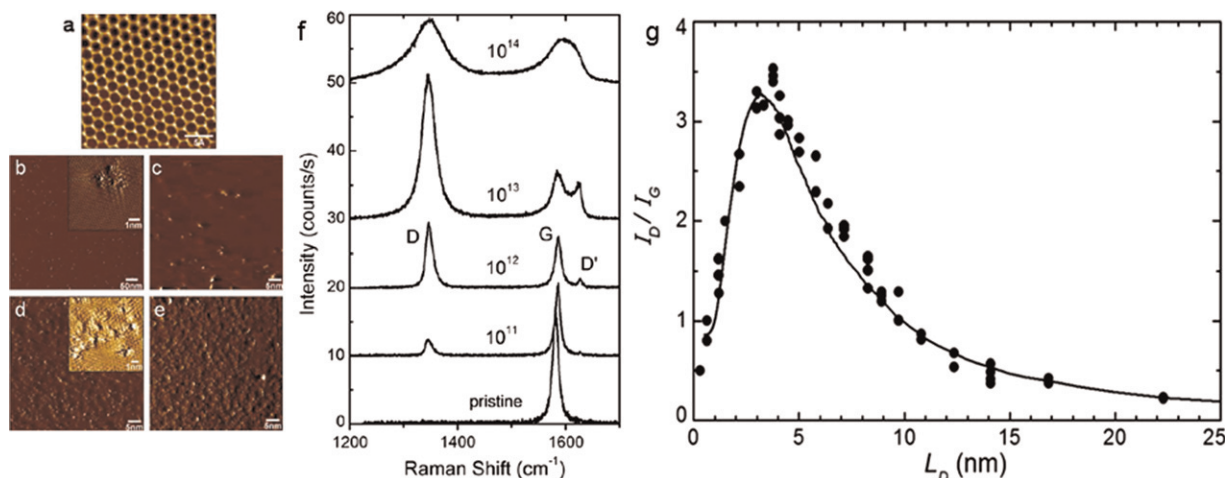
f0035   **Figure 6**   The ion bombardment technique is used to gradually induce disorder in graphene. Scanning tunneling microscopy (STM) measurements can provide an accurate measure of the defect density. From (a–e) the panels display results at zero, 10^{11}, 10^{12}, 10^{13} and 10^{14} Ar^+ / cm^2 ion doses. (f) Evolution of the first-order Raman spectra of a monolayer graphene sample deposited on an SiO_2 substrate, subjected to the same ion bombardment conditions. (g) The I_D/I_G data points from three different mono-layer graphene samples as a function of the average distance L_D between defects, induced by the ion bombardment procedure (data points), fit by a theoretical model (lines) (Lucchese *et al.*, 2010).

the industrial products are focused. In the graphene field, the mechanically exfoliated samples are still the preferable prototype metrological material, even though such samples are unlikely to reach commercial markets. The present needs of industry also require standards for property measurements, not usually addressed by the academic research community, such as resiliency for battery applications, strength/weight ratio measurements for sporting goods applications, metallicity or conductivity enhancement for electrical shielding for building materials and related applications. The development of standards for the nanoworld is at such an early stage at present that it is not yet clear how these standards should be developed, and how these standards should be used.

p0105   The accumulated experience from TEM experts shows that it is not difficult to find a defect along a ~ 100 nm segment of SWNTs grown by the usual chemical vapor deposition processes. However, the type of defect (an impurity, a vacancy, or a dislocation) is important in changing the physical–chemical properties. Accurate and accessible measurement techniques for detailed defect characterization are not yet available. Optics provides a powerful pathway as a fast and reliable approach for nanotube characterization, as demanded for applications, but the optical efficiency of a given nanotube is highly dependent on its morphology and environment. Fruitful outcomes have been achieved when combining SPM and TEM with optical spectroscopy techniques, giving us the opportunity to correlate vibrational modes with local changes in the microscopic structure or chemical attachment of functional groups on individual SWNTs. Systematic characterization by multiple techniques is important for metrology science, but is not directly applicable to large-scale industrial needs, where easy and quick tests of the stability of the manufacturing process are necessary. Consistency issues between properties measured on the nano- and bulk scales have to be further pursued in order to gain a further understanding of size effects in this context.

p0110   Safety issues have to be seriously considered before any product goes to market. It is usually a difficult task to determine whether or not a material is dangerous for health or environment because the conclusions have to be drawn from indirect measurements. Many safety and biocompatibility of issues regarding nanotube materials still remain unresolved, since toxicity still arises in unexpected situations, depending highly on the degree and type of functionalization, aggregation state, and the presence of metal-catalyst particles remaining from the synthesis process among others. The bio-nanotube interface needs special consideration to advance the development of bio-nanotube metrology for biomedical applications. Strong interdisciplinary scientific effort will be needed for the implementation of a viable metrology program in this area.

p0115   Finally, as discussed here, carbon nanotubes and graphene serve as prototype materials, but there is a large number of other materials that will have to be explored. For example, Si is broadly used as a standard for electronic applications. However, Si is unusual in being an indirect gap semiconductor with six electron pockets at a relatively low symmetry point in the Brillouin Zone. A material like GaAs would be better, as a direct gap material, similar to many other III–V compounds, if one is considering heat transfer materials. PbTe, which can be a standard nanomaterial for thermoelectrics has anomalous defects that are especially good for scattering phonons. In short, one material may be a good standard reference material of one property but not appropriate for another property. The world of 2D systems has expended substantially in recent years, with the appearance of monoatomic analogs of graphene, such as phosphorene, silicene, and germanene, and diatomic nanoscale systems, such as the monolayered hexagonal boron-nitride and the tri-layered transition metal dichalcogenides (TMDCs), of the form MX_2, where M stands for groups 4–10 of transition metals and X stands for the chalcogen atoms S, Se, or Te. Beyond these, other classes of 2D materials, such as perovskite-based oxides, van der Waals solids, topological insulators, and others are now showing great promise for

MATS 02591

applications that are not well addressed by nanocarbons. From this perspective we can only conclude that nanometrology as a research field is just at its early stage.

References

bib1   Araujo, P.T., Maciel, I.O., Pesce, P.B., *et al.*, 2008. The nature of the constant factor in the relation between radial breathing mode frequency and tube diameter for single-wall carbon nanotubes. Phys. Rev. B 77, 241403.

bib3   Archanjo, B.S., Fragneaud, B., Cancado, L.G., *et al.*, 2014. Graphene nanoribbon superlattices fabricated via He ion lithography. Appl. Phys. Lett. 104, 193114.

bib2   Archanjo, B.S., Maciel, I.O., Martins Ferreira, E.H., *et al.*, 2011. Ion beamnanopatterningandmicro-Ramanspectroscopyanalysis on HOPG for testing FIB performances. Ultramicroscopy 111, 1338.

bib4   Beams, R., Cancado, L.G., Oh, S.-H., Jorio, A., Novotny, L., 2014. Spatial Coherence in Near-Field Raman Scattering. Phys. Rev. Lett 113, 186101.

bib5   BIPM, 2004. What is metrology? Available at: http://www.bipm.org/en/convention/wmd/2004/ (accessed 18.11.2008).

bib6   Cancado, L.G., Jorio, A., Ismach, A., *et al.*, 2009. Mechanism of near-field Raman enhancement in one-dimensional systems. Phys. Rev. Lett 103, 186101.

bib8   Dresselhaus, M.S., Jorio, A., Hofmann, M., Dresselhaus, G., Saito, R., 2010. Perspectives on carbon nanotubes and graphene Raman spectroscopy. Nano Lett. 10, 751.

bib9   Ehrenberg, M., 2014. Scientific Background on the Nobel Prize in Chemistry 2014: SUPER-RESOLVED FLUORESCENCE MICROSCOPY. Available at: http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2014/advanced-chemistryprize2014.pdf (accessed 02.01. 2015).

bib10   Hata, K., Futaba, D.N., Mizuno, K., *et al.*, 2004. Water-assisted highly efficient synthesis of impurityfree single-walled carbon nanotubes. Science 306, 1362.

bib11   ISO, 2005. International Organization for Standardization. Available at: http://www.iso.org (accessed 18.11.2008).

bib12   Itkis, M.E., Perea, D.E., Niyogi, S., *et al.*, 2003. Purity evaluation of as-prepared single-walled carbon nanotube soot by use of solutionphase near-IR spectroscopy. Nano. Lett. 3 (3), 309–314.

bib13   Janssen, T.J.B.M., Tzalenchuk, A., Lara-Avila, S., Kubatkin, S., Fal'ko, V.I., 2013. Quantum resistance metrology using graphene. Rep. Prog. Phys. 76, 104501.

bib14   Jorio, A., Dresselhaus, M.S., 2007. Nano-metrology: A link between state-of-the-art academic research and ultimate industry needs for technological innovation. MRS Bulletin 34 (12), 988–993.

bib15   Jorio, A., Dresselhaus, M.S., Dresselhaus, G., 2008. Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications, Springer Series in Topics in Applied Physics, vol. 111. Berlin: Springer.

bib16   Jorio, A., Saito, R., Dresselhaus, G., Dresselhaus, M.S., 2011. Raman Spectroscopy in Graphene Related Systems. Weinheim, Germany: WILEY-VCHVerlag GmbH & Co. KGaA.

bib17   Kyle, J.R., Ozkan, C.S., Ozkan, M., 2012. Industrial graphene metrology. Nanoscale 4, 3807.

bib18   Lee, J.E., Ahn, G., Shim, J., Lee, Y.S., Ryu, S., 2012. Optical separation of mechanical strain from charge doping in graphene. Nat. Comm. 3, 1024.

bib19   Lucchese, M.M., Stavale, F., Martins Ferreira, E.H., *et al.*, 2010. Quantifying ion-induced defects and Raman relaxation length in graphene. Carbon 48, 1592.

bib20   Maximiano, R.V., Beams, R., Novotny, L., Jorio, A., Cancado, L.G., 2012. Mechanism of near-field Raman enhancement in two-dimensional systems. Phys. Rev. B 85, 235434.

bib21   Maciel, I.O., Anderson, N., Pimenta, M.A., *et al.*, 2008. Electron and phonon renormalization near charged defects in carbon nanotubes. Nat. Material 7, 878–883.

bib22   Miyauchi, Y., Saito, R., Sato, K., *et al.*, 2007. Dependence of exciton transition energy of single-walled carbon nanotubes on surrounding dielectric materials. Chem. Phys. Lett. 442 (4–6), 394–399.

bib23   Niehus, H., Calderon, H.A., Freitag, B., Stavale, F., Achete, C.A., 2008. Atomically resolved interface structure of a vanadium sesquioxide (0001) film grown on Cu3Au(001). Surf. Sci. 606, L59–L63.

bib24   Nikolaev, P., Gorelik, O., Allada, R., *et al.*, 2007. Soft-bake purification of single-walled carbon nanotubes produced by pulsed laser vaporization. J. Phys. Chem. C 111 (48), 17678–17683.

bib25   Novoselov, K.S., Fal'ko, V.I., Colombo, L., *et al.*, 2012. A roadmap for graphene. Nature 490, 192.

bib26   O'Connell, M.J., Bachilo, S.M., Huffman, , *et al.*, 2002. Band gap fluorescence from individual single-walled carbon nanotubes. Science 297, 593–596.

bib27   Paillet, M., Michel, T., Meyer, , *et al.*, 2006. Raman active phonons of identified semiconducting single-walled carbon nanotubes. Phys. Rev. Lett 96, 257401.

bib28   Purewal, M.S., Hong, B.H., Ravi, A., Chandra, B., Hone, J., Kim, P., 2007. Scaling of resistance and electron mean free path of single-walled carbon nanotubes. Phys. Rev. Lett 98, 186808.

bib29   Rasool, H.I., Ophus, C., Klug, W.S., Zettl, A., Gimzewski, J.K., 2013. Measurement of the intrinsic strength of crystalline and polycrystalline graphene. Nature Comm. 4, 2811.

bib30   Saito, R., Hofmann, M., Dresselhaus, G., Jorio, A., Dresselhaus, M.S., 2011. Raman spectroscopy of graphene and carbon nanotubes. Adv. Phys. 60 (3), 413.

bib31   Valdez, J., 2005. Features and future of the international system of units (SI). Adv. Imag. Electron Phys. 138, 251–320.

bib32   Zhang, R., Zhang, Y., Dong, Z.C., *et al.*, 2013. Chemical mapping of a single molecule by plasmon-enhanced Raman scattering. Nature 498, 82–86.

Further Reading

bib7   Dresselhaus, M.S., Dresselhaus, G., Jorio, A., 2007. Raman spectroscopy of carbon nanotubes in 1997 and 2007. J. Phys. Chem. C 111 (48), 17887–17893.