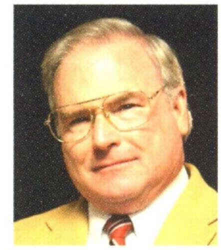
Nanometrology Solutions Using an Ultra-High Resolution In-lens SEM

Michael T. Postek, Andras E. Vladár and John S. Villarrubia

National Institute of Standards and Technology *, Gaithersburg, MD 20899 USA



Michael T. Postek

Andras E. Vladár

Abstract

The imaging and measurement of nanostructures such as particles, carbon nanotubes, and quantum dots have placed new demands on the high resolution imaging capabilities of scanning electron microscopes. A barrier to accurate dimensional metrology is the detrimental effects induced by the electron beam interactions of these small particles in secondary electron detection mode which dominate in the imaging. Such effects are minimized in the transmission electron detection mode of the SEM and can lead to accurate metrology of nanoparticles. Work is being done in the Precision Engineering Division of the National Institute of Standards and Technology (NIST) to develop infrastructural metrology and ultra high resolution imaging for measurements of nanoparticles using the Hitachi S-5500 STEM. Such metrology development is critical to the characterization of nanoparticles for many industrial applications and the emerging research for environmental, health and safety.

Introduction

Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers. In this size realm, unique materials changes can occur which can facilitate new and novel material applications. Therefore, the *accurate*† determination of the dimensions of nanomaterials, in this regime, is critical. Yet, the accurate metrology needed does not currently exist. The difference between a measurement of a nanoparticle at 5 nm or at 6 nm may be the transition zone where a unique nanomaterial property begins to become exhibited. Therefore, the size must be accurately known in order to understand and effectively use these new properties. So, it is extremely important that accurate measurements are made because the prime characterization is based upon dimension. Several of the workshops associated with the U.S. National Nanotechnology Initiative (NNI) have recommended the rapid evolution of current instruments and the development of revolutionary instrumentation for the measurement and characterization of nanomaterials [1,2,3,4].

The imaging and measurement of nanostructures such as gold particles, carbon nanotubes, and cellulose nanocrystals have placed new demands on the high resolution imaging capabilities of scanning electron microscopes. Sample preparation remains an issue but, a significant barrier to accurate dimensional metrology remains the detrimental effects induced by the electron beam interactions as the electron beam scans the small particles. In secondary electron detection mode, electron beam interaction effects can still dominate in the imaging depending upon the instrument conditions employed. Such effects are minimized in the transmission electron detection mode of the SEM and can lead to the accurate metrology of nanoparticles. Such metrology was demonstrated for SCALPEL masks [5, 6] and x-ray masks [7]. Thus, a scanning transmission electron microscope is a good tool for exploring these materials. Within the Precision Engineering Division of NIST the development of infrastructural metrology and ultra high resolution imaging and measurements of nanoparticles using the Hitachi S-5500 is being done. Such metrology development is critical to the characterization of nanoparticles for

† Accuracy is "closeness of agreement between a measured value and a true quantity value of a measurand." (*International Vocabulary of Metrology—Basic and General Concepts and Associated Terms*, ISO/IEC Guide 99-12:2007). The true value is generally unknown, so accuracy is not typically assigned a numerical value. Measurements with lower uncertainty are said to be more accurate.

many industrial applications and the emerging research for environmental, health and safety research.

Ultra-high resolution STEM.

Nanotechnology has opened up many new applications for the scanning electron microscope as well as the scanning transmission electron microscope. The highest possible instrument performance is needed to work routinely with nanostructures. Therefore, the ultra-high resolution provided by the Hitachi S-5500 is easily justified. For the best results, ultra-high resolution scanning electron microscopes must be employed at both high and low accelerating voltages and instrument performance must be maintained at the highest levels possible. In addition, performance testing must be performed prior to any critical work in order to ensure data fidelity.

Secondary Electron Imaging.

Secondary electron imaging is the most common mode of imaging in the SEM and STEM. Unfortunately, a generally ignored problem creates a barrier to accurate dimensional metrology. This is the detrimental effects induced by the electron beam interactions on the small particles being observed. The effects of these interactions can dominate the measurements. Postek, 1990 [8] clearly demonstrated that measurements of the secondary electron image of semiconductor structures collected at high resolution in the high resolution field emission SEM were larger than images similarly collected of backscattered electrons under the same conditions; on the same sample; with the same micro-channel plate electron detector. Therefore, the secondary electron "blooming" of the edges, so characteristic of SEM imaging, detrimentally contributes to the dimension of the measured structure. Sample edge information must be de-convoluted from the image through modeling before accurate structure measurements can be made [9]. However, highly precise measurements are possible and have been the mainstay of semiconductor metrology for several years.

Backscattered Electron Imaging.

Imaging of the electrons backscattered in the SEM can be very helpful in detecting differences in atomic number in nanomaterials and locating regions for analysis (see upcoming figures). Backscattered electron imaging is also useful in imaging nanomaterials where charging is observed in the secondary electron image. Viewing in backscattered electron mode does not eliminate the charging, but permits a backscattered electron image to be captured without distortion as long as the charging is minimal. Backscattered electrons contribute to the secondary electron image through their direct collection or the generation of additional secondary electrons as they re-emerge from the material being viewed.

Electron Beam Modeling.

Electron beam interaction modeling has made great strides in recent years. This is due in part to a successful series of workshops strongly supported by Hitachi High Technologies (and others) held at the yearly SCANNING Microscopy meeting. Much recent work in this area has been done by Joy [10, 11], Villarrubia [12, 13], Lowney [14, 15], Davidson [16], Ding and Shimizu [17, 18], Kieft and Bosch [19], and their coworkers. The work consists of modeling the beam-sample interaction to understand the actual structures represented by the combined sources of secondary and backscattered electrons making up the standard secondary electron image.

Secondary electron imaging is used in some applications, particularly where samples are too thick for transmission imaging and in time-critical applications where the additional secondary electron yield is advantageous. In this mode, a structure's edge is bright, owing to the fact that more electrons can escape from the upper and side surfaces than escape when only the upper surface is available, as is the case far from an edge. The intensity change caused by a sample feature occurs within a finite neighborhood feature. The size of the neighborhood and the form of the intensity variation within it depend upon the details of electron scattering and secondary electron production. The neighborhood size represents a limit on the "easy" spatial resolution in this mode. Locating features with smaller uncertainties requires modeling. This is one of the motivations of the modeling work referenced in the previous paragraph.

Scanning Transmission Electron Detection.

The scanning transmission electron detection has been available for many years, but not been a common mode of operation in the SEM. Any SEM can be equipped to collect transmitted electrons [20] and a number of detectors from very simple to very elaborate have been commercially available. The advanced design of the Hitachi S-5500 incorporates a scanning transmission electron detection system. In this mode, the instrument can function in a manner similar to a transmission electron microscope having a scanning beam accessory. Electron opaque nanoparticles can be observed in the instrument at high resolution and lattice fringes can be resolved [21]. Opaque nanoparticles can be viewed essentially as a shadowgraph. These particles can be measured with a high degree of precision because the edge "blooming" characteristic of the secondary electron image is not present in the image. Electron beam interaction and electron scatter does occur, but measurement of transmitted electron images of x-ray photomasks [7] pointed out the greater ease of modeling the image. If dimensional information from nanoparticles is needed, transmission electron detection provides a viable alternative to the secondary electron detection mode. Transmission electron detection in the SEM or even the STEM is a mode which has lain reasonably dormant and with the introduction of the S-5500 can now be revived as a viable technology for nanoparticle metrology.

The transmitted-electron detection mode of the SEM or STEM offers the investigator another independent source of information regarding the specimen under study. The necessary thin specimen can often be prepared using existing conventional thin-sectioning techniques developed for the TEM. The STEM mode can provide information about the internal ultra-structure in specimens. The STEM results can also be coupled with x-ray microanalysis results to provide additional high resolution information about the elemental information and distributions. STEM and x-ray microanalysis of small particulate specimens are both facilitated when the specimens are suspended on TEM grids to minimize the substrate effects that would otherwise be present if they were mounted on a mounting stub. Finally, with the added information available from the use of the STEM mode, it should be no surprise that this mode has proven useful in testing and evaluating SEM performance.

Materials and Methods

Instrumentation.

The National Institute of Standards and Technology is developing infrastructural metrology and ultra high resolution imaging and measurements of nanoparticles using the Hitachi S-5500. The Hitachi S-5500 has the advantage of having true in-lens operation (**Figure 1**) so that the resolution obtained can be the highest possible for this type of instrument. This of course, results in the requirement for relatively small samples. Fortunately, nanotechnology provides the ideal solution — very small samples. The sample is inserted directly into the final lens pole piece thus insuring the highest possible resolution (0.4 nm at 30 keV accelerating voltage) and an excellent low accelerating voltage operation specification of 1.6 nm at 1 keV.

Example Applications

Carbon Nanotubes.

Single-walled carbon nanotubes (SWCNTs) are one of the many promising nanomaterials currently being manufactured. SWCNT have demonstrated unique electronic and mechanical properties which lend themselves to a variety of applications, such as field-emission displays, nanostructured composite materials, nanoscale sensors, and elements of new nanoscale logic circuits [22-26]. There is a growing interest in the nanomanufacturing of bulk SWCNTs and hence there

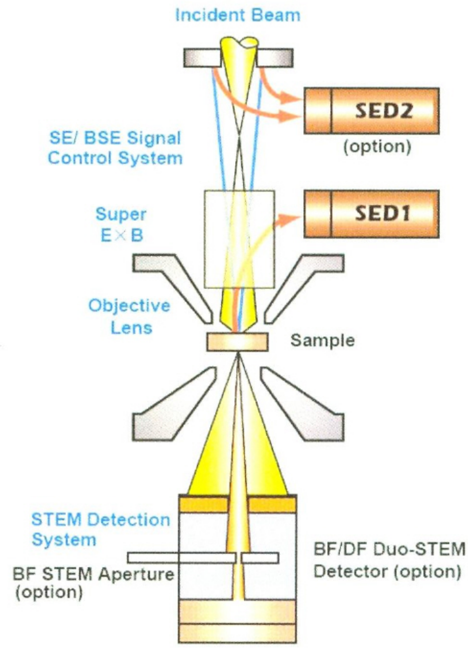


Figure 1. Diagrammatic view of the S-5500 column and placement of the sample in the pole piece of the lens and location of the secondary, backscattered and transmitted electron detectors.

is a growing need for appropriate nanostandards and infrastructural measurement methodology. The relatively large number of suppliers of SWCNT had grown over the past few years and as such, this material is an excellent test vehicle for determining the complications associated with imaging and metrology for reference materials for nanotechnology.

While some instruments are able to resolve single SWCNT under very high resolution imaging conditions, in most cases, only bundles of two to three SWCNTs are the minimum-sized objects are imaged. The ability to obtain complementary images in secondary, backscattered and transmitted electron detection modes makes this determination much easier. If the instrument is not resolving the fine structure, it is unlikely that the resolution will be high enough to give accurate information about tube length, diameter or other properties. Therefore, instead, STEM imaging of SWCNT alone, as opposed to in devices or composites is typically used for the purpose of investigating bundles of SWCNT and the carbonaceous and other impurities such as metal catalysts attached to those bundles. The ability of STEM imaging, coupled with energy dispersive x-ray microanalysis, to identify the type and location of the impurities present in the sample material can provide a useful complement to other analytical techniques that can report quantitative data for the overall degree of sample impurity. **Figure 2** is an ultra-high resolution secondary electron

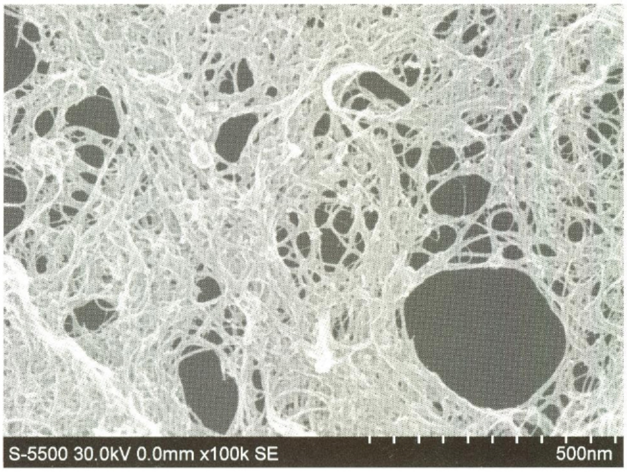


Figure 2. Secondary electron image of a sample containing single walled carbon nanotubes. (Field of view = 1280 nm).

image taken in the S-5500 at relatively low magnification. At this level of detail, the carbon nanotubes appear as a tangled mass with very little differentiation between tubes and contaminants. This can be contrasted to **Figure 3** which is a high angle backscattered electron image of the same field. The heavy atomic number contaminants are visible as bright specks in the image although at this magnification identification is still difficult to determine if they are single particles or groups of particles. **Figure 4** is a complementary transmitted electron image of the same field. In this image the darker structures can be seen to be consistent with the location of the higher atomic number particles. At this point energy dispersive x-ray microanalysis of this sample could reveal information about the elemental composition of these particles.

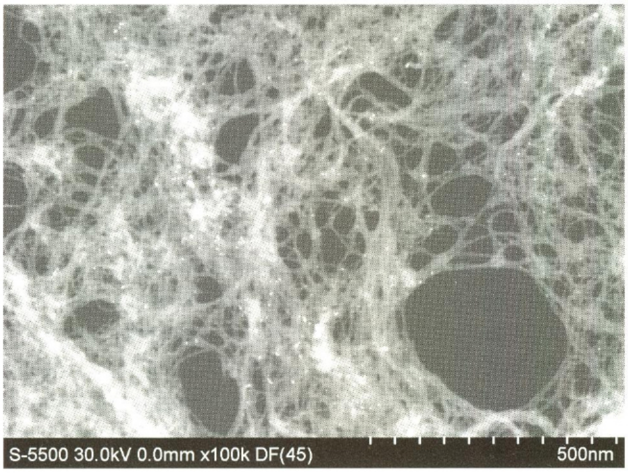


Figure 3. High angle backscattered electron image of the same field as the previous figure. Note the bright metal catalytic particles. (Field of view = 1280 nm).

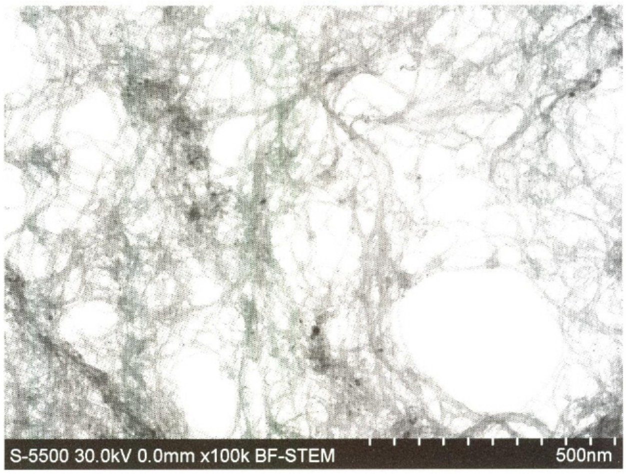


Figure 4. Transmitted electron image note that the high electron density particles (dark) coincide with the bright particles of the previous figure. (Field of view = 1280 nm).

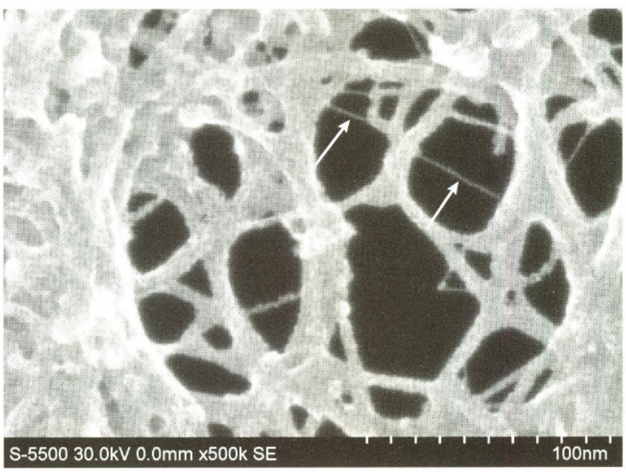


Figure 5. Single walled carbon nanotube containing material. Note the single walled carbon nanotubes extending across the voids in the material (arrows). (Field of view = 256 nm).

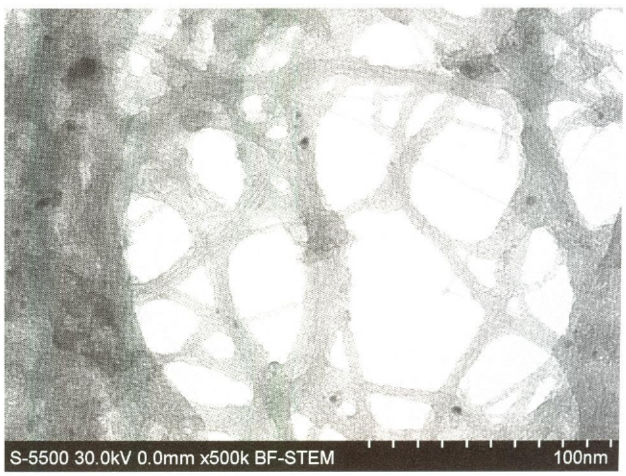


Figure 6. Bright-field transmitted electron image of the same field as the previous image. Note the detail in the single walled carbon nanotubes is now beginning to be resolved as the electron beam penetrates through the material. (Field of view = 256 nm).

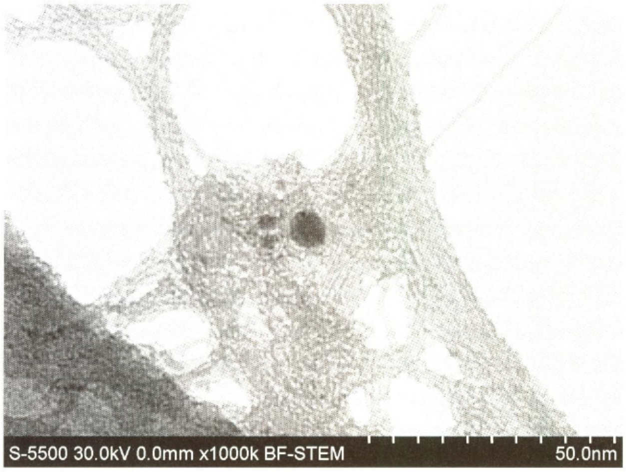


Figure 7. Bright-filed transmitted electron image. Note the details of the bundles of single-wall carbon nano tubes are resolved as the electron beam penetrates through the material. (Field of view = 128 nm).

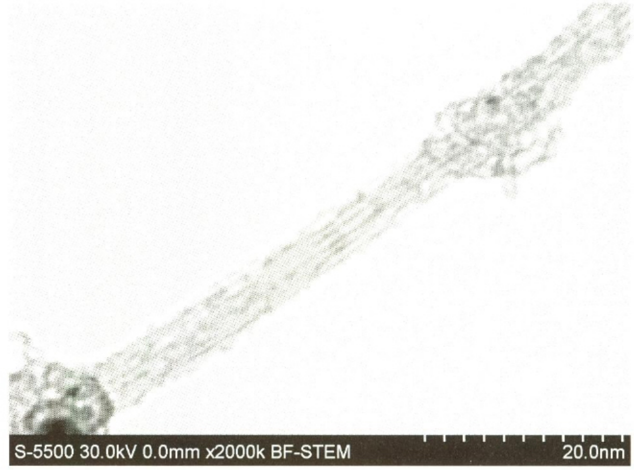


Figure 8. Bright-field transmitted electron image of a bundle of six single-wall carbon nano-tubes. (Field of view = 64 nm).

At higher magnifications single walled nanotubes can be readily revealed stretching from one group of nanotubes to another across voids in the material as shown in **Figure 5** (arrows). In a complementary transmitted electron image detail in the single walled nanotubes is beginning to be resolved as the magnification is increased (**Figures 6 to 8**).

Gold Nanoparticles.

Gold nanoparticles are used in many nanotechnology related research projects such as instrument calibration and conjugation to antibodies for biomedical research. NIST has also just released a series of gold nanoparticle Reference Materials (RMs). These gold nanoparticle reference materials are 10 nm (RM 8011) [27], 30 nm (RM 8012) [28] and 60 nm (RM 8013) [29]. These RMs are intended primarily to evaluate and qualify methodology and/or instrument performance related to the physical and dimensional characterization of nanoscale particles used in pre-clinical and biomedical research and clinical treatment. These nanoparticles have been viewed in the S-5500 STEM (**Figures 9 and 10**). These images demonstrate one of the more difficult aspects of research on nanoparticles which is sample preparation. The media suspending the particles has left a residue on the surface of the samples which has dried around the particles

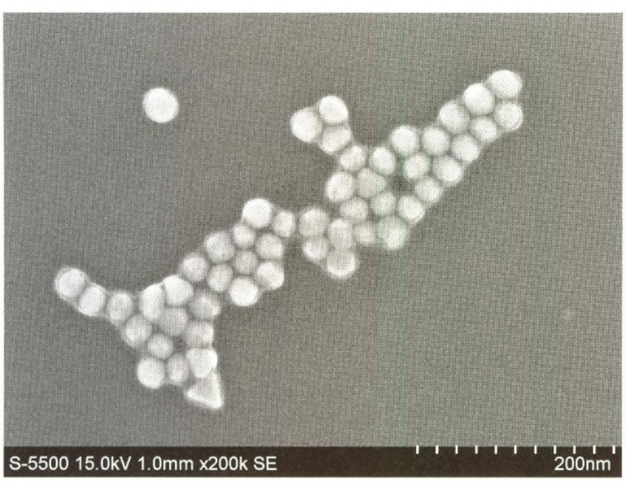


Figure 9. Secondary electron image of 30 nm nominal size colloidal gold nanoparticles. The individual particle structure is somewhat obscured by the surface coating derived from material in the solution. (Field of view = 640 nm).

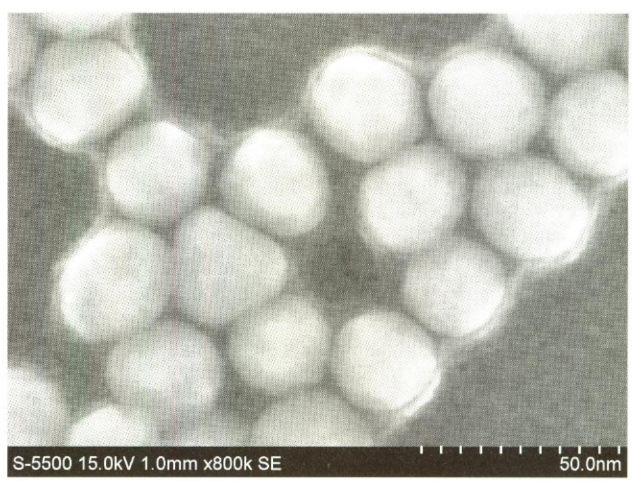


Figure 10. Secondary electron image of colloidal 30 nm nominal size gold nanoparticles at ultra-high resolution. The individual particle structure is somewhat obscured by the surface coating derived from material in the solution but the faceting of the individual particles is beginning to be resolved. (Field of view = 162 nm).

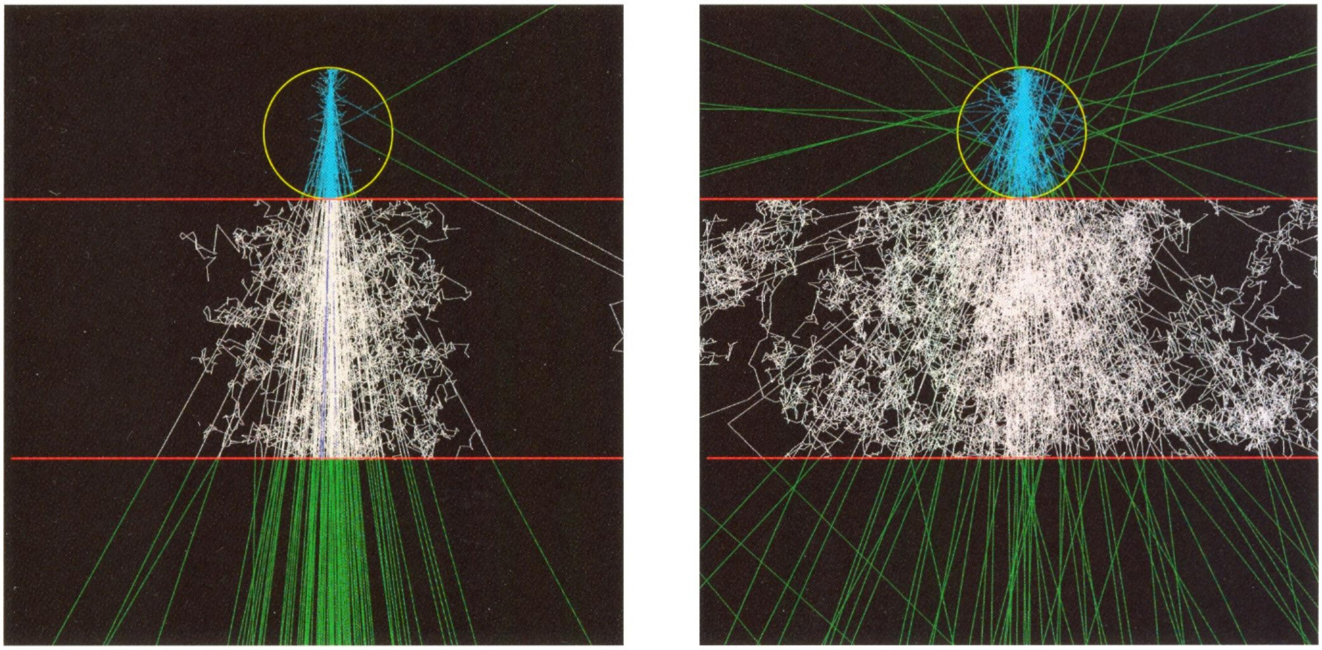


Figure 11. Simulated scattering and transmission of 25 keV (left) and 5 keV (right) electrons through a 10 nm gold sphere (circle) on a 20 nm carbon film (horizontal lines). The trajectories in the sphere and film include secondary electrons, but these low energy electrons are omitted in the vacuum regions above and below the sample.

and obscured some of the gold particle information. Whereas detail in the background remains sharp since the contaminant remained adhering to the particles (**Figure 10**). **Figure 11** shows simulated trajectories in transmission mode from such particles, suspended on a thin membrane. For nanoparticle characterization sample preparation has again become an important aspect of successful microscopy. Preliminary measurements of these particles were made and were included with the Report of Investigation accompanying the Reference Material. The accurate metrology that provides small uncertainties is currently being researched.

Concluding Remarks

It is well known that accurate dimensional metrology and characterization of currently studied nanomaterials remains a problematical issue. But, high measurement precision is possible in the STEM using either secondary or transmitted electron detection. Transmission electron detection can lead to accurate measurements because of the more straightforward modeling of the transmitted electron signal and modeling of the secondary electron image is soon to be a reality, as well. Coupling the instrument to the modeling will be a task which needs to be undertaken by the instrument manufacturers. Hitachi High Technologies has had the vision to recognize this important task and placed a Guest Researcher (Ms. Maki Tanaka) at NIST to learn about electron beam interaction modeling. Several excellent publications resulted from this work.

For any nanoparticle, effective sample preparation is also a barrier which needs to be overcome as minor contaminants can readily obscure sample detail. The ability to view simultaneously nanomaterials in an STEM with secondary, backscattered and transmitted electron detection modes at ultra high resolution is a capability which is available today and can be successfully utilized in nanomaterial characterization and dimensional metrology.

Acknowledgements

We wish to thank and acknowledge Mr. Hideo Naito, Mr. Robert Gordon and Mr. Roger Teppert of Hitachi High Technologies, USA for their assistance in obtaining the instrumentation and Mr. Greg Rigby, Neil Wagoner and Mel Hawes for maintaining the instrument at such high levels of performance.

References

1) Subcommittee on Nanoscale Science, Engineering, and Technology (NSET) of the Committee on Technology of the National Science and Technology Council. 2006. Instrumentation and metrology for nanotechnology: Report

of the National Nanotechnology Initiative workshop January 27-29, 2004. Washington, DC: NSET. http://www.nano.gov/html/res/pubs.html.

2) NSET. 2007a. The National Nanotechnology Initiative strategic plan. Washington, DC: NSET. http://www.nano.gov/html/res/pubs.html.

3) NSET 2007b. Manufacturing at the nanoscale. Report of the National Nanotechnology Initiative workshops, 2002-2004. Washington, DC: NSET. http://www.nano.gov/html/res/pubs.html.

4) IWG, 2008. Interagency Working Group on Manufacturing Research and Development. Instrumentation, Metrology and Standards for Nanomanufacturing http://www.nano.gov/html

5) Farrow, R. C., Postek, M. T., Keery, W. J. Jones, S. N., Lowney, J. R., Blakey, M., Fetter L, Hopkins, L. C., Huggins, H. A., Liddle, J. A., Novembre, A. E., and Peabody, M. 1997. Application of transmission electron detection to SCALPEL mask metrology. J. Vac. Science and Technol. B. 15(6):2167-2172.

6) Liddle, J. A. Blakey, M. I., Saunders, T., Farrow, R. C., Fetter, L. A., Knurek, C. S., Novembre, A. E., Peabody, M. L., Windt D. L. and. Postek M. T. 1997. Metrology of SCALPEL masks. J. Vac. Science and Technol. B. 15(6):2197-2203.

7) Postek, M. T., Lowney, J. R., Vladár, A. E., Keery, W. J., Marx, E. and Larrabee, R. D. 1993. X-ray Lithography Mask Metrology: Use of Transmitted Electrons in an SEM for Linewidth Measurement. NIST J. Res. 98:415-445.

8) Postek, M. T. 1990. Low Accelerating Voltage SEM Imaging and Metrology using Backscattered Electrons. Rev. Sci. Instrum. 61(12):3750-3754.

9) Postek, M. T., Villarrubia, J. and Vladár, A. 2005. Advanced Electron Microscopy Needs for Nanotechnology and Nanomanufacturing. J. Vac. Sci. Technol. B, Vol. 23, No. 6, Nov/Dec 2005 3015-3022.

10) Joy, D. C. and Luo, S. 1989. An Empirical Stopping Power Relationship for Low-Energy Electrons. Scanning 11, 176-180

11) Lin, Y. and Joy, D.C. 2005. A new examination of secondary electron yield data. Surf. Interface Anal. 37, 895-900

12) Villarrubia, J. S., Vladár, A. E. and Postek, M. T. 2005. A Simulation Study of Repeatability and Bias in the CD-SEM. J. Microlith. Microfab. Microsyst. 4, 033002.

13) Villarrubia, J. S., Vladár, A. E., and M. T. Postek. 2005. Scanning electron microscope dimensional metrology using a model-based library. Surf. Interface Anal. 37, 951-958.

14) Lowney, J. R. 1996. Application of Monte Carlo simulations to critical dimension metrology in a scanning electron microscope. Scanning Microscopy 10, 667-678.

15) Lowney, J. R. 1996. Monte Carlo simulation of scanning electron microscope signals for lithographic metrology. Scanning 18, 301-306.

16) Davidson, M. P. and Vladár, A. E. 1999. An inverse scattering approach to SEM line width measurements. Proc. SPIE 3677, 640-649.

17) Ding, Z.-J. and Shimizu, R. 1996. A Monte Carlo Modeling of Electron Interaction with Solids Including Cascade Secondary Electron Production. SCANNING 18, 92-113.

18) Mao, S.F., Li, Y.G., Zeng, R.G. and Ding, Z.-J. 2008. Electron inelastic scattering and secondary electron emission calculated without the single pole approximation. J. Appl. Phys. 104, 114907.

19) Kieft, E. and Bosch, E. 2008. Refinement of Monte Carlo simulations of electron-specimen interaction in low-voltage SEM. J. Phys. D: Appl. Phys. 41, 215310.

20) Postek, M.T., Howard, K.S., Johnson, A.J., and McMichael, K. 1980. Scanning Electron Microscopy—A Student Handbook. Ladd Research Industries, 305 pp.

21) Ngo, V. V., Hernandez, M., Roth, B. and Joy, D. C. 2007. STEM imaging of lattice fringes and beyond in a UHR in-lens field-emission SEM. Microscopy Today, March Issue pp. 12-16.

22) A. F. Mamedov, A. F., Kotov, N. A., Prato, M., Guldi, D., Wicksted, J. P. and Hirsch, A. 2002. Molecular design of strong single-wall carbon nanotube/polyelectrolyte multilayer composites. Nature Materials 1, 190-194.

23) Zhou, A. O., Shimoda, H., Gao, B., Oh, S., Fleming, L. and Yue, G. 2002. Materials science of carbon nanotubes: fabrication, integration and properties of macroscopic structures of carbon nanotubes. Acc. Chem. Res. 35, 1045-1053.

24) Kong, J., Franklin, N. R., Zhou, C., Chapline, M. G., Peng, S., Cho, K. and Dai, H. 2000. Nanotube molecular wires as chemical sensors. Science, 287, 622-625.

25) Avouris, P. 2002. Molecular electronics with carbon nanotubes. Acc. Chem. Res., 35, 1026-1034.

26) Dai, H. 2002. Carbon nanotubes: synthesis, integration, and properties. Acc. Chem. Res. 35, 1035-1044.

27) https://www-s.nist.gov/srmors/view_detail.cfm?srm=8011

28) https://www-s.nist.gov/srmors/view_detail.cfm?srm=8012

29) https://www-s.nist.gov/srmors/view_detail.cfm?srm=8013