AC 2012-5101: PREPARING THE 21ST CENTURY GLOBAL WORKFORCE IN MICRO- AND NANOSCALE FABRICATION AND CHARACTERIZATION IN THE FIRST TWO YEARS OF ENGINEERING EDUCATION

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Preparing the 21st Century Global Workforce in Micro- and Nanoscale Fabrication and Characterization in the First Two Years of Engineering Education

Abstract

There is a world-wide demand for smaller and faster electronic devices. As a result, there is an increasing need for a global workforce familiar with the basics of micro- and nanoscale fabrication and characterization. This workforce will come primarily from post secondary institutions. For this reason, it is important for nanotechnology instructors at non-research based post secondary institutions to provide laboratory exercises that introduce students to the fundamental concepts associated with fabrication and characterization on the micro- and nanoscale. Additionally, these laboratory exercises need to encourage student understanding and appreciation of differences that exist among US and international research institutions pursuing nanotechnology related goals. Presented in this manuscript are two laboratory exercises used to introduce students to top-down and bottom-up fabrication and characterization. Both laboratory exercises utilize one or more of the following characterization techniques; atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and UV-VIS spectroscopy. At the end of each laboratory exercise, post lab assessments were administered to gauge student understanding of the concepts involved in each laboratory exercise. Additionally, a two-page literature review of nanotechnology related research conducted in the United States and internationally was assigned in an effort to provide global awareness regarding nanotechnology research and development efforts globally.

Introduction

Nanotechnology related research has increased globally over the past several years [1]. Due to the technological promise of nanotechnology, the US Government established the National Nanotechnology Initiative (NNI) in 2001[2]. Soon after the establishment of the NNI, similar initiatives were created in Australia, Canada, Europe, and Japan[2]. To prepare first and second year undergraduate engineering students for entry into the global nanotechnology workforce, two laboratory exercises were created that incorporate three educational objectives regarding nanotechnology education, based on Bloom's Taxonomy[3]. These objectives involve hands-on experiences with top-down and bottom-up methods of fabrication, comparing the two fabrication methods, and learning how to use advanced nanoscale instrumentation[3]. Additionally, the laboratory exercises include a literature review assignment to promote student appreciation and awareness of international nanotechnology research and developments.

Educational Objective 1: Micro- and Nanofabrication Experiences

Exposing college level science and engineering students to laboratory exercises in top-down and bottom-up fabrication is necessary due to the need for micro- and nanoscale artifacts for fundamental investigations and technological applications[4]. Meenakshi et al.[5]report that the increasing importance of nanofabrication in the fields of microelectronics, optoelectronics, and biomedical applications has prompted the creation of undergraduate curricula related to these topics. Top-down fabrication involves using macroscale systems to create micro- and nanoscale features, and bottom-up refers to using individual atoms or molecules to fabricate micro- and nanoscale features[6]. The following paragraphs describe simple, low cost laboratory exercises that demonstrate top-down and bottom-up fabrication.

The top-down laboratory exercise involves the use of soft lithography. In soft lithography, a patterned, elastomeric stamp is employed to generate micro- or nanoscale structures on flat substrates[7]. Soft lithography is an ideal introductory nanofabrication exercise because this technique is inexpensive, easy to learn, and the materials are easily accessible[7]. The elastomeric stamps used for soft lithography are made from polydimethylsiloxane (PDMS).

Micro-molding in capillaries (MIMIC) is the soft lithography technique implemented in the top-top down laboratory exercise. In this technique, a patterned stamp is placed on the surface of a substrate and the channels are filled with a polymer or liquid[7] (Figure 1). The polymer cures or the solvent evaporates leaving behind a patterned surface.

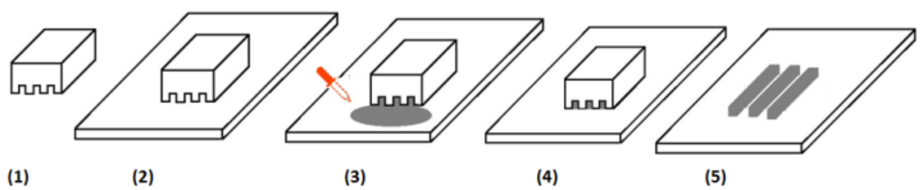

Figure 1. The MIMIC procedure. A clean dry stamp (1) is place in direct contact (patterned side down) with a flat, clean solid substrate (2). A fluid, i.e. polymer precursor, is placed at the opening of the channels and the fluid is drawn into the channels via capillary action (3). The solvent component of the fluid is allowed to dry (4) and the stamp is removed leaving behind patterned material (5).

The bottom-up laboratory exercise relies on a single replacement reaction between copper metal and dilute silver nitrate solutions to create silver nanowires. This silver nanowire synthesis is reported by Jiang et al.[8]. Their report describes a synthesis of silver nanowires using a single replacement reaction involving the oxidation of neutral metal atoms (Fe^0 and Cu^0), and the reduction of metal cations (Ag^+). The net ionic equation for the single replacement reaction is shown in Equation 1.

$$\text{Equation 1: } M^0_{(s)} + A^+_{(aq)} \rightarrow A^0_{(s)} + M^+_{(aq)}$$

Educational Objective 2: Compare and contrast top-down and bottom-up nanofabrication

Post lab assessments are included to gauge student understanding of top-down and bottom-up fabrication. It is expected for students to understand that soft lithography (MIMIC) is a top-down nanofabrication process because the PDMS stamp, a macroscale system, is used to make nanoscale structures that require the use of an AFM to see. Students are also expected to understand that the silver nanowire laboratory exercise involves bottom-up fabrication due to the reorganization of atoms and ions to form silver nanowires. The post lab assessments also gauge student understanding of the MIMIC process, AFM operation and measurements, single replacement reactions, SEM operation, EDS analysis, and sputter coating.

Educational Objective 3: Student exposure to surface characterization techniques.

The third educational objective as reported by Sweeny and Seal[3] involves student use of nanoscale characterization instrumentation. In the top-down fabrication lab, the nanoscale patterns generated using soft lithography requires characterization using AFM (Figure 2). This technique involves rastering a pyramidal tip with a nominal radius of 10 nm across a sample of interest with a piezoelectric scanner[9]. During the course of AFM characterization, students are exposed to the two most common operating modes of AFM, contact mode and tapping mode. In contact mode AFM, images of nano- and microscale structures are produced by monitoring the deflection of a cantilever as the tip makes direct, uninterrupted contact with the sample surface[10]. Tapping mode AFM involves oscillating the cantilever at its resonant frequency while in close proximity to the sample surface. As the cantilever oscillates, the tip makes intermittent contact with the sample surface. Changes in the vibrational amplitude of cantilever oscillation are used to generate tapping mode AFM images[10].

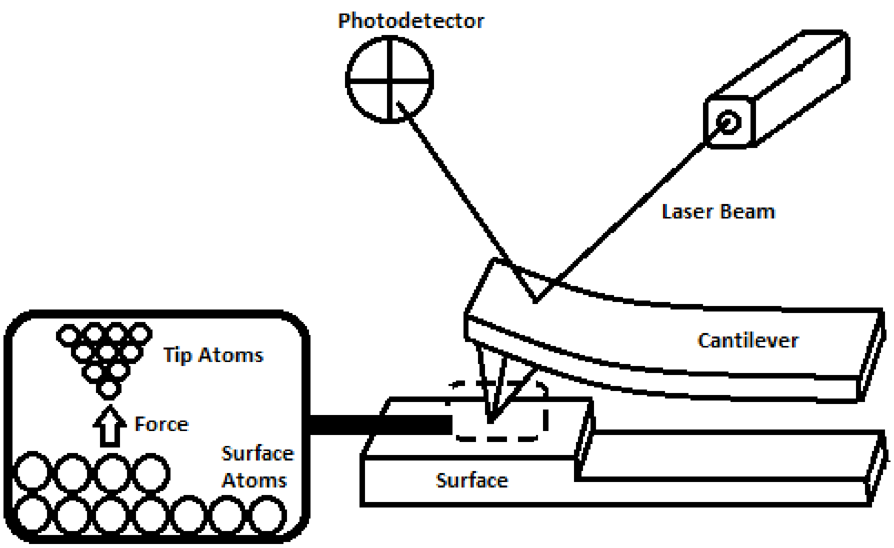

Figure 2. Schematic illustrating AFM operation.

In the bottom-up laboratory exercise, students use a variety of microscopic and spectroscopic techniques to characterize silver nanowires. These characterization techniques include AFM, SEM, EDS, and UV – VIS spectroscopy. SEM utilizes a beam of electrons to examine sample surfaces (Figure 3). When striking the surface of samples, electrons and x-rays are released. Sensors amplify and process the removed electrons and x-rays to produce topographic and elemental maps respectively[11]. EDS is a measure of the energy of x-rays given off when the electron beam of a SEM strikes sample surfaces. The energy of the x-rays is dictated by the nature of the material bombarded with electrons[11]. Therefore, EDS is able to identify which elements are present in a sample.

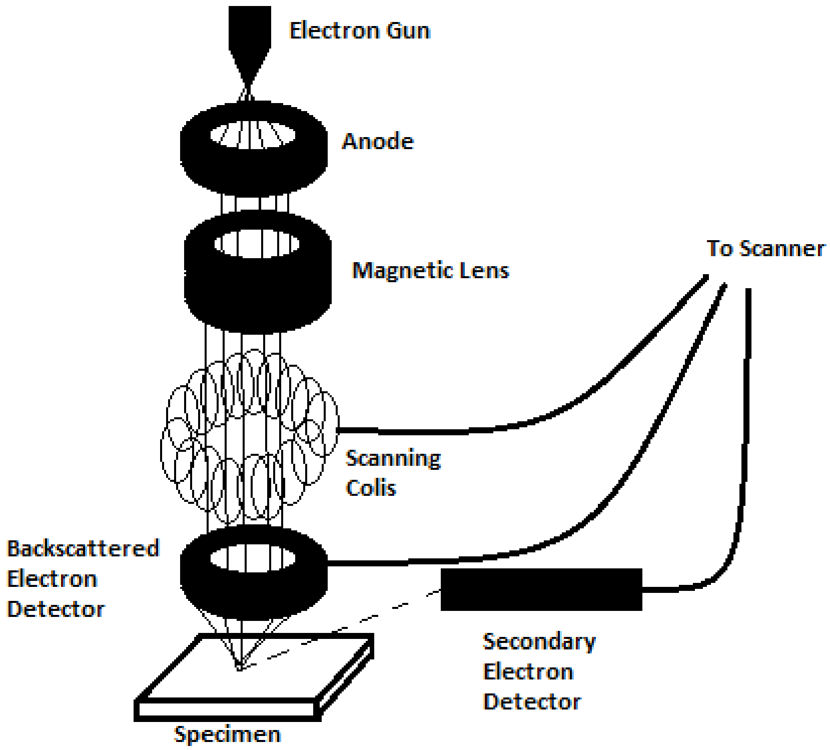

Figure 3. Schematic illustrating SEM operation.

An additional spectroscopic measurement in the bottom-up fabrication lab includes UV-VIS spectroscopy. In these measurements, a spectrophotometer (Figure 4) sends electromagnetic radiation in the visible spectrum through a sample (I_0)[11]. This radiation passes through the sample (I_T) reaching a detector that generates a signal indicating the wavelength(s) of light absorbed by the sample or the percent of light transmitted through the sample[11].

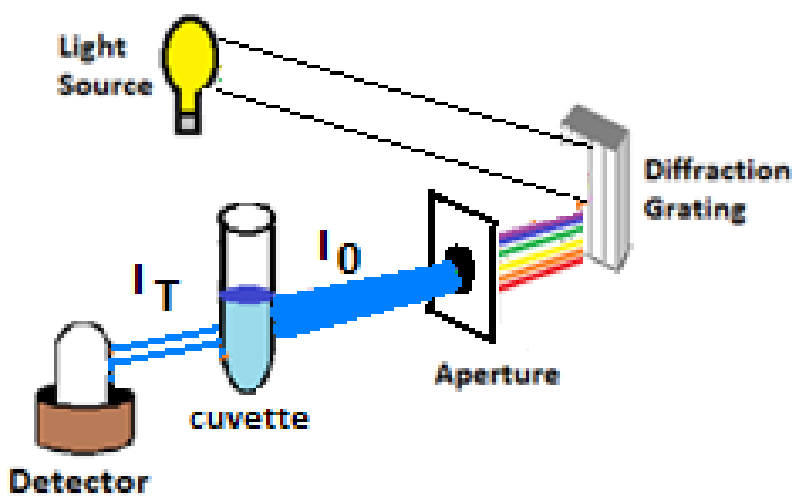

Figure 4. Schematic illustrating UV-VIS spectrophotometer operation.

Educational Objective 4: Global engineering perspectives

A fourth education objective deals with promoting student understanding and appreciation of global efforts in nanotechnology research. The importance of incorporating global perspectives in engineering education is supported by Jesiek et al.[12]. They state that global engineering education is important because it promotes continued innovation in engineering curriculum and ensures the employability and mobility of engineering graduates. The authors state further that studying papers published in international journals and conference proceedings can provide evidence for how boundaries around scientific research worldwide are established and maintained. Encouraging students to consider global perspectives while in engineering programs results in students becoming globally competent engineers. A globally competent engineer is able to work effectively with people who approach scientific and engineering challenges differently[13].

In an effort to promote student appreciation of international perspectives on engineering, a post lab literature review was assigned. In this assignment, students were required to write a literature review that compares US and international developments in scanning probe microscopy or research involving intensive use of scanning probe microscopy.

Results

Execution

In the top-down laboratory exercise, six students in an introductory scanning probe microscopy course worked individually. In the bottom-up laboratory exercise, fourteen students enrolled in an introductory nanotechnology course worked individually. Students majoring in engineering or the physical sciences were among those participating. Students signed up for an hour and a half worth of lab time outside of class for imaging and spectroscopy characterization.

Educational Objective 1: Micro- and Nanofabrication Experiences

Results of the top-down nanofabrication laboratory exercise are shown in Figures 5a and 5b. Figure 5a shows a student AFM image of the corrugations on the surface of CD-R gold. After orienting a patterned stamp perpendicular to the grooves on the corrugated CD-R gold, filling the channels of the patterned stamp with an alcoholic salt solution, and allowing evaporation of the alcohol solvent, nanoscale crystal patterns were formed. Student AFM analysis of the resulting sample revealed linear, magnesium sulfate crystal structures perpendicular to the gold bars (Figure 5b). The salt structures can be distinguished from the gold bars based on a qualitative examination of the pattern in Figure 5b. Students are taught that in 2-D AFM images, height differences are indicated using a color gradient. Higher features are lighter and lower features are darker. There are features in Figure 5b that are darker and perpendicular to lighter structures, therefore the assumption can be made that the darker features are the salt structures.

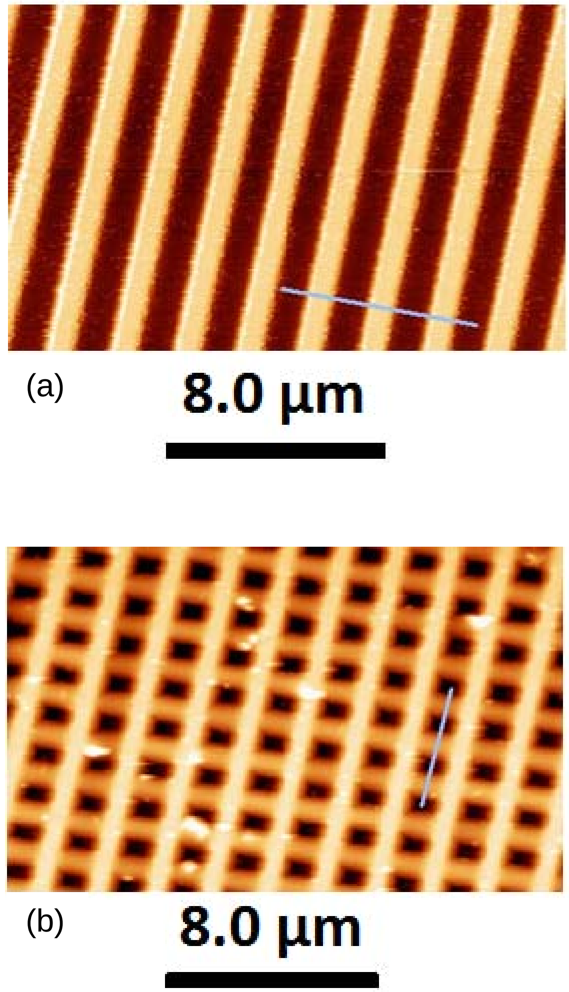

Figure 5. AFM image of CD-R gold (a) and a salt pattern on CD-R gold (b).

Results of the bottom-up nanofabrication exercise are shown in Figure 6a. Figure 6a shows a student generated AFM image of silver nanowires. This image suggests that silver nanowires are formed when students add approximately 1.5-2 mL of dilute silver nitrate solution to a plate sputtered with copper metal. Silver wires with varying lengths and diameters were generated according to Equation 2:

$$\text{Equation 2: } Cu_{(s)} + 2\ AgNO_{3(aq)} \rightarrow Cu(NO_3)_{2\ (aq)} + 2\ Ag_{(s)}$$

A cross sectional profile (Figure 6b) generated from student AFM data indicates that the silver nanowires have diameters of approximately 280 nm. A student generated SEM image (Figure 7) indicates that wires with varying diameters are formed during the course of the reaction.

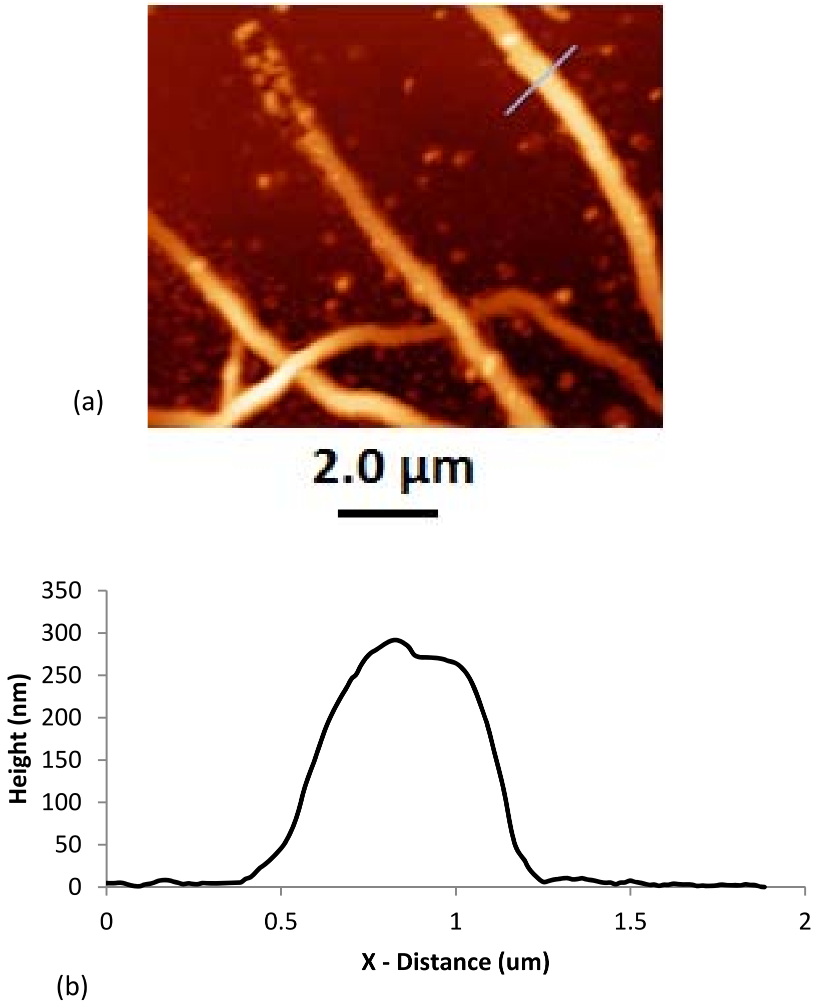

Figure 6. A 10 um x 10 um AFM scan of silver nanowires (a) and a cross sectional analysis of silver nanowires (b).

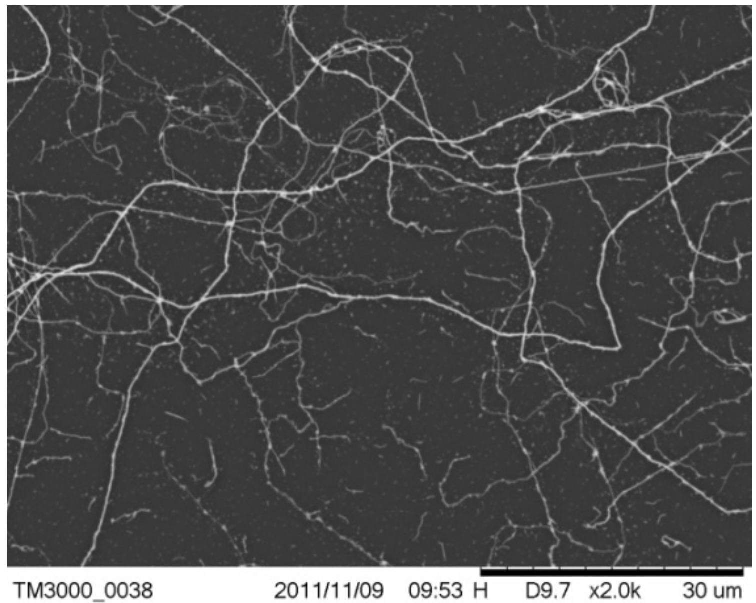

Figure 7. 2000X SEM images of silver nanowires.

Educational Objective 2: Compare and contrast top-down and bottom-up nanofabrication

Post lab assessments were given to the students after completion of both laboratory exercises. Both post lab assessments were used to gauge student understading of soft lithography, the MIMIC process, AFM operation, AFM measurements, single replacement reactions, SEM operation, EDS analysis, and sputter coating. The results of the post lab assessment for the top-down laboratory exercise suggest that the students understood the operation of MIMIC as well as the role of AFM in surface characterization (2-D and 3-D renderings, cross sectional profiles). However the post lab assessment for the bottom-up laboratory exercise indicated that the students had difficulty grasping concepts associated with the single replacement reaction responsible for generating the nanowires.

Educational Objective 3: Student exposure to surface characterization techniques.

During the course of the SEM imaging, students concurrently performed an EDS analysis of the silver nanowires (Figure 8). They found that the samples generated a peak at 3 keV. A question on the post lab assessment for this laboratory exercise required students to compare their experimental EDS value to the reported EDS value for silver nanowires found in the literature. Students discovered that 3 keV is the accepted EDS value for silver nanowires[14-18].

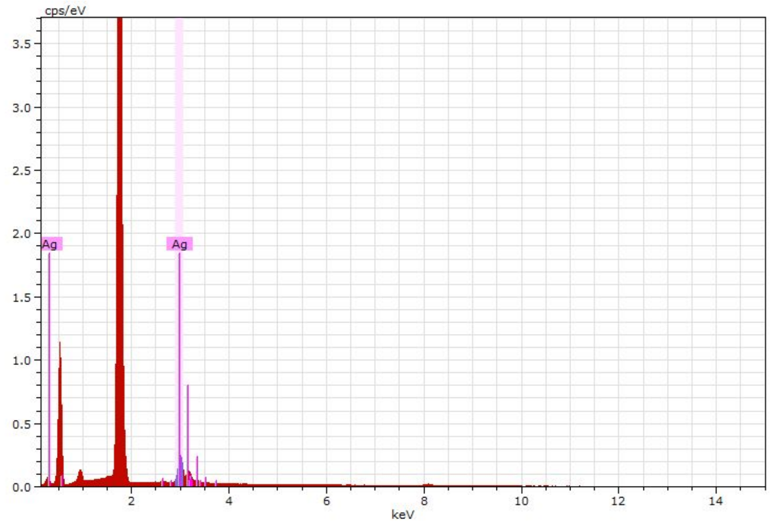

Figure 8. EDS spectra of silver nanowire sample.

The silver nanowire laboratory exercise also included student exposure to UV-VIS characterization. Students accomplished this analysis using a Vernier SpectroVis Plus spectrophotometer. The most intense absorbance peaks were observed at 402 nm and 459 nm. The maximum absorbance at 402 nm is consistent with reported UV-VIS analyses of silver wires[19-20]. It is believed that the maximum absorbance observed at 459 nm is due to the presence of larger silver wires, particularly silver wires with thicker diameters[21].

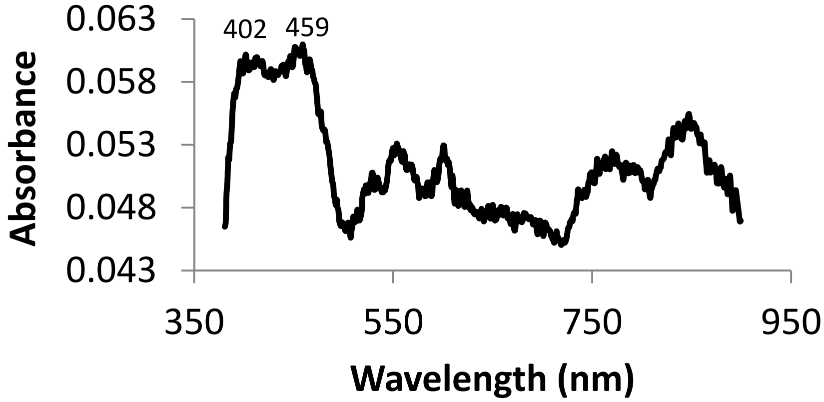

Figure 13. UV-VIS spectra of silver wires dispersed in de-ionized water.

Educational Objective 4: Global engineering perspectives

Students successfully compared nanotechnology related research and development occurring in the United States and internationally. In the assigned literature review paper, students realized that US and international research institutions pursued interests with similar methodologies. Students realized that although cultural and language differences exist, global pursuits in understanding the fundamental concepts and utility of nanotechnology involves using similar research strategies and identical characterization techniques.

Summary

All of the learning objectives as stated by Sweeny and Seal[3] were met in the laboratory exercises described in this manuscript. Students successfully used top-down and bottom-up nanofabrication schemes to generate structures that required specialized microscopy to view. Students were able to view the resulting structures using AFM and SEM. Students also obtained additional characterization experience by using EDS and UV-VIS spectroscopy to confirm production of silver nanowires. Results of post lab assessments administered at the end of each laboratory exercise suggest that students understood the difference between top-down and bottom-up nanofabrication, the role of the sputter coater, SEM operation, AFM operation, and the basics of EDS. The results also indicate concepts not readily understood by the students dealt with the single replacement reaction between the copper metal and dilute silver nitrate solutions. To increase student understanding of the chemistry behind the reaction used to make silver nanowires, animations, video clips, and an additional single replacement demonstration (i.e. reaction between iron and copper sulfate) will be used in the future to reinforce the concept of single replacement reactions. Student literature reviews indicate that students realized that nanotechnology related endeavors in the United States are being pursued internationally as well. The literature reviews suggest that students also realize that US and international researchers follow similar methodologies and use identical microscopic and spectroscopic characterization techniques in nanotechnology related research.

Literature Cited

1. Heinze, T. *Nanotechnology Law and Business*. **2004**, *1*, 1-19.

2. Sweeny, A. E.; Seal, S.; Vaidyanathan, P. *Nanoscience and Nanotechnology*. **2003**, *23*, 236-245.

3. Sweeny, A. E.; Seal, S. Nanoscale Science and Engineering Education; American Scientific Publishers: Stevenson Ranch, 2008.

4. Porter, L. A.; Choi, H. C.; Schmeltzer, J. M.; Ribbe, A. E.; Elliot; L. C. C.; Buriak, J. M. *Nano* Letters. **2002,** *2*, 1369.

5. Meenakshi, V.; Babayan, Y.; Odom, T. W. *J. Chem. Educ.* **2007,** *84*, 1795-1798.

6. Lyman, B. M.; Farmer, O. J.; Ramsey, R. D; Lindsey, S. T.; Stout, S.; Robison, A.; Moore, H. J.; Sanders, W. C. Journal of Chemical Education. 2012, 89, 401-405.

7. Xia, Y.; Whitesides, G. M. *Annu. Rev. of Mater. Sci.* **1998,** *28*, 153-184.

8. Jiang, Z. Y.; Xie, Z. X.; Zhang, S. H.; Xie, S. Y.; Huang, R. B.; Zheng, L. S. *Chem. Phys. Lett.* **2003**, 374, 645-649.

9. Meyer, E.; Hug, H. J.; Bennewitz, R. Scanning Probe Microscopy The Lab on a Tip; Springer: Berlin, 2004.

10. Eaton, P.; West, P. Atomic Force Microscopy; Oxford, New York, 2010.

11. Joshi, M.; Bhattacharyya, A.; Ali, S. W. *Indian J. of Fibre Text. Res*. **2008**, *33*, 304-317.

12. Jesiek, B., Borrego, M., & Beddoes, K.. "Expanding Global Engineering Education Research Collaboration," *SEFI Annual Conference Proceedings*, 2008.

13. Downey, G. L.; Lucena, J. C.; Moskal, B. M.; Parkhurst, R.; Bigley, T.; Hays, C.; Jesiek, B. K.; Kelly, L.; Miller, J.; Ruff, S. *Journal of Engineering Education*. **2006**, *95*, 1-16.

14. Caswell, K. K.; Bender, C. M.; Murphy, C. J. *Nano Lett*. **2003**, 3, 667-669.

15. Wiley, B. J., Im, S. H., Li, Z. Y.; McLellan, J., Siekkinen, A., Xia, Y. *J. Phys. Chem. B.* **2006**, 110, 15666-15675.

16. Ditlbacher, H., Hohenau, A.; Wagner, D., Kreibig, U., Rogers, M., Hofer, F., Aussenegg, F. R., Krenn, J. R. *Phys. Rev. Lett.* **2005**, 95, 1-4.

17. Zhang, D.; Qi, L.i; Ma, J.; Cheng, H. *Chem. Mater*. **2001**, 13, 2753-2755.

18. Jiang, Z. Y.; Xie, Z. X.; Zhang, S. H.; Xie, S. Y.; Huang, R. B.; Zheng, L. S. *Chem. Phys. Lett.* **2003**, 374, 645-649.

19. Yang, Z.; Qian, H.; Chen, H.; Anker, J. N. *J. Colloid Interface Sci*. **2010**, 352, 285-291.

20. Yin, Y.; Lu, Y.; Sun, Y.; Xia, Y. *Nano Lett*. **2002**, 2, 427-430.

21. Zhou, J.; Zhou, G.; Wang, R.; Lu, M. *Mater. Sci. - Pol*. **2009**, 27, 73-78.