

Review

Analysis and Modifications of 1D Nanostructures by Lukáš Kachtík

Doctoral thesis presented to the Brno University of Technology

Lukáš Kachtík's thesis deals with the microstructural analysis of 1D nanostructures, with the goal of identification and quantitative assessment of critical parameters. Three materials systems, InAs and Ge nanowires, oxidized WS₂ nanotubes, and WS₂ nanotubes, are addressed. The analysis is based on TEM and Raman Spectroscopy. The InAs NW study and oxidation study of the WS₂ nanotubes is taking the minor part of the thesis. The InAs nanowire analysis stays superficial and could have been omitted from the thesis. More depth could have been gained for instance for the size-phase relationship observed in pure InAs nanowires, meaning that thin nanowires condense in the hexagonal structure not observed in bulk InAs, not mentioned in the thesis.

The rewarding part to read is the attempt to extract crucial parameters of the WS₂ TMDC nanotubes from Raman measurements and TEM diffraction and to correlate between these methods. Having worked a lot with similar questions, I do understand the effort that is required to find a one-to-one correlation between, for instance, the details of a Raman spectrum and the size or number of shells of a nanotube.

I enjoyed reading the chapter on Raman Spectroscopy on the WS₂ nanotubes, as it clearly demonstrates the difficulties when working with a real-world sample that cannot be prepared reproducibly with a structural monodispersity. To address the latter issue, Lukáš Kachtík did correlate SEM, TEM, and Raman measurements to find that even with careful attention to reproducibility and detail in the measurements, the statistically solid result is not straightforward to achieve. There are amendments that the thesis could have benefitted from in chapter 3: (1) The conclusions which focus to take, and which substrate are adequate when based on an engineering approach. Formulating a hypothesis why the measurements are condition-dependent and substrate-related would have been a welcome extra to promote a scientific discussion. (2) The ground truth for the relation of the ratio of the in-plane and out-of-plane Raman vibrational modes in nanotubes is not known. Therefore I'd have expected to see reference measurements on bulk platelets of WS₂, to be able to judge how much the measurements reflect expectations on a known and more ideal system and how much of a reproducibility error we have to account for in an otherwise ideal sample.

Most rewarding was the study of the chirality by TEM and the decoration of the outermost shell by Au nanoparticles. The analysis of the diffraction patterns is scientifically sound and correct and the writing-up of it is a good tutorial. Most important Lukáš Kachtík found a solution to process electron diffraction data, and to do this in a statistical manner to prove that scrolling of the nanotube shells is one of the growth phenomena and moreover, that the shell terraces are terminated in a zig-zag configuration. The only point I am missing here is the verification by high-resolution STEM images of such kind of surface terrace termination for direct verification, for a few selected cases.

Minor comments concern the conciseness of the citations in the introductory chapter 1 and a description of the utilized TEM equipment:

- on page 4 the discussion of the knock-on damage relates to a recent materials study while the mechanisms are disclosed by the McKinley Feshbach publication dated to 1948.
- Radiation damage mechanisms are described superficially on page 5 while a brief citation to Ray Egerton's publications would have been better.

- An explanation of the difference between a diffraction pattern and an FFT for Fig. 1.3 is in place.
- Section 1.2 on Energy- dispersive X-ray spectroscopy ends with “ .. but still an operator needs to be aware of its limitations.” The obvious limitation relating to Fig. 1.7 is the overlap between Mo and S lines, it would be in place to mention it in this section to support the argument.
- The description of the equipment for Raman spectroscopy is extensive, but there is no specification of the TEM instrumentation that was used. I suggest to complete with this description at the end of section 1.2 before section 1.3.

In summary, I am pleased with the thesis, its technical preparation, and the scientific approaches. *I recommend Ph.D. graduation.*

Questions for the defense exam

- (1) Relating to the focus effect of the Raman characterization of the A1g/E2g ratio (Fig. 3.8.): Did you measure the effect of the laser power from a constant focus? Can you rule out non-linear effects emerging from a focussed beam, e.g. for the absorption? Can you elaborate on an explanation?
- (2) Relating to the modulation of the E2g component with polarisation angle, Fig. 3.13: There is symmetry in the polar plot of the magnitude of E2g vs the polarization angle, the expected two-fold symmetry with maxima around 90 degrees/270 degrees. But there is also a fourfold symmetry with a Larmor angle of 45 degrees. Can we understand these symmetries?
- (3) Chirality vectors (m,n) in graphene were adopted for the TMDC nanotube in the thesis. Can you directly translate (m,n) vectors used in the terminology for graphene to the hexagonal TMDCs? Think about the unit cell definitions.
- (4) Chirality determination from TEM diffraction patterns: Your automated processing did not use the six-fold symmetry. How could you use symmetry to get a more reliable quantification of the chiral angle?
- (5) Can you see chirality from an FFT of an image?
- (6) Challenging bonus question: You've shown iDPC images of oxidized nanotubes in Fig. 4.3. Do you think that differential phase contrast images at atomic resolution can help distinguish a chiral outer shell on a WS₂ nanotube from an armchair or zig-zag tube?

In Israel, April 12th, 2023

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Dr. Lothar Houben, Ph.D.