Lawrence Berkeley National Laboratory
Lawrence Berkeley National Laboratory

Title

Sub-Angstrom electron microscopy for sub-Angstrom nano-metrology

Permalink

https://escholarship.org/uc/item/6x20k458

Authors

O'Keefe, Michael A.
Allard, Lawrence F.

Publication Date

2004-01-18

eScholarship.org Powered by the California Digital Library
University of California

Sub-Ångstrom Electron Microscopy for Sub-Ångstrom Nano-Metrology

Michael A. O'Keefe* and Lawrence F. Allard[#]

**Materials Sciences Division, LBNL 2-200, Berkeley, CA 94720, USA*

[#]High Temperature Materials Laboratory, ORNL 4515-6064, Oak Ridge, TN 37831, USA

National Nanotechnology Initiative Workshop on
Instrumentation and Metrology for Nanotechnology
Gaithersburg, Maryland
Jan. 27-29. 2004

https://metrology.nano.gov./

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory is an equal opportunity employer.

Ernest Orlando Lawrence Berkeley National Laboratory – LBNL-54332

Sub-Ångstrom Electron Microscopy for Sub-Ångstrom Nano-Metrology

Michael A. O'Keefe* and Lawrence F. Allard[#]

**Materials Sciences Division, LBNL 2-200, Berkeley, CA 94720, USA*
[#]High Temperature Materials Laboratory, ORNL 4515-6064, Oak Ridge, TN 37831, USA

The revolution in nanoscale science and technology requires instrumentation for observation and metrology – we must be able to see and measure what we build. Because nano-devices operate on the level of a few molecules, or even a few atoms, accurate atomic-scale imaging is called for. **High-resolution aberration-corrected electron microscopes (both TEM and STEM) can provide valuable measurements at the sub-Ångstrom level.**

In general, resolution is accepted as the ability to determine if an image feature represents two objects rather than one. Rayleigh's original resolution criterion, the accepted standard in optics, was derived as a yardstick for judging when two sources of light (stars) could be distinguished from a single source [1]. In the field of microscopy, resolution has continued to be based on the ability to determine if detail in an image represents distinct (separated) objects. In high-resolution electron microscopy these objects are atoms. A resolution of $|\mathbf{d}|$ is achieved when atoms separated by a (projected) distance $|\mathbf{d}|$ can be perceived as separate objects. Although demonstration of resolution $|\mathbf{d}|$ requires the presence of the corresponding spatial frequency $1/|\mathbf{d}|$ in the TEM image spectrum, the mere presence of the $1/|\mathbf{d}|$ frequency is not sufficient to validate a corresponding resolution of $|\mathbf{d}|$ [2]. Similarly, in a scanning transmission electron microscope (STEM), a probe size of $|\mathbf{d}|$ is a necessary, but not sufficient, requirement to achieve a resolution of $|\mathbf{d}|$.

Test samples with atoms separated by known amounts can be used to measure sub-Ångstrom resolutions. Specimens with diamond cubic and zincblende structures can be oriented to provide pairs of atoms in "dumbbell" configurations with well-characterized separations ranging from 1.6Å to 0.5Å. Figure 1 shows spacings available from some test specimens [3], together with images obtained at resolutions of 0.89Å and 0.78Å in the LBNL One-Ångstrom Microscope (OÅM), a modified HRTEM [4]. Similar images have been obtained using HR-STEMs [5, 6]. Many nanodevices use interfaces on [110] and [112] planes.

To properly characterize nanomaterials, it is important to be able to see all the atoms, even the light ones. Improved resolution has the advantage of narrowing the peaks corresponding to heavy atoms, thus allowing the lighter atom peaks to become visible. The OÅM has demonstrated that sub-Ångstrom resolution gives us the ability to image lithium, the lightest of all metal atoms. Figure 2 shows peaks corresponding to the positions of cobalt, oxygen and lithium atoms in the lithium battery material, $LiCoO_2$ [7].

Characterization of catalyst nanoparticles requires knowledge of the internal structures of the particles as well as their shapes. As well as revealing atom column positions, sub-Ångstrom phase-image microscopy can also provide a good estimate of the number of atoms making up each column in a single-atom-species particle [8]. Figure 3 shows a gold nanoparticle with each atom column visible as a white peak. The arrangement of the atom columns reveals the shape of the 70Å diameter particle, as well as the fact that it is multiply-twinned.

Over the next decade, extension of TEM and STEM resolutions to half-Ångstrom levels by next-generation aberration-corrected electron microscopes will advance the capabilities of these essential tools for atomic-scale structural characterization [9]. Because improvements in resolution allow for separation of atom columns in many more projection directions, these microscopes will provide much improved three-dimensional characterization of the shape and internal structure of nanodevices and catalyst nanoparticles (perhaps even true 3-D imaging), and hence provide essential feedback in the nano-theory/construction/measurement loop [10].

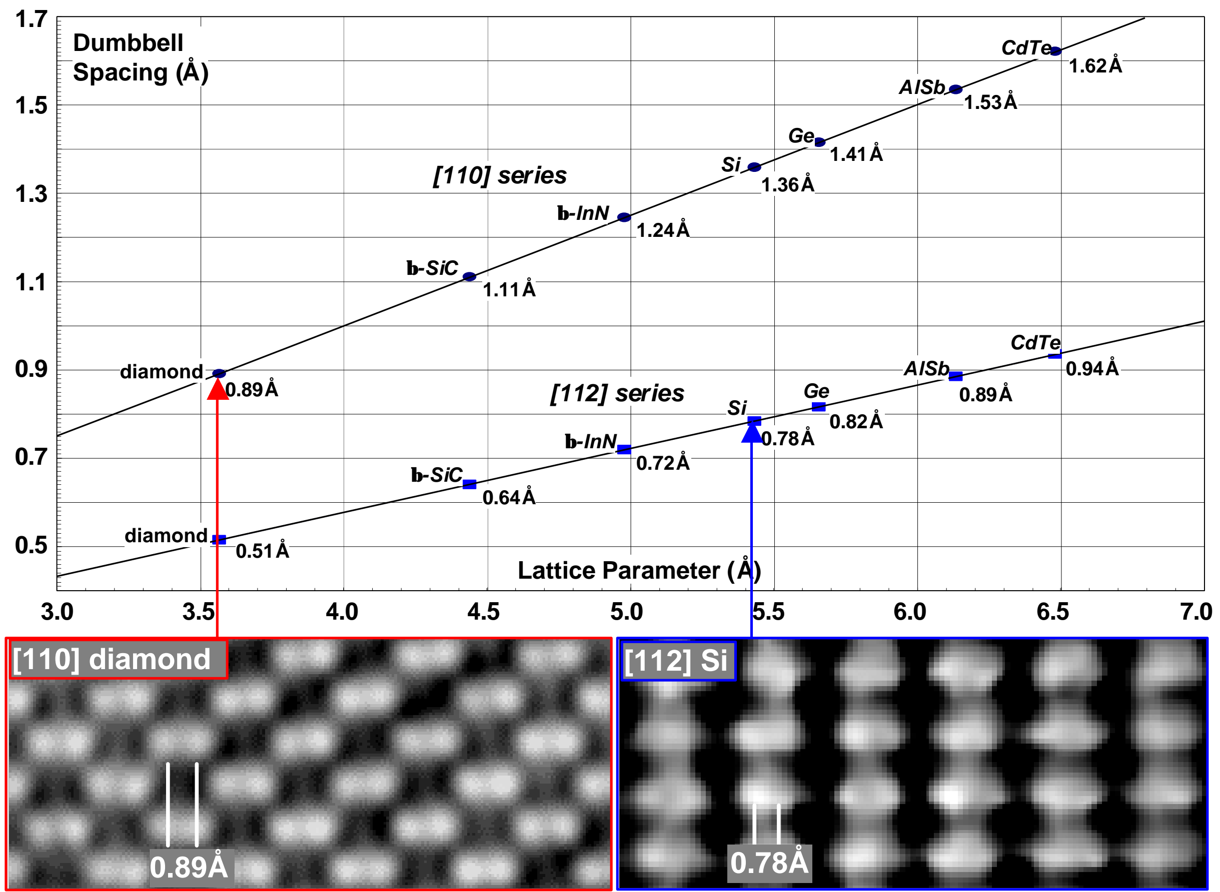

Fig. 1. Test specimens can provide separations of atom columns in atomic "dumbbells" ranging from 1.62Å to 0.51Å for samples in [110] and [112] orientations. Images obtained on the OÅM [4] show the 0.89Å carbon atom spacing in [110] diamond (left) and the 0.78Å silicon atom spacing (barely) in [112] silicon (right).

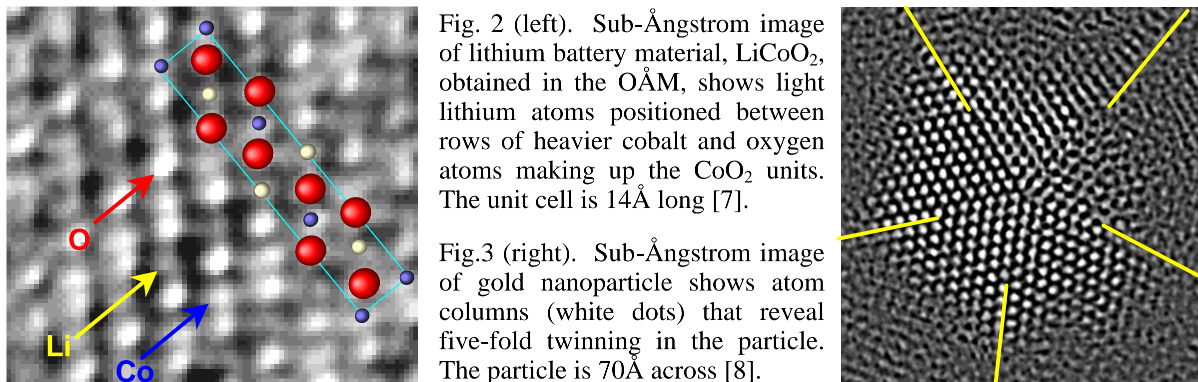

Fig. 2 (left). Sub-Ångstrom image of lithium battery material, $LiCoO_2$, obtained in the OÅM, shows light lithium atoms positioned between rows of heavier cobalt and oxygen atoms making up the CoO_2 units. The unit cell is 14Å long [7].

Fig.3 (right). Sub-Ångstrom image of gold nanoparticle shows atom columns (white dots) that reveal five-fold twinning in the particle. The particle is 70Å across [8].

[1] Lord Rayleigh, *Philosophical Magazine* **47**, 310: (1874) 81-93.
[2] O'Keefe, M.A. *37th Ann. Proc. EMSA*, San Antonio, Texas (1979) 556-557.
[3] D W Palmer, www.semiconductors.co.uk, 2002.06 <http://www.semiconductors.co.uk/>
[4] O'Keefe, M.A. et al. *Ultramicroscopy* **89**, 4: (2001) 215-241.
[5] Batson, P. E., Dellby, N. & Krivanek, O. L., *Nature* **418**, (2002) 617-620.
[6] Nellist, P.D. & Pennycook, S.J., *Microscopy and Microanalysis* **6**, 2: (2000) 104-105.
[7] Shao-Horn,Y., Croguennec, L., Delmas, C., Nelson, E.C. & O'Keefe, M.A. *Nature Mat.* **2**, (2003) 464-467; advance on-line publication 15 June 2003 (doi: 10.1038/nmat922).
[8] O'Keefe, M.A., Nelson, E.C. & Allard, L.F. Microscopy & Microanalysis **9**, 2: (2003) 278-279.
[9] O'Keefe, M.A., *Third TEAM Workshop, San Antonio,* and *Microscopy & Microanalysis* **9** (2003) 2: 936-937.
[10] Supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Science Division, DOE (contract DE-AC03-76SF00098), and Asst. Sec. for EERE, Office of FreedomCAR and Vehicle Tech. for the HTML User Program, ORNL, managed by UT-Battelle, LLC for DOE (contract DE-AC05-00OR22725).