

## Improving Atomic-Scale Elemental Mapping Resolution of STEM-EDS through Optimizing Experimental Conditions

Ping Lu<sup>1</sup>, Renliang Yuan<sup>2</sup> and Jian Min Zuo<sup>2</sup>

<sup>1</sup>Sandia National Laboratories, Albuquerque, NM 87185-1411 USA

<sup>2</sup>Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 1304 W Green St, Urbana, IL 61801, USA

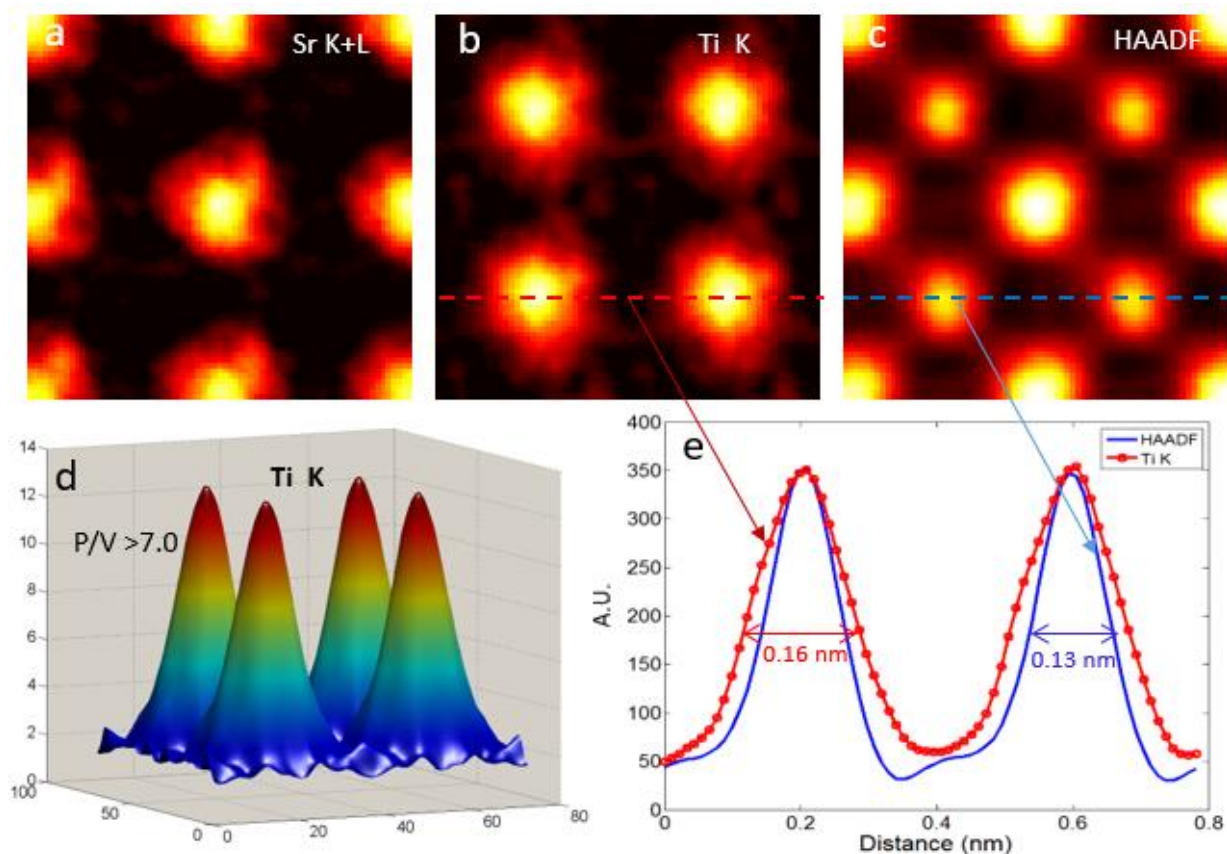
Atomic-scale elemental mapping in aberration corrected scanning transmission electron microscopy (STEM) using energy-dispersive x-ray spectra (EDS) provides a real-space approach to resolve materials structures [1-3]. The technique offers a benefit of easy interpretation with a one-to-one correspondence between image and structure, and provides a mean to resolve the crystal structure that cannot be resolved otherwise by the traditional imaging or diffraction techniques [1]. However, the technique has a severe shortcoming due to the poor efficiency of x-ray generation and collection, and as a result a typical data collection requires more than a few 100 seconds, subjecting the samples to high irradiation of electrons. Utilizing the method of lattice-vector translation (or lattice-averaging) [2,3], we have demonstrated that the rapid atomic-scale chemical elemental mapping by STEM-EDS can be obtained with the acquisition time of ~2 seconds or less. The technique provides averaged atomic-scale elemental maps from an area of ~ few 10 nm<sup>2</sup>, enabling the elemental mapping of electron-beam sensitive materials as well as the time-resolved chemical mapping [3].

Additional limitation of atomic-scale STEM-EDS that prevents its applications is due to its relatively poorer resolution than that of the STEM image. While the sub-Ångström resolution has been routinely obtained in STEM image using high-angle annular dark-field (HAADF) detector, the resolution for the STEM-EDS (defined as the shortest distance between the *identical* atomic-columns that can be resolved in a projected crystal structure) has been so far limited to around 2 Å, even when the STEM-EDS mapping is carried out under similar electron optical conditions [1,2]. In this work, we report our efforts to improve the STEM-EDS resolution by optimizing experimental conditions, and through the studies by modeling. We find that a key parameter for achieving the highest resolution STEM-EDS mapping is the specimen thickness, and it is necessary to be below a certain crystal thickness. Using the SrTiO<sub>3</sub> (STO) crystal in [001] projection as an example, we demonstrate that atomic-scale EDS mapping with a resolution approaching to HAADF image can be obtained when the specimen thickness is limited to be less than 20 nm for 200 keV electrons. This thickness effect can be explained based on the x-ray delocalization in the crystal by using multislice image simulations.

A FEI Titan<sup>TM</sup> G2 80-200 STEM with a Cs probe corrector and ChemiSTEM<sup>TM</sup> technology (X-FEG<sup>TM</sup> and SuperX<sup>TM</sup> EDS with four windowless silicon drift detectors) operated at 200 kV was used in this study. An electron probe of size less than 0.13 nm, convergence angle of 18.1 mrad, and current of ~75 pA was used for data acquisition. HAADF images were recorded under similar optical conditions using an annular detector with a collection range of 60-160 mrad. Figures 1a, 1b, and 1c show Sr (K and L) map, Ti K map and HAADF image, respectively, obtained simultaneously from a thin STO crystal in [001] direction. The crystal thickness is about 16 nm, which was determined by using position-averaged convergent beam electron diffraction [4]. Under the thin specimen condition, high-quality EDS maps, exhibiting narrow and high peak-to-valley (P/V) ratio peak about the respective atomic columns, can be obtained. Figure 1d shows the 3D surface-plot of Ti K map, showing the narrow Ti peaks with a P/V ratio of greater than 7.0.

The line-profiles across Ti columns along [100] direction (Fig.1e) show the width of Ti EDS peak match closely with that of HAADF image. The full-width at half-maximum (FWHM) for Ti EDS peak reaches about 0.16 nm, slightly broader than 0.13 nm for HAADF, which is expected from the effective ionization potentials [5]. Both the higher P/V value ( $>7.0$ ) and narrower FWHM width (about 0.16nm) achieved under our experimental conditions represent a significant improvement from the current state of atomic-scale EDS mapping [6].

1. Lu, P., Zhou, L., Kramer, M.J., & Smith, D.J. *Sci. Rep.* **4**, 3945 (2014).
2. Lu, P., Romero, E., Lee, S., MacManus-Driscoll, J. L., & Jia, Q. *Microsc. Microanal.* **20**, 1782-1790 (2014).
3. Lu, P., Yuan, R.L., Ihlefeld, J. F., Spoerke, E.D., Pan, W., & Zuo, J. M. *Nano Letter* **16**, 2728-2733 (2016).
4. LeBeau, J.M., Findlay, S.D., Allen, L.J., & Stemmer, S. *Ultramicroscopy* **110**,118 (2010).
5. D'Alfonso, A.J., Freitag, B., Klenov, V. & Allen, L.J. *Phys. Rev.* **B 81**, 100101 (2010).
6. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the US Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.



**Figure 1.** (a) EDS Sr (K+L) map; (b) EDS Ti K map; (c) HAADF image, obtained from a thin STO crystal ( $\sim 16$ nm) in [001] projection; (d) 3D surface-plot of Ti K map; and (e) line-profiles of EDS and HAADF across Ti column along [100] direction.