Z-contrast scanning transmission electron microscopy and its applications on grain boundary structure/property studies

Miyoung Kim[1,2], Gerd Duscher[2,4], Nigel D. Browning[5], Sokrates T. Pantelides[2,3], and Stephen J. Pennycook[2,3]
[1]Analytical Engineering Center, Samsung Advanced Institute of Technology
[2]Solid State Division, Oak Ridge National Laboratory
[3]Dept. Physics and Astronomy, Vanderbilt University
[4]Dept. Materials Science and Engineering, North Carolina State University
[5]Dept. Physics, University of Illinois at Chicago

It has been proven by theoretically and experimentally that incoherent scattered electrons obtained from high inner-angle annular detector successfully provide atomic number (Z) contrast, which allows intuitive interpretation of images[1]. Since high-angle scattering occurs close to the atomic site, most contribution to the image comes from 1s-state of the atom and the resulting image is often interpretated as a convolution of the probe intensity profile with the object function. Another advantage of using high-angle annular detector is that low-angle scattered electrons are used for electron energy-loss spectra simultaneously while high-angle scattered electrons are used for the Z-contrast image; Therefore, it is possible to locate the probe over a selected atomic column with very high accuracy, which enables an atomic column resolved analysis. The combination of atomic resolution imaging and electron energy-loss spectroscopy has been proved to be powerful for determining impurity sites and changes of local density of states around dislocation cores/interfaces. Here, an application of Z-contrast imaging and EELS on grain boundaries of perovskite materials will be shown.

Grain boundaries comprise arrays of dislocations that induce significant local strains even if the long-range strain fields are negligible. These short-range strains may be sufficient to lead to the spontaneous generation of point defects at high concentrations, changing the local stoichiometry and causing a valence imbalance. This is the origin of the electrical barriers at grain boundaries in SrTiO3, where a combination of atomic-resolution Z-contrast microscopy, electron energy-loss spectroscopy and first-principles theory shows the grain boundaries to be intrinsically non-stoichiometric[2]. Total energy calculations reveal that the introduction of non-stoichiometry into the grain boundaries is energetically favorable and results in structures that are consistent with atomic resolution Z-contrast images. Electron energy-loss spectra provide direct evidence of the Ti:O ratio change at grain boundaries compared to the bulk, which leads to excess electrons in the conduction band. In p-type bulk this leads to a p-n-p type of band structure. The same effect occurs in the structurally related high temperature superconductor, YBCO[3]. As the charge carriers in this material are holes, the excess electrons at the boundary lead to a depletion zone which is non-superconducting. A structural unit model of the grain boundary structure is able to quantitatively explain the exponential decrease in superconducting critical current with grain boundary misorientation.

References

[1] S.J. Pennycook and P.D. Nellist, Impact of electron and scattering probe microscopy on materials research, 161-207, edited by D.G. Rickerby, Kluwer Academic Publisher (1999)

[2] M. Kim *et. al.*, Phys. Rev. Letts, 86, 4056 (2001)

[3] S.J. Pennycook *et. al.*, Proceeding of Materials Research Society, Fall Meeting, Boston (2000) in press