Characterization and Quantification of Point Defects from Multivariate Analysis of HAADF-STEM Images

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Keywords: Point Defects, Z-contrast, Image Processing, Pattern Recognition

Point defects are increasingly important engineering targets as miniaturization and performance demands on materials grow. Scanning transmission electron microscopy (STEM) is a technique capable of resolving the atomic structure changes of point defects. The advent of aberration-corrected STEM has brought about great increases in spatial resolution, probe intensity, and depth resolution, all of which improve interpretability of images [1,2,3]. Despite these increases, some challenges to image interpretation remain. Such challenges include low signal to noise ratio due to low-dose imaging techniques, or when a small atomic number difference between the dopant and the bulk gives a small contrast difference that is difficult to distinguish from noise. Multivariate statistics have been used to quantify HRTEM images for some time, but this technique has seen limited application to STEM images due to the comparatively easy task of interpreting Z-contrast images directly [4,5,6]. Under low SNR imaging conditions, the statistical approach becomes especially valuable. Identification of the structure responsible for the observed contrast is assisted using first principles structure calculations and multislice image simulation.

Transition metal (Co, Mn) doped zinc oxides have been used to test these techniques. Such transition metal doped zinc oxides are under investigation for their properties as high-temperature dilute magnetic semiconductors. Metal ions have been shown to substitute for zinc directly on lattice sites, and the magnetic properties are thought to arise from exchange among small clusters of transition metal dopant atoms [7,8]. Identifying and quantifying the size and spatial distribution of these atoms or clusters will aid in explaining the structure-property relationship in these materials. Multivariate statistical analysis is used to perform the identification and quantification.

Analysis begins by choosing a repeat unit of interest in the original image, based on the scale of the defect to be examined. Windows are cropped from the original image using a cross-correlation algorithm to locate matches of the chosen repeat unit template. These windows are allowed to overlap. A single template can be used to crop windows from many large images to improve statistics. Dimensional reduction is performed on the set of cropped windows, yielding a set of eigenimages that represent groups of correlated pixels in each cropped window. These eigenimages are then matched with simulated STEM images to identify the structure represented by the eigenimage. Input structures for the image simulations are obtained by energetically optimizing ZnO supercells in which one or more zinc sites has been substituted with a transition metal (Co or Mn). These calculations are performed using the CASTEP module of the Accelrys Materials Studio suite [9]. Image simulations are carried out using QSTEM [10]. Once identified, the scores for each of the eigenimages for any window are used to classify and quantify the number and type of defect observed in the overall parent image.

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11. This research was supported by the US Department of Energy, under grant number DEFG02-03ER46057 . The authors also acknowledge support of the National Center for Electron Microscopy, Lawrence Berkeley Lab, which is supported by the U.S. Department of Energy under Contract # DE-AC02-05CH11231.

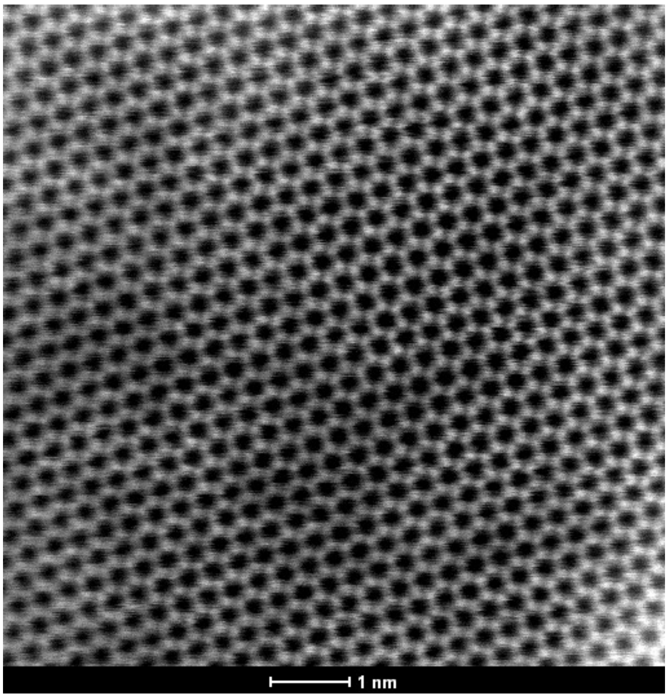

Figure 1. Example HAADF-STEM image of Co:ZnO.

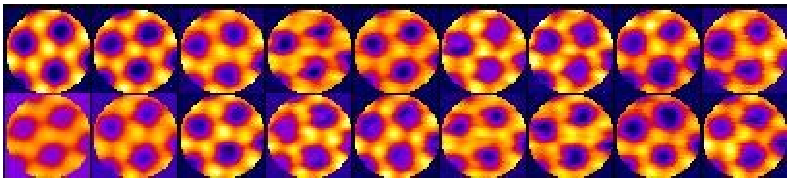

Figure 2. Pseudocolor rendition of set of importance images showing classes of variation in the original image. These images are formed by adding or subtracting the maximum and minimum value of each eigenimage to the average image.

DOI: 10.3217/978-3-85125-062-6-011,