CRADA Final Report

CRADA 0700 Pixon LLC

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Abstract

Digital images captured with electron microscopes are corrupted by two fundamental effects: shot noise resulting from electron counting statistics and blur resulting from the nonzero width of the focused electron beam. The generic problem of computationally undoing these effects is called image reconstruction and for decades has proved to be one of the most challenging and important problems in imaging science. This proposal concerned the application of the Pixon method, the highest-performance image-reconstruction algorithm yet devised (Puetter et al. 1995, 1999, 2005), to the enhancement of images obtained from the highest-resolution electron microscopes in the world (Pennycook et al. 2003, Nellist et al. 2004), now in operation at Oak Ridge National Laboratory.

Statement of Objectives

Our primary aim was to enable a rigorous statistical way of improving the quality of images from the scanning transmission electron microscope (STEM). This aim required that we advance understanding of the physics of the imaging process and the statistics of the noise and data acquisition. In order to achieve this aim, there were 6 technical goals in the Phase I program. These were to show the feasibility and the utility of:

(1) calibration of the microscope and understanding and measuring the instrumental noise,
(2) modeling and measurement of the Point Response Function, or PRF,
(3) compensation for systematic noise and artifacts,
(4) performing initial 2-dimensional non-parametric image reconstructions,
(5) extending results to parametric modeling,
(6) performing the first exploratory 3-dimensional image reconstructions.

Phase II was not funded.

Benefits to the Funding DOE Office's Mission

The ability to examine samples through electron microscopy benefits many different aspects of science. As specific examples, atomic resolution images allow us to gain new insight into catalysts, high-temperature superconductors, tough ceramics, new semiconductors, and other exotic materials. These materials provide prospects for new clean-energy generation, reduced loss in power transmission, lighter, more efficient engines, and faster computers; all of which are directly relevant to the mission of the Department of Energy. The limitations of electron microscopy are due to the finite resolution and the inevitable shot noise. Phase II of this proposal would have directly attacked these two limitations and allowed us to obtain better images from the experimental data in order to understand these exciting materials in more detail.

The STEM offers a truly unique way to analyze nanomaterials and nanostructures of all kinds. These nanomaterials are of ever increasing importance to the economy of the nation; consider the nanometal particles in every catalytic converter or the nanoscale components in a high-speed microprocessor. This proposal had the potential to benefit a wide range of applications and groups in ORNL and other DoE funded facilities. For example, even a single image can cut down the number of possible structures that need to be calculated theoretically, making an otherwise intractable problem solvable with finite computer resources. Had this proposal been funded to commercialization, it then could have been useful in almost any area where nanoscale analysis is required.

Technical Discussion of Work Performed by All Parties

Goal 1 was achieved through a detailed noise analysis model. This goal presented some interesting technical challenges: The noise depends on details of the signal generation, amplification, acquisition, and digitization. As a demonstration of this model, see Fig. 1 below. Goal (2) has been met through quantum mechanical simulations of the probe propagation through specimens. These simulations give the probe profile as a function of specimen thickness, and would have been useful in Phase II to allow us to reconstruct in 3-dimentsions. Comparison with data obtained on the Si <112> test specimen showed that these mathematical models of the probe are reliable; as an example, see Fig. 2. Having demonstrated significant progress towards goals (1) and (2), and understanding some of the areas necessary for goal (3), we were then in a position to tackle goal (4), some initial reconstructions, of which we present two examples below. Of the 6 goals listed above, goals (5) and (6) were considered less important. Consequently during the course of the Phase I program they were de-emphasized and goal (5) was essentially abandoned in favor of additional progress on the other goals. We did, however, make progress on goal (6) and have made encouraging progress on 3-dimensional image reconstruction, and this is an area we had hoped to continue to work on in Phase II.

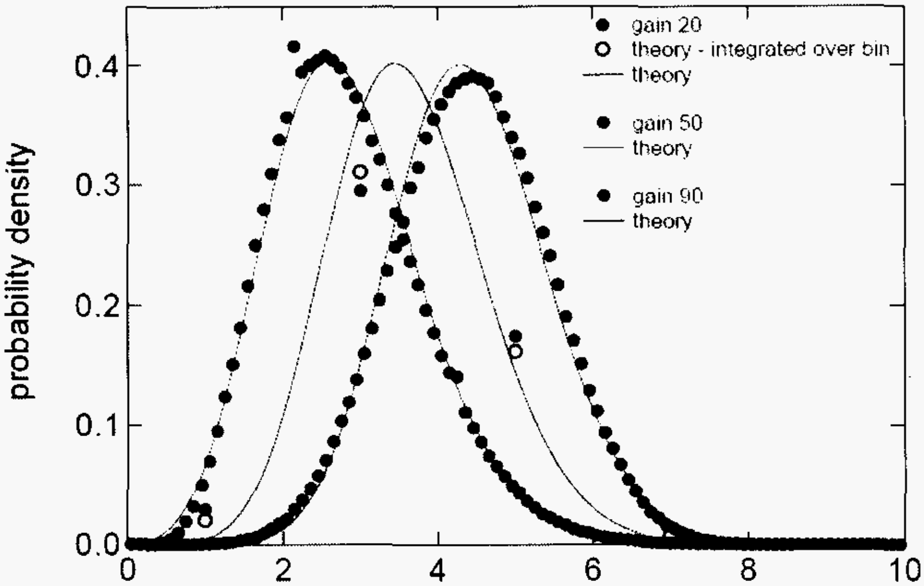

Figure 1. Comparison of the noise models to the response of the photomultiplier demonstrating the reproduction of the noise histogram at different gain settings. The horizontal axis represents the suitably normalized digitized intensity.

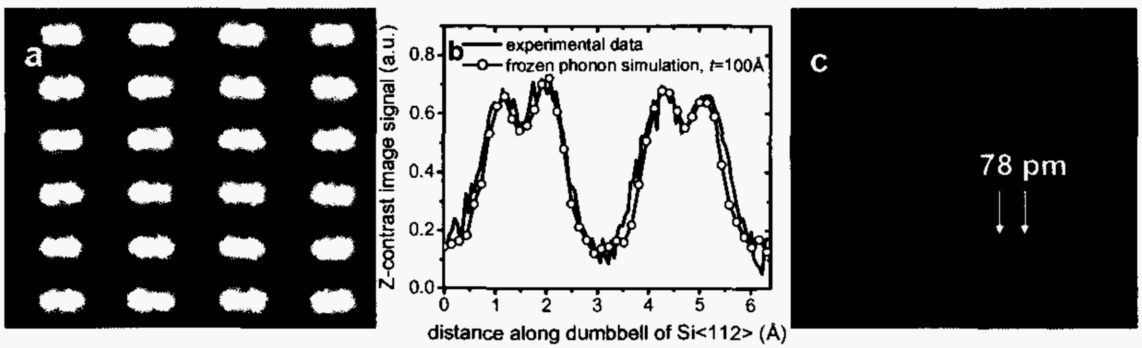

Figure 2. Demonstration of simulations compared to real images. (a) Simulation of Si[112] image using measured microscope parameters including pseudo-random noise. (b) Comparison of a linetrace through real and simulated images. (c) Experimental image of Si[112] after a smoothing process.

Example Reconstruction 1: CdSe Nanocrystal

Nanoparticles exhibit many unique catalytic or otherwise exciting phenomena. CdSe nanocrystals have unique optical properties arising from quantum confinement of electrons and holes. Their optical emission is tunable through control of nanoparticle size, and can reach 100% quantum efficiency with suitable surface passivation (core-shell structures). Nanocrystals are finding major applications in biomedical research for labeling proteins in living cells. Presently there is little understanding of the structure/property relationship for individual nanocrystals, but initial results using Z-contrast STEM and Pixon reconstruction have shown how the size, sublattice polarity, surface facets and complete three dimensional shape can be obtained. Figure 3 shows raw data and a Pixon reconstruction of a CdSe nanocrystal. After reconstruction, the lattice polarity can be seen, which is a critical factor in determining the chemical nature of the exposed facets and, in turn, the growth process itself. The image can be directly compared to a ball and stick model. The thickness profile of the nanocrystal can be obtained from the intensities of each atomic column to give information on the 3-dimensional shape (Pennycook et al., 2003).

Example Reconstruction 2: Nature Article - Observation of Rare Earth Segregation in Silicon Nitride Ceramics

Silicon nitride (Si_3N_4) ceramics are used in numerous applications because of their superior mechanical properties (Chen et al. 1993; Hoffmann & Petzow 1994). Their intrinsically brittle nature is a critical issue, but can be overcome by introducing whisker-like microstructural features. However, the formation of such anisotropic grains is very sensitive to the type of cations used as the sintering additives. Understanding the origin of dopant effects has been key to the design of high-performance Si_3N_4 ceramics for many years. In our Nature paper (Shibata et al. 2004), the Pixon method was used to delineate in a clear manner the dopant atoms (La) within the nano-meter scale intergranular amorphous films typically found at grain boundaries. The Pixon images clearly reveal that the La atoms preferentially segregate to the film/crystal interfaces—see Fig. 4. First-principle calculation confirms the strong preference of La to the crystalline surfaces that controls grain growth reaction at these specific surfaces essential for forming elongated grains and a toughened microstructure.

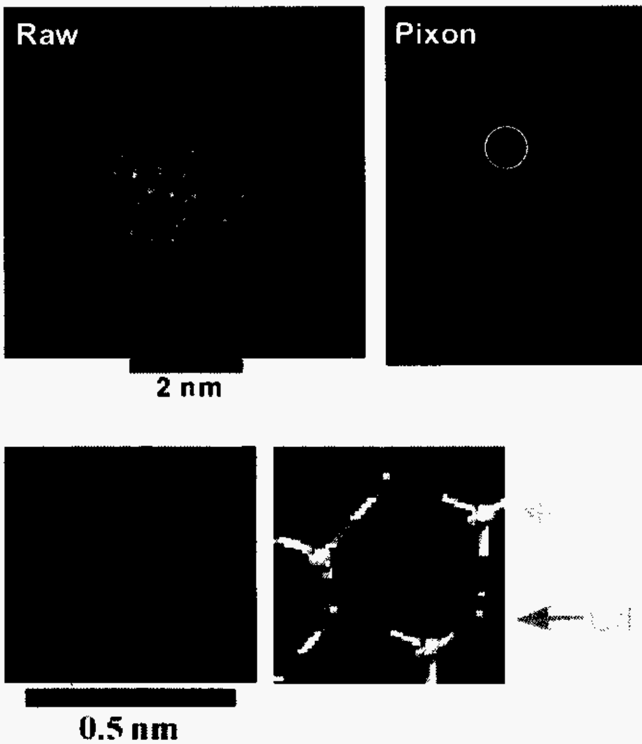

Figure 3 Raw data from a CdSe nanocrystal with Pixon reconstruction showing "ball and stick" resolution. The reconstruction allows nanocrystal orientation, polarity and 3D structure to be seen, critical data for understanding the optical properties, growth process and determining means to chemically functionalize the surfaces with proteins.

In summary, Phase I was very successful. All of the high priority tasks were successfully completed. We have learned what is necessary to calibrate STEM microscopes, measure and characterize their noise, develop a useful model for the PRF, and apply this information to achieve sub-diffraction limit 2-dimensional images.

Shibata et al._Figure 2

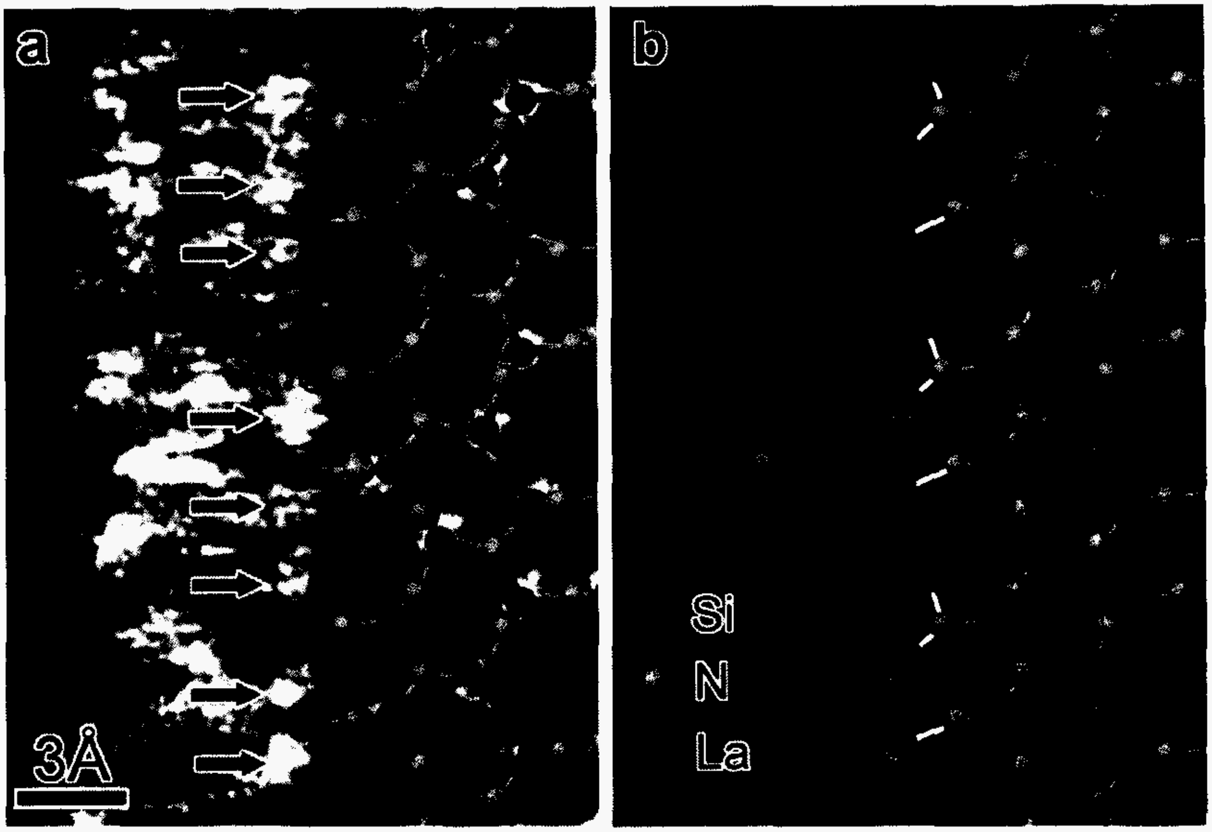

Figure 4. Magnified HAADF-STEM images of the interface between the intergranular film (IGF) and the prismatic surface of a β-Si_3N_4 grain. The β- Si_3N_4 lattice structure is superimposed on the images. **Panel a:** La atoms are observed as the bright spots (denoted by red arrows) at the edge of the IGF. The positions of La atoms are shifted from that of Si atoms based on the extension of the β- Si_3N_4 lattice structure; these expected positions are shown by open green circles. **Panel b:** The Pixon reconstructed image of Panel a, showing the La segregation sites more clearly. The predicted La segregation sites obtained by the first-principles calculations are shown by the open white circles. These theoretical predictions agree well with the experimental result. The slight deviations from some of the theoretically predicted sites probably indicate the influence of atoms in the IGF.

Subject Inventions (As defined in the CRADA)

Phase I of this project was primarily aimed to determine whether the application of Pixon techniques to Z-contrast STEM imaging would present any advantages over other imaging / deconvolution combinations. It appears that this is indeed the case, although specific inventions would have been the subject of Phase II, which was not funded.

Commercialization Possibilities

The previous sections have argued the fundamental importance of electron microscopy in mesoscale physics and the development of nanotechnology; indeed these subjects are core emphases of the Department of Energy's basic-science portfolio. Fundamental advances in these areas are essential to continuing US dominance in computing electronics and in attaining an early presence in entirely new nanotech markets, especially as quantum limits on Moore's law are reached in the next decade. In the near term, commercial objectives of this project are to provide an optimal image-processing software package to the electron-microscope industry. This objective follows a pathway to commercialization—already established by ORNL—for new electron-microscope technologies: The use of an annular dark-field detector in STEM, largely pioneered at ORNL, is now a feature offered with microscopes available from both FEI, Hitachi and JEOL. Approximately 250 transmission electron microscopes are sold annually worldwide. ORNL was instrumental in the development of aberration correctors for the STEM, which are now being offered by several manufacturers, and was the first institution in the world to install an aberration corrector in a 300-kV STEM.

Perhaps the key difficulty in transmission electron microscopy is interpreting the data. Other deconvolution codes exist and are commercially available from a variety of sources. However, the Pixon technique is almost unique in that it allows us to produce models with rigorous statistical confidence, based on detailed modeling of the imaging process and its inherent noise. Thus we were really gaining insight both into the physics of electron microscope imaging as well as into the more important materials problems. We have no plans to immediately commercialize this work, but it is clear that with some further development such commercialization would be possible.

Plans for Future Collaboration

At this moment we have no plans for future collaboration. However it isapparent that this method has many exciting prospects and we would like to explore it more in future.

Conclusions

It is clear that existing deconvolution techniques leave something to be desired; the aim of electron microscopy is to obtain images that advance our understanding of basic or important scientific problems. We believe that the Pixon technique represents a powerful method to help achieve this aim and, had phase II of this project been funded, we would have made some significant progress. However, we have developed some improved models for the noise in the STEM imaging process and gained some more insight into the imaging physics. We believe that the insight gained during phase I of this project will greatly assist us in the future *quantitative interpretation* of microscope data and therefore represents a very important step that will benefit many of the wide variety of applications where STEM is used.

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