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UHV-STEM STUDIES OF MATERIALS

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By

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The work carried out under DOE grant # DE-FG02-87ER45322 that terminated May 14th 2000 was directed towards the understanding and exploitation atomic scale electron beams (~0.2 nm) and associated imaging and electron spectroscopy modes that enabled determination of local electronic properties at grain boundaries, interfaces, and other examples of microstructural features. In addition, since the use of STEM capabilities was a new approach at the outset of these studies, development and validation of appropriate interpretative background and techniques was necessary. I note the appearance of a book (reference 46 below) reflecting experience partly generated under this program that makes the experience generated here widely available (and being quite widely used). This book may well become a classic reference in this field. In addition, digital image acquisition and storage made feasible wide use of the instrument permitting graduate students with little background in microscope operation to operate and use the instrument comfortably. Other experimental adaptations were also made during the course of this program.

It is gratifying to find that the high spatial resolution EELS and ultra small electron probe work supported under this program has now become a mainstream element in electron probe nanocharacterization studies. That it is now the leading edge became clear at the Long Beach meeting in 2001 where indeed a symposium was generated in honor of Professor Silcox. Although several groups and scientists are part of this development (most notably Dr. S. Pennycook of Oak Ridge National Laboratory and Dr. Philip E. Batson at IBM Watson Laboratories) it is probably a stretch to assert that this program and the efforts of alumni of the program such as Dr. David A. Muller, now of Lucent Technologies Bell Laboratories, have also played a major role in creating this change. Professor Silcox drew upon many results from the program in a presentation to the second NTEAM workshop at Berkeley National Laboratory July 17th 2002 concerning the role that the four DOE Electron beam laboratories might play in future years as the revolution in instrumentation arising from recent successes in solution of a sixty year old problem in correcting aberrations in electron lenses.

In the opinion of the principal investigator under this program, the revolution now under way as a result of these developments will have a significant impact on the ability to identify structures in materials, to measure chemical and electronic effects on a local scale and to follow through the classic materials paradigm from structure to properties in ways that hither-too have not been possible. My biggest concern is whether the talent will be there to follow through on the paradigm shift in the field of electron beam microcharacterization being made feasible by the new systems. I urge that DOE Office of Science consider funding the research needed within the University community to ensure that the field can attract high quality students able to handle the physics and chemistry needed for the interpretation of the more classical materials research problems that now can be approached by these new methods.

The following notes briefly outline themes and connect them to references in the attached list of publications from this group on work carried out during the duration of this grant.

1. Development of a multislice simulation program for use in convergent beam situations and with scanned probe microscopy and spectroscopy [1-5, 7].

2. A "frozen phonon" approximation was introduced and experimentally verified [10,12,14,15, 44].

3. Demonstration of high resolution Annular Dark Field performance [6,8,9].

4. Determination of spherical aberration coefficient in STEM [13,16].

5. Simulation and experimental verification of imaging zone axis images [17-21,23, 26].

6. Identification of diamond as distinguished from amorphous carbon using energy selected maps of the 2 π^* and 2 σ^* states of carbon with a 5 Å spatial resolution on a cross section sample [22,24]. These observations are valuable for the insight they bring to the growth of diamond films.

7. Imaging 6 Å diameter, micron long fibers of $(Mo_3Se_3)_n$ using ADF imaging. This provided evidence of the success of the chemical separation and of the morphology of the fibers. The success of this approach has resulted in two other papers in Science (under non-DOE support) describing incorporation of molecular inorganic molecules in polymer matrices (See J. H. Golden et.al., Science 268, 1463-1465 (1995) and 273, 782-784 (1996))

8. Identifying changes in the d-hole local density-of-states at grain boundaries in boron- doped and undoped Ni_3Al in collaboration with the DOE-supported group of Professor Stephen Sass [4 to 9, 29 to 34, 39, 41]. This gives the basis for a model that estimates changes in the bonding at the boundary that are reflected in the changes in fracture behavior and environmental susceptibility. Interpretation of this data called for development of significant theoretical (in collaboration with Dr. D.J.Singh of the Naval Research Laboratory) and experimental (in collaboration with Dr. Philip E. Batson of IBM Watson Laboratory) material on bulk alloys to give a base for the interpretation of the grain boundary data [36, 37, 38]. Additional studies of structural changes arising from 100keV electron irradiation [27] also arose from this work.

9. Quantitative image analysis of the atomic densities in quantum wells of In GaAs at a level approaching one atom sensitivity with the group of Professor Lester Eastman (Cornell E.E. Dept.) [10]. This gives details of the composition within the well and how they arise from the growth process.

10. Use of nanodiffraction to measure local lattice parameters to +/- 0.005 Å and thus determination of the strain distribution around a quantum wire (also with the group of Professor Lester F. Eastman (Cornell E.E. Dept.) [11]. The observed strain compares well with a linear elasticity calculation. Further, that strain can be used to estimate the changes in band gap arising from the strain and to account quantitatively for a consequent shift in the photoluminescence as observed.

11. Exploration of the atomically sharp interfaces of MgO structures embedded in a copper matrix as a result of the internal oxidation of copper/magnesium alloys in collaboration with Professor David Seidman's DOE supported program at Northwestern University resulted in

demonstrating metal induced gap states at the interface. These states "leaked" from the copper over the oxygen atoms in the neighboring plane and shielded the charge on the oxygen atom. Comparison with theoretical calculations showed that this effect (omitted in some calculations) resulted in the reduction of the atomic scale dipole moment at the interface to one third of the unshielded value [35,37,42].

12. The existing theories of the spatial resolution of EELS were probed and experiments carried out to verify the conclusions. The resolution was found to be significantly better than had generally been believed on qualitative arguments [28].

13. Continuation of our studies of image formation in ADF STEM led to several conclusions. These included a significant depth dependence of the probe structure as it progresses through the specimen [13,14]. This has important conclusions for analysis. The effective incoherent source size is an important practical limitation on resolution and provides an explanation of why the resolution degrades somewhat as the tip ages. Simulations [15] suggest that strain provides an explanation for some ADF image features and that multiple scattering can be a practical factor in generating some false detail in images. A review of ADF STEM was also published [16] and a comparison of ADF STEM images with BF STEM and BF CTEM images reported [17].

14. Experimental improvements to the instrument during this period include; an ADF detector that was over 100 times more sensitive than the detector it replaced [18] and which is now (2002) an accessory generally available for electron microscopes throughout the world through Fischione Co. and other manufacturers, a PEELS system based on the Cambridge system (McMullen [19] that permits the choice of three detector systems, an upgrade to the image acquisition system (WINSTEM) that is now user-friendly and based on Windows 95 and a new specimen chamber and stage that permits the tilt of specimens at a 2 Å resolution level.

15. During the course of this program, Dr. Kirkland continued his earlier development of computer simulation programs for the interpretation of electron microscopy images by extending them to include STEM imaging. This has resulted in the publication of a book on Advanced Computing for Electron Microscopy [45].

Publication List:

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