Arizona State Univ.
FG 02-87 ER 45305

DOE/ER/45305--T2

DE93 009750

Project Summary

Title: High Resolution Interface Nanochemistry and Structure

2. Summary of Results During Previous Three Years

(a) Development of methods and instrumentation for interface/boundary chemical analysis.

The critical experimental conditions for high spatial resolution nanospectroscopic analysis of interfaces/boundaries are incident probe size, current density and alignment, inelastic scattering cross sections, spectrum collection time and specimen/probe temporal stability. They are given in ref. 34. References in this section are listed in Section 2.g.,

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below. Experimental measurements of probe current distributions as a function of divergence half angle and defocus for a field emission gun TEM/STEM are given in ref. 19. Reference No. 19 also contains theoretical calculations of probe current density using both the coherent and incoherent treatments; results shown that the incoherent treatment is required for large divergence angles and that either treatment suffices for small divergence angles. This paper defines the optimum probe electron optical parameters for nanospectroscopy, particularly probe focus to avoid beam tails. A copy is enclosed. This reference is the only fundamental comprehensive study of field emission TEM/STEM probe optics performed to date, and is directly applicable to the new generation of FEG/TEM/STEM microscopes. Reference No. 16 defines the spatial resolution and detection sensitivity limits for nanospectroscopy. Reference No. 10 describes the computer system designed and built for position and time resolved nanospectroscopy of interfaces and boundaries in the work described below. These papers together define current electron optics/nanospectroscopic methods for interface/boundary chemical analysis, primarily using EELS for oxygen, nitrogen and carbon analysis and secondarily using EDXS analysis for heavier elements.

(b) Interface and Boundary Structure in Ceramic Matrix Composites.

An extensive investigation of the chemistry and structure of interfaces and matrix grain boundaries in four silicon carbide whisker reinforced-Si₃N₄ matrix composites was conducted during the last three years. The starting materials and processing cycle for each of the four were identical, but the whiskers were from different sources. The main reference for these results is No. 15. Nos. 12 and 24 are also useful. These composites were synthesized using 6 wt. % of an equimolar mixture of (Al₂O₃ + Y₂O₃) as a densification aid. Electron energy loss (EELS) nanospectroscopy was used to investigate the nitrogen and oxygen distribution at SiC(w)/Si₃N₄ interfaces and Si₃N₄ grain boundaries. Several important new results have been obtained:

- (1) The thin amorphous or disordered regions along Si₃N₄/Si₃N₄ matrix grain boundaries always contained a high oxygen concentration, but Si₃N₄/SiC(w) interface regions with the same appearance in high resolution images did not always exhibit a high oxygen concentration. That is, the oxygen distribution was continuous in matrix grain boundaries but discontinuous in whisker/matrix interfaces. We do not expect a unique value for whisker/matrix interface strength to exist for these composites.
- (2) Relatively wide oxygen and nitrogen gradients were observed in crystals adjacent to interfaces/boundaries, clearly indicating that the chemical width is much greater than the structural width of these interfaces/boundaries. These are the first observations of differences between chemical and structural width in ceramic matrix composites. High spatial resolution nanospectroscopy methods described above are required to observe them. Chemical widths are presumed to be processing dependent. They will introduce gradients in other parameters adjacent to interfaces/boundaries such as lattice constant and strength and will have significant effects on composite properties.
- (3) High angle annular dark field (HAADF) STEM imaging was used for the first time to determine the distribution of heavy elements, in this case yttrium, in the same interfaces/boundaries. The yttrium distribution follows the oxygen distribution, i.e. it is discontinuous in the SiC(w)/Si₃N₄ interfaces and continuous in the Si₃N₄ grain boundaries, and has the same chemical width as oxygen. The HAADF method is not spectroscopic, but it does have better spatial resolution than x-ray spectroscopy. (Ref. No. 2).

- (4) Fresnel fringes are clearly visible along all interfaces/boundaries in out of focus images in these materials, whether or not strong oxygen segregation exists at some particular location. The existence of Fresnel fringes has in the past been taken to be an *unequivocal* indication of chemical segregation at the interface/boundary. However, Fresnel fringes indicate only a difference in mean elastic scattering potential which can result from local changes in atom density at an interface/boundary as well as from differences in atom chemical species. This effect was investigated quantitatively using segregation-free silicon $\Sigma=13(510)[001]$ tilt grain boundaries. High resolution imaging was used to determine boundary atomic structure in order to calculate the mean scattering potential at the boundaries and the resulting Fresnel fringes, which matched experimental images very well. Thus, Fresnel fringes are a necessary accompaniment to out of focus interface/boundary images where an abrupt difference in scattering potential occurs but are not sufficient to establish the existence of chemical segregation. Refs. 13, 14, 20 and 25 describe this work.
- (5) The thickness of the amorphous or disordered region at the interfaces/boundaries varies from one interface/boundary to another in a single specimen, thus these microstructures are probably far from equilibrium. By comparison to the $\text{Al}_2\text{O}_3/\text{SiC(w)}$ composite examined, which was synthesized without sintering aids and exhibited thinner disordered regions at all boundaries/interfaces, sintering aids are the primary source of amorphous films at interfaces/boundaries (ref. 27).

(c) Quantitative Composition Measurements of Thin Films and Inclusions.

Ceramic microstructures in general contain many complex features which are thought to result from the use of sintering aids during synthesis and possible reducing or neutral atmospheres during densification. We have investigated a number of these using the nanospectroscopic methods developed on this project.

- (1) The origins and composition/structure of ubiquitous graphite fiber/amorphous matrix inclusions, both intergranular and at triple junctions, in ceramics and ceramic composites are of long-standing interest. We first detected oxygen in these inclusions in SiC in 1981 using what are now regarded as primitive EEL spectroscopic methods (Skiff and Carpenter, Proc. 40th Ann. Mtg. EMSA, p. 564). Using our current methods we have detected and analyzed these inclusions in α -SiC (Ref. 26), in ceramic matrix composites (Ref. 27), in reaction bonded SiC (Ref. 6), and in liquid phase densified SiC (Ref. 18). The amorphous matrix of the inclusions invariably contained oxygen, a small amount of carbon, silicon, and other metal impurities from starting materials or sintering aids. The crystalline graphite fibers in the amorphous matrix were invariably pure carbon. These inclusions, which in some cases are large enough to act as stress concentrators, evidently form from the last liquid to solidify and contain graphite fibers precipitated by heterogeneous nucleation on the surfaces of surrounding crystals from the carbon saturated last liquid. The last liquid contains appreciable amounts of both silicon and oxygen and does not crystallize on cooling.
- (2) Existence of Substoichiometric Si Oxides. It is generally assumed by most researchers that amorphous silicon oxides have composition SiO_2 , based on the experiences of many researchers with thermal oxide on Si wafers and with glass technology. Our EELS methods enabled direct measurement of Si/O ratios in various thin films, grain boundary regions and inclusions. Amorphous, thin, silicon-oxygen films containing 15 to 50 at % oxygen can be easily prepared, and when heated in an inert environment will precipitate Si nanocrystals in an

amorphous matrix of increased oxygen content (Refs. 3, 28, 32). The inclusions and oxygen-containing interface/boundary regions described above are not SiO_2 ; these regions contain other metallic and nonmetallic solutes and reduced oxygen concentrations relative to SiO_2 .

- (3) SiC particles compacted with Al rich sintering aids (Al_2O_3 and Al_4C_3) and hot pressed ($T > 1800^\circ\text{C}$) in nitrogen atmosphere densify by liquid phase sintering without formation of amorphous intergranular films from the residual liquid upon cooling. All intergranular films in this material are crystalline and although they do contain oxygen, they contain much more Al than Si. Evidently the presence of large amounts of both Si and oxygen in the residual liquid is required for amorphous intergranular film formation (Ref. 18).

(d) Theoretical Calculations for Electron Energy Loss Near Edge Fine Structure and Grain Boundary Structure and Grain Boundary Structure.

- (1) The validity of the Random Phase (RPA) and the Dipole Approximations (DA) for Si-L_{2,3} near edge fine structure calculations was examined by calculating the edge as a function of scattering half-angle with and without RPA and DA using an *ab initio* self consistent linear PAO combination scheme to calculate the band structure of crystalline Si and the Born approximation to calculate the differential inelastic cross section. The results showed little sensitivity to the RPA, but the DA began to fail for scattering half angles > 12.5 mr and caused about 50% error for scattering half angles ≈ 100 mr. Our experimental data is collected with a maximum scattering half angle of 10 mr; thus, we do not introduce significant error in our comparisons of theory and experiment by use of the RPA and DA (Ref. 23).
- (2) The major changes that occur in low loss EELS absorption peaks (valence band excitation) across the series $\text{Si} \rightarrow \text{SiC} \rightarrow \text{Si}_3\text{N}_4 \rightarrow \text{SiO}_2$ are broadening of the low loss peak and a decrease in maximum intensity. We have done the first theoretical calculations for these edges, based on a single electron excitation model using extended Huckel band calculations to obtain valence shell crystal states and the Born approximation to calculate cross sections. The relationship of this model to plasmon excitation is discussed. The results predict the experimental trend but are not quantitative. These calculations are more difficult than core edge computations because molecular wave functions are required for initial states.

Self-consistent-field band calculations, such as CNDO/2 parameterization, will result in more accuracy, which will become increasingly important as EELS spectra from interfaces begin to require interpretation (ref. 36).

- (3) We have investigated the application of "complete neglect of differential overlap" (CNDO/2) parameterization to energy band calculation of solids and for calculation of EELS core absorption edges. The CNDO/2 parameterization improved agreement between theoretical and experimental core edges. (Refs 29, 37).
- (4) Comparison of theoretical valence band relaxation and excitonic effect calculations using the *ab initio* pseudo atomic orbital method with experimental x-ray emission and EEL spectra for the Si-L_{2,3} edge from diamond cubic Si (Ref. 17) and the B- and N-K edges from hexagonal BN (Ref. 4) showed that there is

very little valence band electron relaxation before the core hole is filled; when including the excitonic effect in EEL near-edge-structure calculations the valence band should therefore be kept the same as the ground state.

- (5) We have used the Quantum Molecular Dynamic (QMD) method to perform the first theoretical calculations of relaxed equilibrium atom positions in a silicon $\Sigma=13(510)[001]$ tilt grain boundary. The results agreed reasonably well with experimental high resolution electron images of the same boundary. Since the models generally used for HREM image simulations of boundaries are not unique, there is a need for minimum energy boundary structure computations to help interpret experimental high resolution results, especially to determine whether observed boundary and interface structures represent equilibrium or a metastable state influenced by chemical segregation. This work is continuing (Ref. 8.).

(e) Small Probe Radiation Effects in Ceramics.

Early in this research we showed that silicon oxynitride undergoes a very unusual mass loss process during irradiation by a focused high current density electron nanoprobe. All three constituent elements are lost during irradiation, at different rates that vary nonlinearly with dose; the oxygen concentration in the irradiated volume, in particular, goes through a maximum at intermediate doses (Ref. 33). We have derived a macroscopic theory to describe this effect (not yet published), but not yet a fundamental explanation. We also found that SiO_x undergoes differential mass loss at differing rates for each constituent for $x=2.0$, but the irradiated volume oxygen concentration does not pass through a maximum at intermediate doses for this binary ceramic (to be published). The binary silicon oxide becomes more resistant to radiation induced mass loss when $x < 2.0$, in the range $1.0 \geq x \geq 0.18$ (Refs. 5, 28). Current density in the probes we use for high spatial resolution nanospectroscopy is usually $\sim 10^5 \text{ A/cm}^2$. At this current density, we have shown that SiC will begin to undergo mass loss in several seconds, but Al_2O_3 will begin in less than 1 sec (Ref. 31). Similar mass loss occurs for WO_3 , V_2O_5 and TiO_2 when irradiated by high current density focused probes at 100kV; HREM examination implied that small probe irradiation caused primarily oxygen mass loss in these binary oxides. Our results indicate that high current density/small probe irradiation effects occur most easily in insulators, i.e. oxides with large band gaps, and at an intermediate level in covalently bonded materials with smaller band gaps, e.g. SiC and Si_3N_4 . The spectrum collection times we have used so far, 200 to 500 msec, are sufficient for elemental analysis; but dose and dose-rate limits for fine structure analysis have not been determined. EELS fine structure analysis to obtain bonding information, particularly at interfaces, and irradiation effects mechanisms, particularly for ternary and higher important ceramic materials, are clearly important topics for further research.

(f) Students Graduated, and Students and Postdocs. Collaborators.

(1) Ph.D. Students Graduated, fully supported by this Grant

Jon Karl Weiss, PhD, Physics. Thesis Title: Limits of Spatial Resolution and Detectability of EELS Microanalysis in a Field Emission Gun TEM/STEM. Presently self-employed in design, construction and sales of microscope computer control equipment.

Karnoketu Das Chowdhury, PhD, Science and Engineering of Materials (ASU). Thesis Title: Interfaces in Silicon Carbide Whisker Reinforced Silicon Nitride Based Composites: A High Resolution Electron Microscopy Study. Presently

Postdoctoral Research Associate on this project. External employment begins March 1, 1993.

(2) Postdoctoral Research Associates Supported

Hong Ma, PhD, Theoretical Solid State Chemistry. Dr. Ma's primary responsibilities are theoretical scattering and bonding calculations.

(3) Collaborators

Dr. Wolfgang Braue, German Aerospace Research Establishment, Materials Research Institute, Cologne, FRG. Dr. Braue contributes physical ceramics and synthesis input to this project.

Dr. M.J. Kim, Assistant Research Scientist, Center for Solid State Science, ASU. Collaborated on HREM and Fresnel studies of model grain boundaries.

Philip M. Rice, PhD, Science and Engineering of Materials (ASU). Collaborated on grain boundary studies of CVD SiC and Si₃N₄. Presently at Oak Ridge National Laboratory, Metals and Ceramics Division.

J.S. Bow, continuing PhD student in the Science and Engineering of Materials Program.. Mr. Bow is making initial applications of interface analysis methods developed on this project to TiSiC interfaces. He also performed oxidation studies on certain types of SiC.

(g) Project Publications

- (1) "High Spatial Resolution TEM Study of Thin Film Metal/6H-SiC Interfaces," J.S. Bow, L.M. Spellman, M.J. Kim, R.W. Carpenter, and R.F. Davis, Proc. Symp. on Evolution of Surface and Thin Film Microstructure, Mater. Res. Soc. (1992) in press.
- (2) "Chemical Analysis of Matrix Grain Boundaries in SiC Whisker Reinforced Si₃N₄ Based Composites," J. Liu, K. Das Chowdhury, R.W. Carpenter, and W. Braue, Proc. Symp. on Silicon Nitride Ceramics, Mater. Res. Soc. (1992) in press.
- (3) "An HREM Study of Interfaces in Reaction Bonded Silicon Carbide," K. Das Chowdhury, R.W. Carpenter, and W. Braue, Proc. Symp. on Atomic Scale Imaging of Surfaces and Interfaces, Mater. Res. Soc. (1992) in press.
- (4) "Ab Initio Calculation of Band Structure, X-ray Emission, Quantum Yield and Electron Energy Loss Spectra of Hexagonal Boron Nitride," H. Ma, S.H. Lin, R.W. Carpenter, P. Rice, and O.F. Sankey, Jour. Appl. Phys. (1992) in press.
- (5) "The Composition and Structure of SIPOS: A High Spatial Resolution Electron Microscopy Study," M. Catalano, M.J. Kim, R.W. Carpenter, and Joe Wong, Jour. of Mater. Res. (1992) in press.
- (6) "Analytical Electron Microscopy of Reaction-Bonded SiC," K. Das Chowdhury, R.W. Carpenter and W. Braue, Proc. 50th Ann Mtg. EMSA, San Francisco Press, Inc., I, 344-345 (1992).
- (7) "HREM Study of the Ti/6H-SiC Interface," J.S. Bow, L.M. Spellman, M.J. Kim, R.W. Carpenter and R.F. Davis, Proc. 50th Ann. Mtg. EMSA, San Francisco Press, Inc., I, 252-253 (1992).
- (8) "Quantum Molecular Dynamic Simulation of $\Sigma=13$ Grain Boundary in Si," M.J. Kim, H. Ma, R.W. Carpenter, S.H. Lin and O.F. Sankey, Proc. 50th Ann. Mtg. EMSA, San Francisco Press, Inc., I, 212-213 (1992).

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- (10) "A Computer System for Imaging and Spectroscopy, in Analytical Electron Microscopy," J.K. Weiss, Peter Rez and A.A. Higgs, Ultramicros, 41, 291-301 (1992).
- (11) "High Resolution Analysis of Structure and Chemistry of Grain Boundaries in Silicon," M.J. Kim and R.W. Carpenter, Proc. Symp. on Structure and Properties of Interfaces in Materials, Mater. Res. Society Symp. Proc. Vol. 238, 157-162 (1992).
- (12) "Analysis of Oxygen Distribution in Interfaces in Silicon Carbide Whisker Reinforced Silicon Nitride Based Composites," K. Das Chowdhury, R.W. Carpenter and W. Braue, Proc. Symp. on Structure and Properties of Interfaces in Materials, Mater. Res. Society Symp. Proc. Vol. 238, 421-427 (1992).
- (13) "Analysis of Interfaces by Fresnel Fringe Techniques," K. Das Chowdhury, R.W. Carpenter and M.J. Kim, Microscopy: The Key Research Tool, 61-66 (1992).
- (14) "Structure and Precipitation on a $\Sigma=13$ Tilt Grain Boundary in Silicon," M.J. Kim, R.W. Carpenter, Y.L. Chen and G.S. Schwutke, Ultramicroscopy 40, 258-264 (1992).
- (15) "A Comparative High Resolution Study of Interface Chemistry in Silicon-Nitride-Based Matrix Composites Reinforced with Silicon Carbide Whiskers," K. Das Chowdhury, R.W. Carpenter and W. Braue, Ultramicroscopy 40, 229-239 (1992).
- (16) "Factors Limiting the Spatial Resolution and Sensitivity of EELS Microanalysis in STEM," J.K. Weiss and R.W. Carpenter, Ultramicroscopy 40, 339-351 (1992).
- (17) "Ab Initio Study of the Valence-Electron Relaxation-Effect on X-ray Emission Spectra and the Excitonic Effect on Electron-Energy-Loss Spectra of Si-L_{2,3} Edge," H. Ma, S.H. Lin, R.W. Carpenter and O.F. Sankey, Phys. Rev. B44, No. 24, 13393-13397 (1991).
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- (19) "A Study of Small Electron Probe Formation in a Field Emission Gun TEM/STEM," J.K. Weiss, R.W. Carpenter, and A.A. Higgs, Ultramicroscopy 36, 319-329 (1991).
- (20) "Analysis of Pure Tilt Grain Boundary in Silicon by Fresnel Fringe Technique," K. Das Chowdhury, M.J. Kim, Y.L. Chen, and R.W. Carpenter, Proc. 49th Ann. Mtg. EMSA, San Francisco Press, Inc., 1002-1003 (1991).
- (21) "Comparative Oxidation Studies of Polycrystalline HP and CVD Silicon Carbides by TEM," J.S. Bow, M.J. Kim and R.W. Carpenter, Proc. 49th Ann. Mtg. EMSA, San Francisco Press, Inc. 938-939 (1991).
- (22) "Study of the Interfacial Concentration Profile of Two Component Systems in the Solid-Solid Interface," N. Tapia, H. Ma, S.H. Lin, and R.W. Carpenter, Materials Letters 10, 256-260 (1990).
- (23) "Theoretical Comparison of Electron Energy-Loss and X-ray Absorption Near-Edge Fine Structure of the Si-L_{2,3} Edge," H. Ma, S.H. Lin, R.W. Carpenter, and O.F. Sankey, J. Appl. Phys. 68 (1), 288-290 (1 July 1990).
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- (27) "High Resolution Interface Analysis of SiC Whisker Reinforced Si_3N_4 and Al_2O_3 Ceramic Matrix Composites," W. Braue, R.W. Carpenter, and David J. Smith, *Jour. of Materials Science* **25**, 2949-2957 (1990).
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- (29) "Application of a Semi-Empirical Self-Consistent-Field Band Calculation to Near-Edge Fine-Structure Analysis of Core-Shell Electronic Absorption Edges," H. Ma, W.M. Skiff, G.S. Wu, S.H. Lin, and R.W. Carpenter, *J. Appl. Phys.* **65** (12), 5217-5220 (15 June 1989).
- (30) "High Resolution Analytical Electron Microscopy of Si and Ceramics," R.W. Carpenter, *Proceedings of the XVII Electron Microscopy Congress, Societa Italiana di Microscopia Elettronica, Universita degli Studi di Lecce, Italy* (October, 1989) p. 57-61.
- (31) "Scanning Probe Parallel EELS Analysis of Interfaces in Ceramics and Ceramic Composites," J.K. Weiss, R.W. Carpenter, W. Braue, and A.A. Higgs, *Proc. 47th Ann. Mtg. Elec. Micros. Soc. Amer.* (1989) p. 226.
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