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Arizona State University

Center for Solid State Science
Tempe, Arizona 85287-1704
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Continuation Document: Grant DE-FG02-87ER45305
"High Resolution Energy Loss Research: Si Compounds and Ceramics"
PI: R.W. Carpenter ; Co-PI S.H. Lin

1. Progress for January 1, 1988 to January 1, 1989

a. Materials

Analytical and high resolution electron microscopes was used to investigate interfaces, grain boundaries and triple junctions in a number of materials. Interfaces between silicon carbide whiskers and either aluminum oxide or silicon nitride grains in two different ceramic matrix composites were found to be mostly crystalline, and did not contain a continuous amorphous phase. The amount of amorphous phase in these interfaces depended primarily on the amount of sintering aid used. Amorphous multiphase regions at triple grain junctions in several structural ceramics were shown to consists of fibrous graphite microcrystals in an oxygen containing amorphous matrix. We consider it likely that these regions act as fracture nuclei for structural ceramics and composites. Grain boundaries from a large silicon bicrystal with $\Sigma13(320)$ structure were examined by atomic resolution and electron energy loss microscopy; this boundary is composed of theoretically perfect regions and regions to which oxygen had segregated during crystal growth. Detailed microstructural analysis of a liquid phase sintered body made from silicon dioxide, aluminum oxide and silicon nitride showed that silicon oxynitride is apparently nucleated at the liquid/silicon nitride interface; the structure of the silicon oxynitride/silicon nitride interface is strongly anistropic. Radiation effects on energy loss microanalysis were found to be small for silicon carbide and silicon nitride, intermediate for silicon dioxide, and large for silicon oxynitride.

b. Instrumentation

Parallel electron energy loss spectroscopy detection systems were installed and are operating on two high resolution analytical electron microscopes. Spectra with 20Å spatial resolution have been obtained, determined by incident probe size.

Computations of microprobe current density for analytical electron microscopes, including those with field emission sources, using newly written software are near completion. New software for time resolved energy loss spectroscopy using parallel energy loss collections systems has been written and is operating successfully.

c. Theory

We completed and published the first quantum mechanical analysis of the low loss region of energy loss spectra and compared our results to experimental low loss spectra from specimen of silicon, silicon carbide, silicon nitride and silicon dioxide. The CNDO/2R computation scheme was successfully applied to analysis of the silicon-L edge in energy loss spectra. A variation of the quantum Monte Carlo method for computing the thermodynamic properties of interfaces has been investigated and appears useful for analyzing chemical segregation to interfaces.

2. Proposed Research for January 1, 1989 to December 31, 1989

a. Materials

High resolution imaging and very high spatial resolution electron energy loss analysis of interfaces in a number of technologically important materials will be conducted. Effort will be concentrated on interfaces whose structure can be analyzed quantitatively. Interfaces of particular interest are Σ13 boundaries in silicon, interfaces between SiC and Al_2O_3 or Si_3N_4, and interfaces between Si_2N_2O and Si_3N_4. Radiation effects studies using electron energy loss spectroscopy to evaluate dose dependent composition changes for silicon oxynitride and aluminum nitride will be conducted. These important experiments will provide information on the reliability of chemical analysis of these materials when using electron energy loss spectroscopy. A major objective of this type of research is determination of the dependence of boundary or interface chemical segregation or chemical reaction upon structure, i.e. atom configuration at the boundary or interface. This requires high resolution structural analysis of boundaries/interfaces, understanding of the fine structure of energy loss spectra, understanding of radiation effects, and control of the current distribution in electron microprobes through knowledge of the appropriate electron optics.

b. Instrumentation

New software for composition profiling at interfaces/boundaries will be put into use. This software enables digital control of electron microprobe position on a specimen and of dwell time at any particular position on the specimen.

c. Theory

CNDO/2R and pseudo-potential computational techniques will be used to compute electron energy loss absorption edges for Si, SiC, Si_3N_4, SiO_2, Si_2N_2O and AlN. These results will be used for critical evaluation of the most accurate computational method and to interpret experimental radiation effects data.

A program developed by Dr. Mason Skiff to compute energy loss spectra from 128 atom clusters, which may be disordered arrays of atoms, will be used to compute the expected changes in silicon-L near edge fine structure for a spectrum acquired from a clean Σ13 boundary in silicon using an electron probe 20 Angstroms in diameter or smaller. These results will be compared directly to experimental results.

Our quantum Monte Carlo method will be applied to determination of thermodynamic properties of interfaces.

Nutt and Carpenter (Mat. Sci. and Engr. 75, 169 (1985)) showed that Mg segregated to alloy matrix/SiC whisker interfaces in a metal matrix composite, where the matrix was an Al alloy containing a small amount of Mg; the ratio of Mg to Al concentration was measured along a trace normal to the whisker matrix interface. To obtain the interface concentration, we have developed a statistical thermodynamic method to calculate the canonical partition function. The partition function is written as a product of thermal and configurational contributions, using the Bragg-Williams approximation for the configurational part. To determine the composition profile as a function of distance along the interface the effect of the interface free energy and diffusion is taken into account. We will investigate the applicability of this theoretical approach for determination of interfacial chemical segregation in both metal matrix and ceramic matrix composites.

3. Graduate Students and Postdocs who received support from this grant:

   a. Dr. Mason Skiff, Ph.D., Chemistry

   Dr. Skiff was supported on this grant for several months during 1988. He was the primary researcher involved in analysis of ELS low loss spectra, and in writing a program for computation of energy loss spectra from 128 atom clusters for disordered systems. He is now a research staff scientist at the Shell Westhollow Research Center in Houston.

   b. Dr. Moon J. Kim, Ph.D., Engineering Science

   Dr. Kim is currently employed on the project, doing high resolution imaging and energy loss research on Σ13 boundaries in silicon.

   c. J.K. Weiss, B.S. Physics

   Mr. Weiss is performing computations of current distributions in small probes for electron energy loss and x-ray energy dispersive microspectroscopy. He is expected to finish his doctoral dissertation in June 1989. It will also include some applications to ceramic materials.

d. Karnoketu Daschowdhury, B.S. Engineering

Mr. Daschowdhury is performing energy loss radiation effects research on silicon oxynitride as part of his Ph.D. dissertation research. Completion is expected in the summer of 1990.

e. Philip R. Rice, M.S. Physics

Mr. Rice is near completion of his course work for the Ph.D. He is doing research on microstructure, energy loss and radiation effects in aluminum nitride ceramic bodies.

f. Hong Ma, B.S. Chemistry

Mr. Ma is doing CNDO/2R and pseudo potential calculations for theoretical interpretation of energy loss spectra from a number of ceramic compounds, and will do cluster energy loss calculations for interpretation of energy loss spectra this year, using CNDO/2R or extended Huckel formation. His dissertation research is expected to be complete in December of 1989.

g. Prof. B. Fain, Visiting Professor Chemistry

Prof. Fain, from Tel-Aviv University in Israel, spent part of his sabbatical leave with us last year. He contributed to study of interfaces using spectroscopy.

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Progress Report

Grant: DE-FG02-87ER45305
Title: High Resolution Energy Loss Research: Si Compounds and Ceramics
For the period January 1, 1988 to January 1, 1989, for continuation funding from June 1, 1989 to May 31, 1990.

By: R.W. Carpenter ________, and S.H. Lin ________

1. Experimental Results

(a) Ceramic Matrix Composite (CMC) Interfaces.

Two CMC microstructures have been examined in detail using electron energy loss spectroscopy (ELS) and high resolution electron microscope imaging (HREM). The CMC were (1) Al_2O_3 matrix without sintering aid addition, and (2) Si_3N_4 with 6 wt.% (Al_2O_3+Y_2O_3) sintering aid addition. Both of these matrices were reinforced with 20 vol.% β-SiC Tokamax whiskers, and both were fabricated by hot pressing. The whisker/matrix interfaces in both composites were mainly crystalline; there were regions containing an amorphous phase, but it was not continuous, even when examined at 2 Angstrom resolution. Furthermore ELS did not show evidence for chemical segregation at crystalline whisker/matrix interfaces, and the amount of amorphous phase observed depended on sintering aid addition: more sintering aid produced more amorphous phase. These important experimental observations contradict some theoretical speculations in the literature that imply the existence of continuous amorphous phase at interfaces. These results are given in attachment 1,2, and 3.

(b) Amorphous regions containing microcrystals in ceramics.

We have observed regions consisting of an amorphous matrix containing microcrystals at triple junctions in diverse ceramics. Using ELS and HREM we have shown that the amorphous matrix always had an appreciable oxygen concentration, and that the microcrystals were graphite. The other constituents of the amorphous matrix were metals and metalloid elements characteristic of impurity distributions and the base ceramic constituents. We have observed these regions in hot pressed SiC, Al_2O_3/SiC composites, liquid-phase reaction zones in wurtzite-structure SiC alloys, and pressureless sintered SiC. Examples in the latter material are shown in Attachment 4. We were the first to discover the presence of oxygen in these amorphous regions; the explanation of this occurrence poses a difficult and interesting problem in high temperature physical chemistry, particularly in those materials/processes with a strongly reducing environment. The mechanical properties of these regions are obviously quite different from those of any structural ceramic. The occurrence of these regions in many different ceramics is process-related and may be related to the well known wide scatter band for fracture strength of most ceramic materials.

(c) Fundamental Study of Boundary Structure/Segregation.

Observations of chemical segregation to boundaries/interfaces with analyzable structure is a comparatively rare event, especially for materials related to ceramics, because specimens of this type are very difficult to prepare. Collaborative research with Prof. Gunter Schwuttke of the Computer and Electrical Engineering Department yielded a large silicon bicrystal with Σ13 {320} structure; this remarkable bicrystal was 4 inches in diameter and 14 inches long, with the plane of the boundary bisecting the crystal along its growth axis. HREM examination showed much of the boundary to be clean, with atomic geometry corresponding to theoretical predictions (Attachment 5). Other regions, however, had images indicating that growth-related oxygen segregation to the boundary may have occurred (Attachment 6). This image shows one of several possible oxygen distributions along the boundary. Subsequent ELS experiments proved that oxygen segregation had occurred during growth (Attachment 7). These are the first observations of oxygen segregation to any growth related boundaries in silicon. This bicrystal is an ideal specimen for determination of the effect of atom geometry on ELS absorption edges using clean boundary regions, for determining the mechanism of oxygen segregation to boundaries, and for comparing the attainable experimental spatial resolution of energy loss spectroscopy with theoretical predictions.

(d) Mechanisms of Liquid-Phase Ceramic Crystal Growth.

We have determined that small inclusions in melt-grown plate-type silicon oxynitride crystals are alpha silicon nitride. Examples of this microstructure are shown in Attachment 8. These oxynitride plates were grown in a melt formed from SiO_2, Si_3N_4, and Al_2O_3. The Si_2N_2O plates appear to have nucleated on the surface of Si_3N_4 particles in the melt. We now have the phase distribution completely defined in this system, and are beginning a high resolution study of interfaces in the system. This microstructure is considered a model for study of liquid phase sintering in nitrogen ceramics.

2. Instrumentation Results.

(a) Electron energy loss spectroscopy.

Two electron energy loss spectrometers with new parallel detection systems have been successfully interfaced to research electron microscopes. One is on a Philips EM-400 fitted with a field-emission electron gun and supertwin objective lens, and the other is on a new JEOL-2000FX. Both microscopes are equipped with effective anticontamination devices and low temperature specimen stages, and so are suitable for very high spatial resolution microanalysis. These spectrometers have achieved an experimental energy resolution of 0.45eV, and are routinely operated at 0.8eV resolution, which is more than sufficient to observe most interesting spectrum fine structure.

(b) Electron nanoprobe experiments and computations.

All software and instrumental modifications for measurement and computations of current distributions in small focussed electron probes are completed. Our experimental measurements so far agree very well with the results of theoretical calculations. First results are summarized in Attachment 9.

(c) Radiation effects: Time-resolved electron energy loss spectroscopy.

The software required to acquire and store many (several thousand spectra; approximately 4Mb memory) sequential electron energy loss spectra from a single specimen area has been written and is operational. This software will be used to examine effects of total dose and dose-rate on energy loss spectra.

3. Theory Results.

(a) Quantum treatment of low loss energy loss spectra.

The low loss region of an energy loss spectrum contains the plasmon or valence shell absorption edges, representing excitation of weakly bound outer electrons to higher energy states. Classical dielectric theory is conventionally used to explain these excitations; this continuum approach requires assumptions of a conduction or "free" electron density, and does not give a physically useful interpretation of the low loss part of the spectrum, especially for semiconductors and insulating ceramics. We developed a quantum theoretical explanation of these absorption processes that provided an accurate physical interpretation of the edges (Attachment 10). This theoretical explanation showed directly the absorption edge shape dependence on energy levels in silicon and its compounds with carbon, nitrogen and oxygen, and produced absolute cross section magnitudes in good agreement (within 30%) with experimental values. The primary limitation on accuracy of this treatment is the semi-empirical extended Hueckel method used to compute energies and wavefunctions, but this does not affect the validity of the physical interpretation. Better quantitative agreement with experimentally measured cross section magnitude can be obtained using self-consistent field methods for wavefunction computation. This work is the first quantum mechanical treatment of low loss spectra.

(b) Quantum Monte Carlo Computations.

The evaluation of thermodynamic functions requires calculation of the partition function. For a system of harmonic oscillators, or linearly or quadratically coupled harmonic oscillators this can be done easily. If the system has only a very small number of degrees of freedom one may be able to solve the Shroedinger equation using a basis set expansion, or other numerical methods, to obtain the eigenvalues, to evaluate the partition function. However, for systems with many degrees of freedom and a complicated potential function these methods are impractical. For our present research we have, in collaboration with Prof. H. Kono's group at Yamagata University (Japan), developed a quantum Monte Carlo (QMC) technique based on the path integral (PI) formulation to evaluate the partition function (see Attachments 11 and 12). In this preliminary work we used Bennett's MC method to calculate the partition function for a system with a double-well potential. We are employing this QMC method to calculate the thermodynamic properties of solid-solid interfaces.

(c) Wave Function Calculations: Complete Neglect of Differential Overlap (CNDO).

We have used a modified 2R parameterization of the CNDO method for energy band calculations in silicon. The resulting wavefunctions were used to calculate near edge fine structure for the Si-L absorption edge in electron energy loss spectra (see Attachment 13). The resulting calculated absorption edge did indeed fit the experimental edge better than did our earlier calculations using the extended Hueckel parameterization for band structure calculations, as we expected. These results show that our earlier theoretical approach was valid; quantitative accuracy of computed electron inelastic scattering cross sections depends primarily on the level of computational sophistication used for wavefunction computation, and the theory is understood. This is an extremely important observation for materials science research.

<u>Publication List for this Project last year</u>.

1. W. Braue, R.W. Carpenter and D.J. Smith, "HREM Interface Studies in SiC-Whisker Reinforced Al_2O_3 and Si_3N_4 Ceramics", p. 734 in Proc. 46th Ann. Mtg. Elec. Micros. Soc. Amer., G.W. Bailey, ed., San Francisco Press, San Francisco, 1988.

2. J.K. Weiss and R.W. Carpenter, "A Study of Small Probe Formation in a Field Emission Gun TEM/STEM", ibid, p. 510.

3. W.M. Skiff, R.W. Carpenter and S.H. Lin, "Analysis of valence shell electronic excitations in silicon and its refractory compounds using electron energy loss microspectroscopy", J. Appl. Phys. <u>64</u> (11) 6328, Dec. 1988.

4. H. Kono, A. Takasaka and S.H. Lin, "Monte Carlo calculation of the quantum partition function via path integral formulations", J. Chem. Phys. <u>88</u> (10), 6390, May, 1988.

5. H. Kono, A. Takasaka and S.H. Lin, "Extraction of ground state properties by discretized path integral formulations", J. Chem. Phys. 89 (5), 3233, Sept., 1988.

6. R.W. Carpenter, "High Resolution Interface Analysis", Mat. Sci. and Engr. <u>A107</u>, 217 (1989).

List of Reprint and Preprint Attachments.

1. Braue, Carpenter & Smith, "HREM Interface Study in Si-C Whisker Reinforced Al_2O_3 & Si_3N_4 Ceramics", Proc. EMSA, 1988.

2. Carpenter, "High Resolution Interface Analysis", Mat. Sci. & Engr. A, Preprint, published in January, 1989.

3. Braue, Carpenter and Smith, "High Resolution Analysis of SiC Whisker..", Preprint, submitted to Jour. Mat. Sci., Feb., 1989.

4. Braue and Carpenter, "Analytical Electron Microscopy of Graphite-Rich Inclusions in Sintered α-Silicon Carbide", preprint, submitted to J. Mat. Sci., January, 1989.

5. HREM Image, Clean Si Σ13 boundary.

6. HREM Image, Oxygen containing Si Σ13 boundary.

7. ELS spectra from oxygen at Si Σ13 boundary shown in attachment 6.

8. Braue, Skiff, Carpenter and Ma, " Energy loss and x-ray analysis of major constituents in silicon oxynitride ceramics," Proc. EMSA, 1987.

9. Weiss and Carpenter, "A Study of Small Probe Formation in a Field Emission Gun TEM/STEM", Proc. EMSA 1988.

10. Skiff, Carpenter and Lin, "Analysis of Valence Shell...", Jour. App. Phys. 64 (1988) 6328.

11. Kono, etal, "Monte Carlo....", J. Chem. Phys. 88, 6390, 1988.

12. Kono, etal, "Extraction of ground state...", J. Chem. Phys. 89, 3233, 1989.

13. Ma, Skiff, Wu, Lin and Carpenter, "Application of a semiempirical self-consistent-field band calculation to near-edge fine-structure analysis of core-shell electronic absorption edges", Preprint, 1989.

Reprints + Preprints removed

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