COMPOSITIONS AND CHEMICAL BONDING IN CERAMICS BY QUANTITATIVE ELECTRON ENERGY-LOSS SPECTROMETRY

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ABSTRACT

Quantitative electron energy-loss spectrometry was applied to a range of ceramic materials at a spatial resolution of <5 nm. Analysis of Fe L_{23} white lines indicated a low-spin state with a charge transfer of ~1.5 electrons/atom onto the Fe atoms implanted into (amorphized) silicon carbide. Gradients of 2 to 5% in the Co:O stoichiometry were measured across 100-nm-thick Co_3O_4 layers in an oxidized directionally solidified CoO-ZrO_2 eutectic, with the highest O levels near the ZrO_2 . The energy-loss near-edge structures were dramatically different for the two cobalt oxides; those for Co_3O_4 have been incorrectly ascribed to CoO in the published literature. Kinetically stabilized solid solubility occurred in an AlN-SiC film grown by low-temperature molecular beam epitaxy (MBE) on $\alpha(6\text{H})\text{-SiC}$, and no detectable interdiffusion occurred in couples of MBE-grown AlN on SiC following annealing at up to 1750°C. In diffusion couples of polycrystalline AlN on SiC, interfacial 8H sialon (aluminum oxy-nitride) and pockets of Si_3N_4 -rich β' sialon in the SiC were detected.

INTRODUCTION

Applications of electron energy-loss spectrometry (EELS) to ceramics have clearly demonstrated the powerfulness of this transmission electron microscopy (TEM) technique for characterization of such materials, especially those containing elements with atomic number $Z < 10$.¹ Examples described here illustrate the sensitivity, accuracy, and limitations of quantitative composition determination and chemical bonding information when applied at a spatial resolution of <5 nm to silicon carbide implanted with iron, to an oxidized directionally solidified CoO-ZrO_2 eutectic, and to aluminum nitride - silicon carbide diffusion couples.

EXPERIMENTAL

Analytical electron microscopy (AEM) was performed at ORNL with a Philips EM400T AEM equipped with a field emission gun (FEG), a Gatan 666 parallel-detection electron energy-loss spectrometer (PEELS) system, and an EDAX 9100 energy dispersive X-ray spectrometer (EDS). Philips CM12/STEM and CM30/STEM AEMs were also used. For microanalysis, specimens were usually cooled to -130°C in Gatan double-tilt cooling holders. High-spatial-resolution PEELS data were acquired in the scanning TEM (STEM) mode with probes of ~2-nm diameter (FWTM) containing ~0.8 nA, and incident and collection half-angles of 8 and 19 (or 30) mrad, respectively. Spectra were also recorded in the TEM mode with probe currents >3 nA, an incident beam divergence of 3 mrad, and probes of ≤10-nm diameter.

Polished single crystal $\alpha\text{-SiC}$ platelets (Carborundum Company, Niagara Falls, NY) of predominately the 6H polytype, with the broad face parallel to the basal (0001) plane, were implanted at room temperature with 160 keV ^{57}Fe to a fluence of 6×10^{16} ions/cm² at the ORNL Surface Modification and Characterization Facility.^{2,4}

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Directionally solidified cobalt oxide - zirconia eutectic material was grown at the Université Paris-Sud by a floating zone melting technique, described previously.⁵

Three AlN-SiC materials, each having α -(6H)-SiC single crystal substrates (Cree Research, Raleigh, NC) oriented 3-4° from [0001] toward [11 $\bar{2}$ 0], were examined in cross section: (1) an AlN-SiC solid solution grown at 1050°C by plasma-assisted, gas-source molecular beam epitaxy (MBE);⁶ (2) diffusion couples of MBE-grown AlN on SiC annealed for 70 h at 1700°C or 25 h at 1850°C; and (3) diffusion couples of polycrystalline sintered AlN (Dow Chemical) on the above specified SiC substrate, annealed at 1600 and 1700°C.

Specimens were prepared for AEM by standard dimpling and ion milling techniques.

IRON-IMPLANTED SILICON CARBIDE

Silicon carbide ion-implanted with iron has been previously characterized by AEM.^{2,4} Implanted iron depth profiles were measured by EDS; no clustering of the iron in the amorphized SiC was detected by TEM. Information about the bonding of the iron was sought from examination of the electron energy-loss near-edge structure (ELNES) for the Fe L_{23} edge. Preliminary data^{2,4} have subsequently been supplemented and quantitatively analyzed. Figure 1 shows a comparison of the Fe L_{23} ELNES in spectra measured with PEELS for a plan-view Fe-implanted SiC specimen sectioned to near the maximum Fe concentration (16 mol%), and for various other iron-based materials. The spectra are normalized so that the level of excitation to the continuum states (say $E > 735$ eV), which is a good measure of the quantity of iron analyzed, is identical for all spectra. The white lines, which arise from transitions to unfilled 3d levels, are much less intense for the Fe-implanted SiC than for the other materials; they are also slightly broader. In more quantitative terms, Pearson et al.⁷ have shown that the normalized white line intensity (WLI) ratio, relative to the intensity in a 50 eV window, 50 eV above the L_3 edge (continuum states), can be used as a measure of the 3d occupancy. Morrison et al.⁸ have derived expressions for measuring 3d hole concentrations from L_3 and L_2 white line intensities. Clearly, the marked differences in the white lines in the spectra of Fig. 1 imply gross changes in the 3d occupancies and thus of chemical bonding. Quantitative measurements of normalized WLI ratios⁷ for the spectra of Fig. 1 are shown in Table 1. The results imply a charge transfer of > 1.5 electrons/atom onto the iron relative to metallic iron. Similarly, from the expressions of Morrison et al.,⁸ the ratio of the number of 3d holes for the implanted iron relative to that for metallic iron is 0.53, again implying ~ 1.4 electrons/atom charge transfer. Additionally, the small L_3/L_2 WLI ratio for the implanted iron implies a low spin state; the ratio of 5/2 to 3/2 state holes for the implanted iron is 20% lower than for metallic iron. The results suggest that the iron in the SiC is not primarily metallically bonded and support the conclusion of earlier conversion electron Mössbauer spectroscopy data that the iron is in covalently bonded sites.⁹

Fig. 1. Fe L_{23} ELNES for Austenite, ferrite, cementite, and Fe-implanted SiC.

Table 1. Analysis of Fe L_{23} white line intensities

	Normalized WLI	Implied 3d occupancy
Fe ₂ O ₃	0.65	4.5
Fe ₃ C	0.41	6.5
Austenite	0.42	6.3
Ferrite	0.37	6.9
Fe in SiC	0.20	8.6

COBALT OXIDE - ZIRCONIA EUTECTIC

The morphology of directionally solidified eutectics (DSE) provides an excellent geometry for studying interfaces in materials, for example by high-resolution TEM.¹⁰ The thin, parallel plates which are formed in the ZrO_2/CoO system also produce flat interfaces on the microscopic scale. However, heat treatment of the eutectic in a high oxygen partial pressure results in a trilayer structure^{11,12} as the CoO transforms to Co_3O_4 . The microstructure consists of alternating lamellae of CoO and calcium-stabilized cubic- ZrO_2 , each with widths of up to $1\text{ }\mu\text{m}$, and a thin (100 to 200 nm), irregular layer of Co_3O_4 spinel extending into the CoO from the flat ZrO_2 interface. The growth direction of the DSE is $[001]_{\text{ZrO}_2} // [1\bar{1}0]_{\text{CoO}}$ and the broad interface is $(100)_{\text{ZrO}_2} // (111)_{\text{CoO}}$. The Co_3O_4 is oriented cube-on-cube with the CoO .

Typical core-loss PEELS data for the stabilized cubic zirconia phase are shown in Fig. 2a. The proximity of the Zr M_3 and overlap with the Zr M_2 preclude accurate use of the $\text{Ca L}_{2,3}$ edge for composition determination but, fortunately, Ca/Zr ratios are easily obtained by EDS. Such measurements indicate that the Ca/Zr atomic ratio is 0.18. However, for other aspects of composition determination, secondary excitation¹³ in EDS gives misleading results, such as the apparent presence of zirconium in the cobalt oxides and higher than actual levels of cobalt in the zirconia. Also, strong X-ray absorption limits the accuracy of oxygen contents from EDS data.

Typical core-loss PEELS data for the cobalt oxide phases are shown in Fig. 2b. To determine compositions accurately,¹⁴ care has to be taken in the treatment of the energy-loss near-edge structure (ELNES), e.g., the $\text{Co L}_{2,3}$ "white lines." A simple approach, that of beginning the integration window just beyond the most pronounced ELNES was used. The measured values of composition depend upon the position of the integration window and the use of the white line correction in the Gatan EL/P (version 2.1) software. A 100 eV integration window offset from the edge threshold by 25 eV gave the most reliable results. Further work, at higher spatial resolution, indicated a reproducible 2 to 5% gradient in the Co:O ratio across the Co_3O_4 phase, with the lowest values (highest oxygen content) near the ZrO_2 interface. This is consistent with the proposed mechanism of phase formation that is based on rapid diffusion of oxygen in the ZrO_2 lamellae and slower lateral diffusion into the cobalt oxide.⁵ The measurement of such composition gradients is possible because the precision of the data is much better than the absolute accuracy.

Inspection of the oxygen energy-loss near-edge structure (ELNES) reveals dramatic differences between the CoO and Co_3O_4 (Fig. 3a). Interpretation of such oxygen ELNES is complex and involves consideration of site symmetry and states arising from hybridization of oxygen 2p levels with metal 3d and 4s or 4p levels.¹⁵ Nevertheless, the differences in oxygen ELNES provide easily identifiable signatures for the two cobalt oxides. The cobalt $\text{L}_{2,3}$ white line ELNES (Fig. 3b) is superficially similar for the two phases, but there is a small shift to higher energies for the Co_3O_4 ($\sim 1.5\text{ eV}$ for L_3 , $\sim 0.6\text{ eV}$ for L_2). The normalized WLI ratio, relative to the continuum states in a 50 eV window, 50 eV above the L_3 edge,⁷ is 0.53 ± 0.02 for the two cobalt oxides, implying similar 3d occupancies. The L_3/L_2 WLI ratios are 3.88 and 2.58 for the CoO and Co_3O_4 , respectively. From the type of analysis employed by Morrison et al.,⁸ the ratios of 5/2 to 3/2 state holes are 1.42 and 0.89 for CoO and Co_3O_4 , respectively, and the ratio of the total number of 3d holes in CoO to those in Co_3O_4 is 0.98, in agreement with the normalized WLI ratio analysis. Quantitative measurements were

Fig. 2. Typical core-loss PEELS data for (a) ZrO_2 (CaO), (b) Co_3O_4 and CoO phases.

Fig. 3. (a) Oxygen K and (b) cobalt $L_{2,3}$ ELNES for Co_3O_4 and CoO phases.

made on single scattering profiles, but difficulty was experienced in implementing even the simple geometric approach used by Pearson et al.⁷ because of the edge shape just beyond the white lines.

Oxygen and cobalt ELNES (with slightly better energy resolution than our present results) for cobalt oxide have recently been published.¹⁶ The results were stated as being for CoO that was made by oxidizing thin evaporated metal films in air at 400°C . However, the published oxygen ELNES is not at all like our results for CoO ; instead, there is excellent agreement with our results for Co_3O_4 . Similarly, the positions of the published Co L white lines are more consistent with our data for Co_3O_4 than CoO . Phase diagram data indicate that Co_3O_4 is the stable oxide below -900°C for oxygen partial pressures of >0.1 atm. Kurata and Colliex¹⁷ have noted similar discrepancies for ELNES of MnO and Mn_3O_4 .

Krivanek et al.¹⁸ extended the EDS-based ALCHEMI (atom location by channeling-enhanced microanalysis) method to demonstrate energy-loss with channeled electrons (ELCE) for MgAl_2O_4 spinel. Tafto and Krivanek¹⁹ further extended the method to demonstrate site-specific valence determination of Fe in a chromite spinel. Similar experiments were performed in an attempt to discriminate the signature of the di- and tri-valent cobalt ions in Co_3O_4 , but no difference in the Co ELNES was detected. The most likely explanation for this behavior is that Co_3O_4 has the inverse spinel structure.¹² There is some supporting evidence from X-ray diffraction data on bond lengths; in addition, Fe_3O_4 has the inverse spinel structure. Further experiments are planned.

ALUMINUM NITRIDE - SILICON CARBIDE

Aluminum nitride and silicon carbide are structural ceramics and wide bandgap semiconductors which have similar hexagonal structures and a lattice mismatch in the basal plane of only 0.9%. AlN-SiC materials are of interest as high temperature structural materials and as ceramic semiconductors for applications such as high power and ultraviolet optoelectronic devices, or for use in severe environments. The tentative AlN-SiC phase diagram of Zangvil and Ruh²⁰ shows a flat miscibility gap at -1950°C between -20 and 80% AlN , with a 2H solid solution above this temperature. The existence of the miscibility gap has been confirmed by several investigators (see Kern et al.⁶), notably Chen et al.²¹ Interdiffusion data exist only for 1950°C and higher. High resolution PEELS was used to detect possible interdiffusion at lower temperatures.

Examination of the AlN-SiC solid solution epilayer grown by MBE at 1050°C revealed predominantly the 2H polytype. Planar defects about 40 nm long and separated by about 5 nm in the growth direction were present on the basal planes. Their formation appears to be linked to the presence of similar sized steps on the growth surface, which are in turn related to the misorientation of the SiC substrate.²² No compositional inhomogeneity was detected by PEELS, the solid solution presumably being kinetically stabilized at the low growth temperature. Quantitative analysis of PEELS data indicated N/C and Al/Si atomic ratios of 0.75 ± 0.05 , in contrast to published⁶ Auger measurements of -0.43 .

Similarly, high spatial resolution PEELS failed to detect any interdiffusion in the diffusion couples of AlN grown by MBE on $\alpha(6\text{H})\text{-SiC}$ and annealed at 1700 or 1850°C , either near the substrate interface or at threading dislocations in the epilayer. Auger depth profiles had indicated apparent

substantial interdiffusion, but large growth-surface steps and concomitantly large variations in epilayer thickness (30%), explain the misleading Auger results.²²

In the diffusion couples of polycrystalline AlN on α (6H)-SiC annealed at 1600 and 1700°C, an additional phase, typically ≤ 50 -nm-thick, was present at the SiC-AlN interface, but only where the AlN was epitactic to the SiC. Typical PEELS data from this phase are shown in Fig. 4; the major constituents are N, O, and Al; there is also a small Si signal. The O/N ratio measured by PEELS ranged from 0.35 to 0.75; beam damage probably contributed to the variability. High-magnification images of the interface phase revealed a 2.3 nm periodicity along the c-axis. The interface phase was thus identified as the 8H sialon phase^{23,24} which is based on the 8H aluminum oxynitride polytypoid of nominal composition $(\text{AlN})_2\text{Al}_2\text{O}_3$.²⁴ With EDS, secondary excitation of the SiC precludes confident identification of the small Si signal as intrinsic to the 8H interface phase; with PEELS there

Fig. 4. PEELS data for 8H sialon interface phase.

Fig. 5. PEELS data for Si_3N_4 -rich β' sialon particles.

is no such concern. Sputtered films from the ion milling are also unlikely since no Si was detected by PEELS on the nearby AlN. The oxygen presumably originates as a surface impurity on the starting materials. The exact epitaxy of AlN grains with the SiC, strongly suggests recrystallization of AlN (2H) from the 8H sialon. Interestingly, this would mean that the dome defects, prevalent in the epitactically oriented grains, nucleate at the dome top, increase in diameter as the grain boundary advances, and eventually pinch off at the oxygen-rich basal fault.

No aluminum was detected in the SiC, even adjacent to the interface, but particles typically 250 nm in diameter, and occasionally up to 1 μm long, form within the SiC at distances up to several micrometers from the SiC-AlN interface. Quantitative analysis of typical PEELS data (Fig. 5) yields Si_3N_4 with small levels of O and Al. Diffraction patterns confirm the Si_3N_4 -rich β' sialon identification and show $[0001]_{\beta'} // [11\bar{2}0]_{6H}$ and $[10\bar{1}0]_{\beta'} // [0006]_{6H}$. Oxygen is suspected of playing an important role in the precipitate formation.

CONCLUSIONS

The results vividly illustrate the efficacy of PEELS for the microanalysis of ceramics. Some questions remain regarding the validity of the normalized WLI ratio method for 3d occupancy measurement in 3d transition metal compounds. The method appeared useful for the Fe in amorphous SiC, but less so for differentiating Co^{2+} and Co^{3+} in cobalt oxides. The ability to measure compositions by PEELS, particularly for elements with $Z < 10$, at a spatial resolution of a few nanometers is unmatched. The absence of secondary excitation processes, which can plague EDS measurements of multi-phase materials, leads to greater confidence in the determined compositions. The Co:O stoichiometry gradients across the 100-nm-wide Co_3O_4 , the absence of AlN-SiC interdiffusion at low temperatures, and the importance of the minor constituents for sialon phase identification, are all examples where PEELS has clear advantages over any other technique.

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