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PULSED LASER ATOM PROBE CHARACTERIZATION OF SILICON CARBIDE

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Abstract - Field-ion microscopy and field evaporation of α -SiC and β -SiC materials have been successfully demonstrated. Since field-ion micrographs could be taken immediately after pulsed field evaporation, the effects of preferential field evaporation of silicon that occurred under ramped field evaporation were eliminated. However, due to the high electrical resistivity of silicon carbide, conventional voltage pulsed field evaporation was not practical and pulsed laser field evaporation was required. No significant variations in performance were found as a function of laser wavelength but the full-width-at-half maximum mass resolution of 0.4 amu was inferior to voltage pulsed field evaporation of metals. In addition, the background noise level was considerably higher. Within the statistical accuracy of the analyses, the compositions were found to be slightly deficient in silicon. These experiments also revealed that the laser power required to field evaporate SiC was greater than for other semiconducting materials.

INTRODUCTION

Silicon carbide is best known as a structural ceramic and is a material that has high temperature and high strength applications. Sintered or hot pressed silicon carbide ceramics are generally polycrystalline forms of α -SiC which contain relatively small amounts of aluminum^[1] or boron^[2] intentionally added as densification aids. Silicon carbide, grown in whisker form, is also used as a high strength reinforcement in composites.^[3] The silicon carbide whiskers are cubic β -SiC and are usually grown by vapor-liquid-solid (VLS) or "rice-hull" processes.^[4-6] In addition, β -SiC has applications for use in semiconductor device applications because of its unique combination of physical and electronic properties. Single crystal thin films of β -SiC are currently grown by chemical vapor deposition onto (100) silicon substrates.^[7]

Several previous attempts have been made to fabricate, image and analyze field-ion specimens of SiC with the atom probe field-ion microscope. As early as 1968, Nishida fabricated a blunt field emission specimen by electrolytic etching in a NaOH solution.^[8] Field-ion specimens of 5 μ m diameter β -SiC whiskers were prepared by heating in an oxypropane flame for a few seconds.^[9] The silica bead that formed was then dissolved in hydrofluoric acid. Kudo et al. prepared field-ion specimens by electrolytically etching β -SiC whiskers in a solution of 45% HF - 22% H₂SO₄ - 22% H₃PO₄ - 11% CH₃COOH.^[10] The same specimen preparation procedure was used by Nakamura and Kuroda in an atom probe investigation of [111] and $\bar{1}\bar{1}\bar{1}$ -oriented whiskers.^[11] Nakamura et al. also prepared specimens by chemically etching whiskers in molten KOH.^[12] Inoue and Nakada produced SiC needles with a end radius of 30 nm from whiskers by etching in a solution of HF and HNO₃.^[13] In the present atom probe field-ion microscopy investigation, several of these chemical methods were attempted on the various forms of SiC used in this study with little success. Therefore, a new approach to specimen preparation of these materials was taken that substituted ion milling for the conventional chemical or electrochemical procedures.

In a previous field-ion microscopy investigation of β -SiC, Smith found that the helium field-ion image was unstable and irregular although the ring structure of a low index pole was apparent when imaged in

hydrogen.^[9] Kudo et al. found that helium images of β -SiC were poor with no atomic order evident and hydrogen images were unstable and irregular.^[10] A previous atom probe characterization of β -SiC whiskers was performed by Nakamura and Kuroda in a conventional voltage pulsed time-of-flight atom probe.^[11] However, only a very limited number of atoms were reported since the flight times were measured from an oscilloscope trace. The field evaporated species detected with a pulse fraction of 10% ($V_{\text{PULSE}}/V_{\text{DC}}$) and a specimen temperature of $\sim 78\text{K}$ in this instrument were C^+ , Si^+ , and Si^{2+} ions and SiC^+ , SiC^{2+} and SiO^+ complex ions. The vacuum in this instrument was $\sim 10^{-6}$ Pa. Carbon was found to evaporate in molecular form with silicon. However, a substantial proportion of ions shown in the mass spectra were unassigned. A voltage pulsed atom probe investigation of β -SiC at room temperature in the presence of approximately 10^{-5} Pa of hydrogen was performed by Nakamura et al.^[12] Under these conditions, the specimen field evaporated as Si^{2+} , C^+ , C^{2+} and H^+ species. No complex species were observed; however, only a small number of ions were shown in the mass spectra.

EXPERIMENTAL

Field-ion specimens of polycrystalline α -SiC, β -SiC thin films grown on (100) Si, and β -SiC whiskers produced from the "rice-hull" and VLS processes were fabricated by ion milling. The bulk α -SiC material was initially cut into square bars (0.5 mm x 0.5 mm x 5 mm) with a diamond cutoff wheel. The specimen blank was ion milled in a Gatan model 600 conventional ion mill in which the sample holder was adapted to accept the field-ion needles. The β -SiC/Si thin film specimens were prepared in a similar manner. This arrangement permitted the needle to be continuously rotated about its specimen axis during ion milling. A 6 kV argon ion beam was used for ion milling. The whiskers were mounted onto blunt tungsten needles with conducting epoxy and were prepared in a Gatan model 645 precision ion milling system (PIMS) as described elsewhere.^[14]

Field-ion microscopy was performed with specimen temperatures between 40 and 120K. Helium and neon image gases were used. However, because of the presence of a C^{3+} species at a mass-to-charge ratio of 4 amu which would be masked by a He^+ species, helium was not used to image specimens that were intended for atom probe analysis.

Both the ORNL atom probe^[15] and Oxford University pulsed laser atom probe^[16] were used to examine the specimens. Chemical analyses were conducted primarily at Oxford University in the pulsed laser atom probe that is equipped with a JK Lasers System 2000 Neodymium-YAG laser. This laser features a 5 ns pulse width and has a power output of up to 120 mJ per pulse. Two wavelengths were used, 532 and 355 nm. Chemical analyses were performed with the image gas removed from the system in a vacuum of better than 10^{-8} Pa.

RESULTS AND DISCUSSION

Ion Milling

Most β -SiC field-ion specimens fabricated by ion milling were sharp, relatively uniform in cross-section, and had a small taper angle. The α -SiC specimens were irregular in cross-section due to preferential ion milling along grain boundaries. A transmission electron microscope (TEM) image of a needle prepared from the β -SiC thin film is shown in Fig. 1. Ion milling consistently produced needles in which the end radius was less than 10 nm.

Field-Ion Microscopy

A neon field-ion micrograph of an α -SiC specimen taken after dc evaporation is shown in Fig. 2. The image was uniform over the specimen surface with little or no ring structure evident, in agreement with previous observations. No difference in behavior was observed between α -SiC and β -SiC. Two field-ion micrographs taken immediately after pulsed laser field evaporation in vacuum are shown in Fig. 3. The quality of these field-ion micrographs was slightly better and a few poles could be identified sufficiently to classify the major 111 pole from its 3-fold symmetry.

The calculated evaporation fields for Si^+ , Si^{2+} , and Si^{3+} are 45, 33, and 60 Vnm^{-1} , respectively, and those of C^+ , C^{2+} , and C^{3+} are 142, 103 and 155 Vnm^{-1} , respectively.^[17] These values indicate that silicon is substantially easier to evaporate than carbon. It is likely that the silicon preferentially evaporates during

dc evaporation leaving the surface of the specimen rich in carbon. The field-ion image of this surface is therefore not representative of silicon carbide but of carbon. Preferential field evaporation of one species is common in alloys that contain elements that differ significantly in their evaporation fields.^[18] After pulsed laser assisted field evaporation, the silicon was not preferentially evaporated from the surface of the specimen and a field-ion micrograph representative of SiC could be obtained.

Atom Probe Analysis

In these high resistivity materials, reliable voltage-pulsed field evaporation proved to be unattainable even with pulse fractions of over 100%. Therefore, chemical analysis was performed in a pulsed laser atom probe. Specimens prepared from the β -SiC whiskers grown by the VLS process were used. The laser power required to field evaporate these specimens was greater than typical for other semiconducting materials. A series of atom probe experiments was performed to investigate whether the wavelength of the laser radiation or the specimen temperature significantly influenced the performance of the instrument or the accuracy of the composition determinations. Two mass spectra of a SiC whisker are shown in Fig. 4. The data in these mass spectra were collected with a specimen temperature of 70K and a laser wavelength of (a) 355 nm and (b) 532 nm. The charge state distributions for carbon and silicon ions are given in Table 1. Only minor differences in the charge state distributions were found between the experimental conditions. The silicon field evaporated almost exclusively as Si^{2+} with small amounts of Si^+ and Si^{3+} . No molecular silicon species were observed. Approximately 80% of the carbon was found to field evaporate as C^{2+} and C^+ ions, although small amounts of C^{3+} and C_2 and C_3 molecular species were also observed. The quantity of ions in the molecular form was typical of that from a refractory carbide. The unusual presence of the triply-charged silicon and carbon ions is a consequence of the refractory nature of the carbide and the high field required to field evaporate the specimen at these temperatures.

Table 1. Distribution of ions between the charge states (in %).

Temperature	Wavelength	Si^{2+}	Si^+	Si^{3+}	C^{2+}	C^+	C^{3+}	C_2^+	C_3^+	C_3^{++}	SiC^+
95K	532	98.1	1.4	0.5	56.5	24.1	2.3	4.0	13.0	0	0
70K	532	94.8	1.4	3.9	53.5	23.0	5.8	8.9	6.5	2.3	0.3
40K	532	97.9	0.7	1.4	55.8	25.4	5.3	9.9	3.1	0.5	0.04
70K	355	99.2	0.6	0.2	58.4	30.6	3.2	4.2	3.3	0.3	0.3

A small number of ions were collected at a mass-to-charge ratio of 40 amu. This species could correspond to SiC^+ or Ar^+ ions. Since less than 0.3% of genuine ions were collected at this mass-to-charge ratio, its contribution may be either neglected or assigned to SiC without significantly altering the results. A few ions were also observed at mass-to-charge ratios of 20, 21 and 22 amu and were assigned to the image gas neon.

The composition determinations based on the assignments shown in Table 1 are summarized in Table 2. The balance of these determinations was carbon. The error quoted is for one standard deviation. The peak at a mass-to-charge ratio of 12 amu was assigned exclusively to the C^+ ion and not the doubly charged C_2 species. This assignment could result in a slight underestimate of the carbon level. The measured compositions under these conditions were consistent with each other within the statistical scatter. The average of the data sets indicated that there is a deficiency in silicon which possibly indicates a slight preferential evaporation of silicon, as would be anticipated from the difference in calculated evaporation fields. The whisker used in this experiment was grown by the VLS process and had a straight and uniform morphology. It has previously been observed that VLS whiskers of this type may possess excess carbon.^[6,19] Therefore, the small deficiency in silicon measured by the atom probe may be real. Additional studies of a variety of SiC specimens of known chemistry are required.

The background noise in the mass spectra was higher than normal for metals in a voltage-pulsed energy-compensated atom probe but similar to that obtained for semiconductors in a pulsed laser atom probe. The primary source of the background noise is residual image gas in the system. The mass resolution of $\Delta M/M$ of $\sim 1/35$ was also inferior to that observed with metal specimens ($\Delta M/M \approx 1/600$) and other semiconducting materials ($\Delta M/M \approx 1/300$). However, the severity of these degradations is not sufficient to limit atom probe analysis.

Table 2. Pulsed Laser Atom Probe Composition Determinations in atomic percent.
The balance of these analyses was carbon.

Specimen Temperature	Wavelength (nm)	Composition (% Si)
95K	532	49.1 $\pm$ 2.1
70K	532	46.5 $\pm$ 0.6
40K	532	47.8 $\pm$ 0.8
70K	355	48.7 $\pm$ 0.7

SUMMARY AND CONCLUSIONS

- * Field-ion specimens of bulk, thin film and whisker SiC materials were successfully prepared by ion milling.
- * Dc field evaporation results in a surface layer rich in carbon and anomalous field-ion micrographs.
- * A pulsed laser atom probe is required for chemical analysis.
- * The measured chemistry did not vary significantly with laser wavelength or specimen temperature.
- * Silicon field evaporated as Si²⁺ with small amounts of Si⁺ and Si³⁺.
- * Carbon field evaporated predominantly as the C²⁺ and C⁺ ions with small amounts of C³⁺ and molecular species.

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Fig. 1. Transmission electron micrograph of a needle prepared from a β -SiC thin film.

Fig. 2. Neon field-ion micrographs of a dc field evaporated α -SiC specimen. (a) at best image voltage and (b) above best image voltage.

Fig. 3. Neon field ion micrographs of a β -SiC whisker after pulsed laser assisted field evaporation. (a) at best image voltage and (b) above best image voltage.

Fig. 4. Pulsed laser atom probe mass spectra from a β -SiC whisker grown by the VLS process. Spectra acquired with a specimen temperature of 70K and laser wavelengths of (a) 355 nm and (b) 532 nm.