

Influence of Alumina Reaction Tube Impurities on the Oxidation of Chemically-Vapor-Deposited Silicon Carbide

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Pure coupons of chemically vapor deposited (CVD) SiC were oxidized for 100 h in dry flowing oxygen at 1300°C. The oxidation kinetics were monitored using thermogravimetry (TGA). The experiments were first performed using high-purity alumina reaction tubes. The experiments were then repeated using fused quartz reaction tubes. Differences in oxidation kinetics, scale composition, and scale morphology were observed. These differences were attributed to impurities in the alumina tubes. Investigators interested in high-temperature oxidation of silica formers should be aware that high-purity alumina can have significant effects on experimental results.

I. Introduction

IN THIS laboratory, we are attempting to understand the basic mechanisms occurring in the oxidation of silicon-based ceramics, i.e., SiC and Si₃N₄. We observed that the impurity effects associated with high-purity alumina reaction tubes on the oxidation of SiC in dry oxygen were very pronounced. These effects are well known in the semiconductor industry for the oxidation of silicon,¹ where high-purity fused quartz tubes are generally used for the oxidation process at temperatures of 1200°C or less. Nevertheless, most studies for the oxidation of SiC, where conclusions have been made about intrinsic oxidation mechanisms, have been conducted in high-purity alumina or mullite tubes owing to the higher oxidation temperatures of interest for SiC (1200–1500°C).

Precedents for the observed impurity effects of high-purity alumina tubes can also be found outside the semiconductor literature. Wagstaff and Richards² noted that contamination in even the highest-purity alumina tubes increased the crystallization rates of silica. The alumina tubes were heated under vacuum at operating temperatures for long times to minimize this problem. Choi, Fischbach, and Scott³ found that parabolic rate constants for the oxidation of silicon in 99.8% pure alumina tubes were about a factor of 7 higher than other values reported in the literature. After changing to silica tubes, they found good agreement with the literature. In recent studies in this laboratory, it was noted that alumina tubes had a large effect on the oxidation behavior of SiC and/or Si₃N₄ in dry oxygen⁴ as well as in 10% water vapor and oxygen.⁵ However, none of these effects have been well documented. In this note, the effects of impurities associated with high-purity alumina tubes are shown in detail in hopes that future studies of oxidation mechanisms of silica formers be conducted in quartz tubes when intrinsic oxidation behavior is desired.

II. Experimental Procedure

CVD SiC coupons (99.999% purity, Morton International, Inc., Woburn, MA) of dimensions 3 cm × 1.5 cm × 0.3 cm were cleaned in detergent, deionized water, acetone, and alcohol. The alumina tubes (99.8% purity, Vesuvius/McDanel, Beaver Falls, PA) and fused quartz tubes (99.995% purity, Quartz Scientific, Fairport Harbor, OH) were cleaned in the same manner as the coupons. The samples were suspended from a microbalance (Cahn 1000, Cahn Instruments, Cerritos, CA) with sapphire rods (<100 ppm impurities, Saphikon, Milford, NH) in 1 in.-diameter reaction tubes. Typical impurity levels for sample and TGA tube materials are shown in Table I. Oxygen gas flowed through the vertical reaction tube at a rate of 100 sccm after first being dried with Drierite (CaSO₄) and Mg(ClO₄)₂. Oxidation was initiated by raising the furnace, already at 1300°C, up around the sample. Oxidation times were typically 100 h. Sample weight change and temperature were recorded digitally as a function of time. After oxidation, the samples were examined by optical microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and secondary ion mass spectrometry (SIMS).

III. Results and Discussion

Macrographs of the CVD SiC coupons after 100-h oxidation in alumina and fused quartz tubes in dry flowing oxygen at 1300°C are shown in Fig. 1. The two coupons are quite different in appearance. The sample oxidized in an alumina reaction tube is light gray in color and has occasional spots on the scale. The

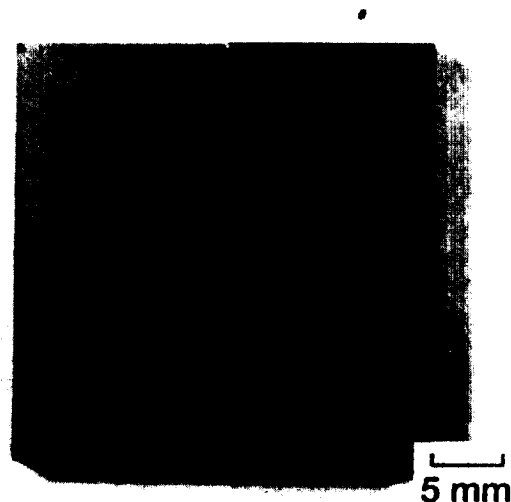


Fig. 1. Macrographs of CVD SiC coupons oxidized for 100 h at 1300°C in dry flowing oxygen. The sample on the left was oxidized in an alumina reaction tube and the sample on the right was oxidized in a fused quartz tube.

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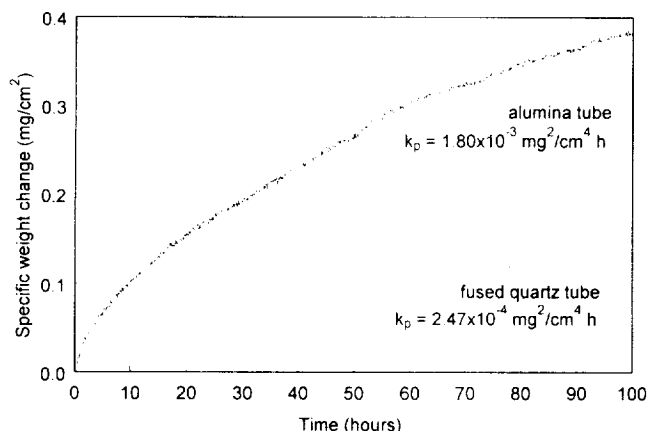
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Table I. Manufacturers' Purity Specifications for the CVD Sample Material and the Reaction Tube Materials

Material (manufacturer)	Purity (%)	Manufacturers' typical values (ppm by weight)
CVD SiC (Morton International)	99.999	Mn (1.2), Fe (7.3), Co (1.0), Ni (0.6), Cu (5.5), Zn (1.5)
High-purity alumina (McDanel/Vesuvius)	99.8	SiO ₂ (600), MgO (350), Na ₂ O (80), CaO (400), Fe ₂ O ₃ (250), Cr ₂ O ₃ (<30), TiO ₂ (40), B ₂ O ₃ (<10), K ₂ O (<10)
Fused quartz (Quartz Scientific)	99.995	Al (16), Ca (0.6), Cr (0.05), Fe (0.3), K (0.7), Li (1), Mg (0.1), Mn (0.1), Na (1), P (1.5), Ti (1.1), Zr (1.5)

**Fig. 2.** Oxidation kinetics for CVD SiC coupons oxidized at 1300°C in dry flowing oxygen.

sample oxidized in the fused quartz tube is much darker in color and has a very uniform surface.

The oxidation kinetics for the two samples mentioned above are shown in Fig. 2. The rate constant for the sample oxidized in the alumina tube is about an order of magnitude higher than that for the sample oxidized in the fused quartz tube. The kinetic results for oxidation in either tube were very repeatable. The parabolic rate constants measured for three samples oxidized in alumina tubes averaged $(1.81 \pm 0.31) \times 10^{-3} \text{ mg}^2/(\text{cm}^4 \cdot \text{h})$. The rate constants measured for three samples oxidized in fused quartz tubes averaged $(2.44 \pm 0.09) \times 10^{-4} \text{ mg}^2/(\text{cm}^4 \cdot \text{h})$.

The SEM cross sections of the oxide scale for the same two samples shown in Fig. 1 are shown in Fig. 3. The scale thickness is $4.7 \pm 0.8 \text{ } \mu\text{m}$ for the sample oxidized in alumina and

$1.6 \pm 0.4 \text{ } \mu\text{m}$ for the sample oxidized in fused quartz. The rate constants can be calculated from the oxide thicknesses assuming a density of 2.32 g/cm^3 for cristobalite as already described.⁶ They are $(1.32 \pm 0.04) \times 10^{-3}$ and $(1.63 \pm 0.01) \times 10^{-4} \text{ mg}^2/(\text{cm}^4 \cdot \text{h})$ for the samples oxidized in alumina and fused quartz, respectively. The disparity between these values and those measured directly by TGA is explained as follows. SEM/EDS observations of oxidized SiC cross sections⁷ have shown that crystalline silica scales crack near the silica/SiC interface leaving a very thin silica layer on the SiC which is indistinguishable from the underlying SiC. Oxide thickness measurements made from the crack to the outer surface result in a slight underestimation of the oxide thickness, and thus k_p .

The XRD results shown in Fig. 4 indicate that both tridymite and cristobalite are present in the scale of the sample oxidized in the alumina tube, whereas tridymite is barely detected in the sample oxidized in the quartz tube. It is known that the formation of tridymite is enhanced in the presence of impurities.⁸

In previous work,⁷ sodium and aluminum impurities were detected by EDS on SiC samples oxidized in 10% water vapor with alumina tubes. Impurity concentrations in the scale on the sample oxidized in the alumina tube with dry oxygen, however, were below the detectability limit of EDS. Oxidized coupons were therefore analyzed using SIMS (Perkin-Elmer PHI-6300 SIMS, work performed by AT&T Analytical Services, Allentown, PA). These results are shown in Fig. 5. The scale grown in the alumina tube has at least an order of magnitude higher sodium content than that grown in the quartz tube. Concentrations were not calculated because of the tendency of Na ions to be moved within the SiO₂ layer by the electron current used for charge neutralization. For the same reason the shape of the Na profile should be considered indeterminate. The Al concentration profiles, if shown relative to ³⁰Si and for the same sputter time (depth) range, are nearly the same in both scales. The different ranges on the abscissa in Figs. 5(A) and (B) prevent this from being easily seen. Ca concentrations (not shown) were lower than Na and Al concentrations and were about the same at the surface of both samples. The Ca concentration in the bulk was about an order of magnitude greater in the scale grown in

**Fig. 3.** SEM micrograph showing the oxide scale thickness for two CVD SiC coupons oxidized for 100 h at 1300°C in dry flowing oxygen. The sample on the left was oxidized in an alumina reaction tube and the sample on the right was oxidized in a fused quartz reaction tube.

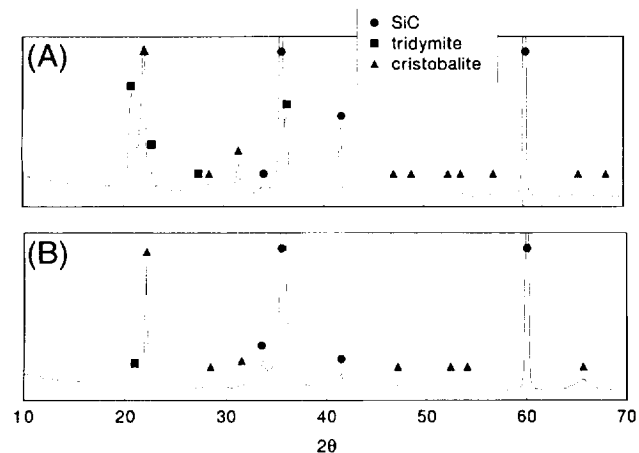
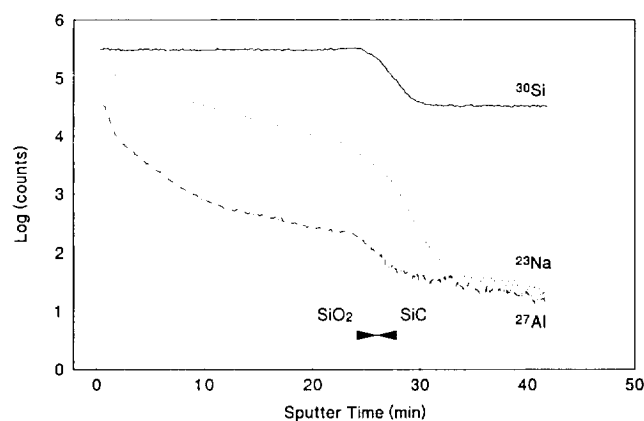


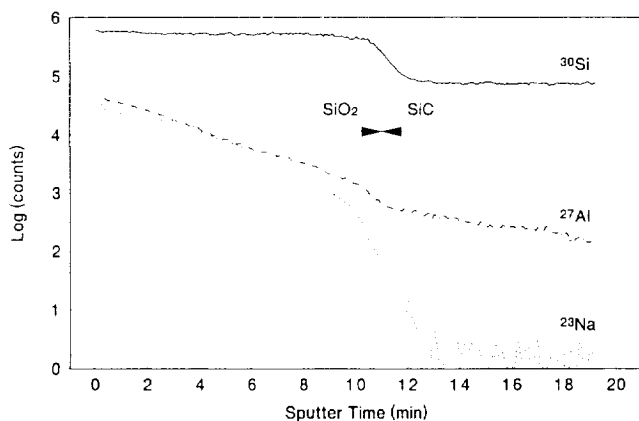
Fig. 4. X-ray diffraction results for two CVD SiC coupons oxidized for 100 h at 1300°C in dry flowing oxygen. Diffraction pattern A was obtained from the coupon oxidized in an alumina reaction tube and pattern B was obtained from the coupon oxidized in a fused quartz tube.

the alumina tube. Levels of Mg, K, and Li were about the same in both coupons. Fe impurity concentrations were not measured because ^{56}Fe could not be differentiated from $^{56}\text{Si}_2$.

It has been demonstrated that sodium accelerates the oxidation of SiC due to the increased permeation of molecular oxygen through the oxide, which may be attributed to the formation



(A)



(B)

Fig. 5. SIMS profiles for Na and Al impurities in the SiO_2 scale on SiC which had been oxidized in an alumina reaction tube (A) and a fused quartz reaction tube (B). Note that the range for the abscissa is different in (A) and (B).

of nonbridging oxygens.⁹ It is therefore believed that sodium impurities from the alumina tube found in the silica scale are responsible for the enhanced oxidation rates compared to those measured in quartz tubes.

From SiC oxidation experiments at lower temperatures (1200°C) where crystallization of silica is less favored, it has been observed that samples oxidized in fused quartz tubes have amorphous scales whereas samples oxidized in alumina tubes are partially crystalline.¹⁰ This is in agreement with the observations of Wagstaff and Richards² that impurities increase the crystallization rate of silica. While the effect of silica crystallization on the oxidation rate of SiC is complicated,¹¹ crystallization is generally believed to decrease oxidation rates.¹² Therefore, impurity modification of the scale rather than crystallization of the scale best explains the enhanced oxidation rates observed here in alumina tubes.

Recent work has been conducted by Ogbuji and Opila⁴ on the oxidation of SiC in fused quartz tubes between 1200° and 1500°C. No change in oxygen transport mechanism was observed to occur in this temperature range. It is suggested that the observed increase in oxidation activation energy found in other studies near 1400°C (summarized in Ref. 4) might be due to reaction tube impurity effects.

An aging effect for impurities in the alumina tubes has been observed. After an alumina tube has been used at temperature for a long time (>2000 h), impurity effects on the oxidation kinetics become insignificant relative to oxidation in fused quartz tubes. This is demonstrated in Fig. 6. The aging effect may be explained by the volatilization of Na impurities over time. Variations in experimental results with time in any impurity-sensitive process conducted in alumina tubes may be due to this aging effect. It is suggested that fused quartz tubes be used when possible to avoid these impurity effects. Fused quartz tubes have been used successfully in this laboratory at temperatures as high as 1500°C.⁴ Use of fused quartz tubes in the 1200° to 1500°C range results in crystallization of the tube; however, this is not a problem until the tube is cooled below the β -to- α cristobalite transition temperature (about 270°C) at which time surface cracking occurs.

IV. Conclusions

It has been demonstrated that the oxidation of pure CVD SiC is very sensitive to ≈ 100 ppm level of impurities. The oxidation kinetics, scale composition, and morphology were all affected by impurities (probably sodium) in "high-purity" alumina reaction tubes. It has been shown that fused quartz tubes provide a cleaner environment for high-temperature oxidation of silica formers in which growth rates are impurity sensitive.

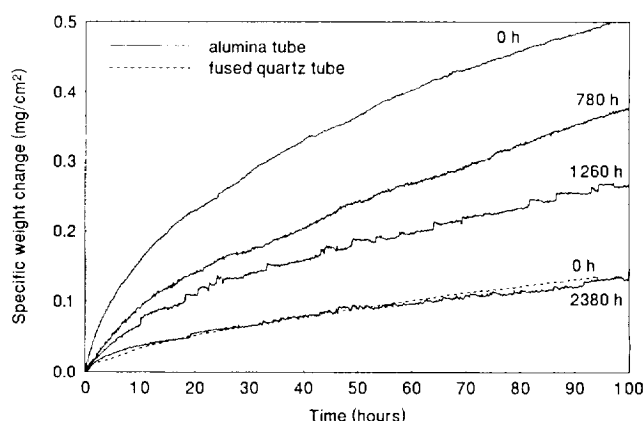


Fig. 6. Effect of Al_2O_3 tube age on the oxidation kinetics of SiC at 1300°C in dry oxygen compared to kinetics obtained in a new fused quartz reaction tube. The time noted by each curve is the approximate time the tube had been at temperatures between 1200° and 1400°C prior to that given oxidation experiment.

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