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Oxygen Diffusion Through Al-Doped Amorphous SiO_2

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Oxygen (O) diffusion through pure and aluminum (Al)-doped amorphous silica is investigated by using secondary ion mass spectrometry to profile the diffusion of an ^{18}O tracer. The oxides are formed by the thermal oxidation of polymer-derived SiCN and SiAlCN ceramics. The authors demonstrate that a small amount of Al dopant can significantly inhibit both the interstitial and network diffusion of O. The activation energy of O network diffusion for Al-doped silica is two times higher than that for pure silica. The results are discussed in terms of the modification of Al doping on the network structure of the otherwise pure silica.

Keywords carbonitrides, diffusivity measurements, error function modeling, experimental study, mass spectrometry, oxide systems, tracer diffusivity

1. Introduction

Oxygen (O) diffusion through vitreous silica (v-SiO_2) has attracted extensive attention in the past few decades due to its scientific interest and practical importance.[1-5] The process is the rate-control step for the thermal growth of dielectric silica thin film on silicon (Si), which enabled the development of the technology for modern microelectronics and optoelectronics.[6] The same process also determines the degradation of Si-based ceramics (e.g., SiC and Si_3N_4) when they are used in high-temperature oxidizing environments.[7] The O transportation through v-SiO_2 can occur through two distinctive processes:[5] molecular O diffusion through the interstitials available in the silica network structures (referred as to interstitial diffusion); and O self-diffusion through the network of bonded O by making use of point defects (referred as to network diffusion). Because O molecules can be dissolved in silica, the two processes can, in principle, become interlinked by an internal exchange between the interstitial molecular O and the network O, leading to a third transportation mechanism, termed "interstitialcy diffusion."

Previous studies on O diffusion through silica have primarily focused on its pure form, and less attention has been paid to silica containing impurities. Zheng et al.[8] reported that a small amount of sodium contamination can increase O interstitial diffusivities by a factor of two, but had no effect on network diffusion. Another way to appreciate the effect of impurities on O diffusion through silica is to study their effect on the oxidation kinetics of Si-based materials. Opila[9] compared the oxidation rates of chemically vapor-deposited SiC in high-purity alumina tubes (~100 ppm impurities) and fused quartz tubes, and concluded that the oxidation rate measured in the alumina tubes is ~10 times higher than that measured in the quartz tubes. A comparison of the oxidation behavior of pure Si-based materials to those with impurities (such as sintering aids) revealed that pure materials always have the lowest oxidation rates.[7,10] These results indicate that the presence of impurities can remarkably enhance the O diffusion. The effect of impurities on O diffusion can be explained by the fact that the impurities cause damage to the silica network structure by generating nonbridging O, which forms an easier path for the transportation of O.[11] This understanding leads to the conclusion that the oxidation resistance of Si-based materials cannot be improved by doping.

Recently, based on oxidation and hot-corrosion studies using microscopic and spectroscopic analysis, An et al.[12,13] discovered that aluminum (Al)-doped, polymer-derived amorphous SiCN ceramics possess much higher oxidation resistance than pure Si-based materials. These results implied that silica containing a small amount of Al could have a lower O transportation rate than its pure counterpart, which contradicts the traditional understanding.

In this article, O diffusion through pure and Al-doped silica is examined by using secondary ion mass spectrometry (SIMS) to profile the ^{18}O tracer concentration. The authors examined the influence of Al doping on the rates of O diffusion through both interstitials and the network. The change in the activation energy of the network diffusion is discussed based on structural modification.

2. Experimental

Fully dense polymer-derived amorphous SiAlCN was prepared by pressure-assisted pyrolysis of a liquid polyalu-

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Table 1 Precursors, compositions, and diffusion parameters

Materials	SiCN	SiAlCN
Starting materials,		
Ceraset to AIP weight ratio	10:0	9:1
Ceramic compositions	$SiC_{0.99}N_{0.85}$	$SiAl_{0.04}C_{0.83}N_{0.93}$
Oxide compositions	SiO_2	$SiAl_{0.04}O_{2.06}$
Do, m^2s^{-1}	3.5×10^{-14}	2.9×10^{-11}
Q, kJ/mole	106 ± 5	201 ± 13

minasilazane precursor.[12-14] The precursor was synthesized by the reaction of polyurea(methylvinyl)silazanes (Ceraset; Kion, Huntingdon Valley, PA) and Al isopropoxide (AIP; Alfa Aesar, Ward Hill, MA).[15] The obtained polyaluminasilazane was then mixed with 3 wt.% dicumyl peroxide (Acros Organics, Morris Plains, NJ) as a thermal initiator. The liquid mixture was cast into a Teflon tube and solidified into a polymeric rod by annealing at 140 °C for 2 h in a vacuum. Discs 2 to 3 mm thick were cut from the rods, and pyrolyzed at 1000 °C for 5 h in a hot-isostatic-press furnace with graphite heating elements. The pyrolysis was conducted under 50 MPa isostatic pressure using ultra-high-purity N_2 as the pressure media. The discs that were obtained are fully dense amorphous SiAlCN ceramics.[12-15] For comparison, fully dense amorphous SiCN was also synthesized using the same procedure as described above, except that pure Ceraset was used as the precursor. The nominal compositions of the SiCN and SiAlCN were measured using a combination of elemental analysis and secondary hydrochloric acid inductively coupled plasma and are listed in Table 1.

The SiCN and SiAlCN specimens were oxidized in dry air at 1200 °C for 200 h in a high-purity quartz tube. The oxide layers that were prepared are fully dense and uniform in thickess.[12-14] The oxide layer formed on the SiCN was pure amorphous SiO_2, while the oxide layer formed on the SiAlCN was amorphous SiO_2-containing Al.[12-16] Elemental mapping obtained using a scanning electron microscope (JSM-6400F; JEOL, Tokyo, Japan) equipped with energy-dispersive spectroscopy (Noran Instrument N649B-1SUS, Middleton, WI) revealed that the Al is uniformly distributed within the oxide layer and the ratio of Si-to-Al in the oxide layer is approximately equal to that in the substrate.[16]

For ^{18}O diffusion experiments, the oxidized specimens were placed in a high-purity quartz tube and heated to a preset temperature. The system was then evacuated to ~10^{-3} torr before introducing the ^{18}O-enriched gas. The samples were then held in the ^{18}O-enriched gas at 0.1 MPa pressure for a given time in the temperature range of 1000 to 1150 °C. After annealing, concentration profiles of the ^{18}O in the oxide scale were determined by SIMS (Adept 1010; Physical Electronics, Eden Prairie, MN) using a 3 kV Cs^+ beam current rastered over a 250 μm square. All data were collected from the central 25 μm^2 region to avoid edge effects. Sputter time was converted to depth by assuming a constant sputter rate.

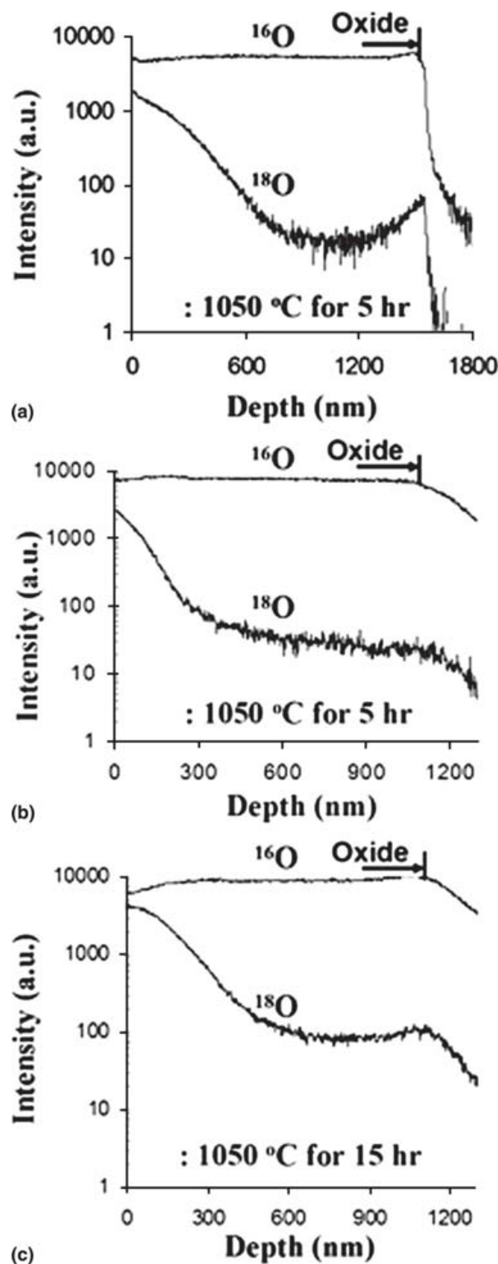

Fig. 1 SIMS profiles of ^{16}O and ^{18}O in the oxide scales formed on (a) the SiCN, and (b, c) the SiAlCN after annealing in ^{18}O-enriched gas at the given conditions as indicated

3. Results and Discussion

If the oxidation is controlled by interstitial diffusion, the ^{18}O isotope will accumulate near the oxide-substrate interface, unless the oxidation is controlled by network diffusion or interstitial-network exchange becomes appreciable and ^{18}O concentration should be uniformly distributed across the oxide.[17,18] Figures 1(a) and 1(b) show the SIMS profiles of ^{18}O and ^{16}O in the oxide scales formed on the SiCN and SiAlCN specimens, respectively, after annealing in ^{18}O-enriched gas at 1050 °C for 5 h. It can be seen that there

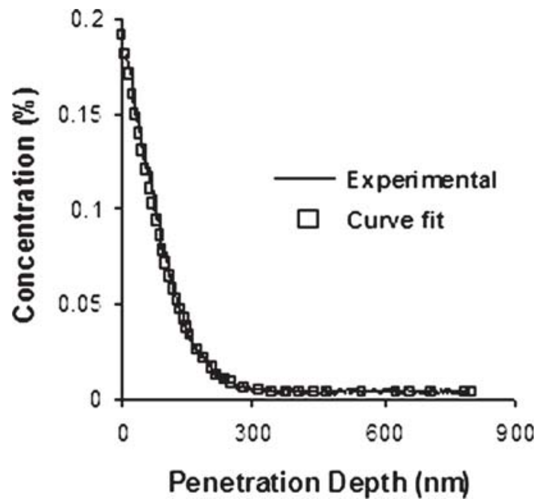

Fig. 2 Comparison between the experimental ^{18}O concentration-penetration profile obtained from the SiAlCN after annealing in ^{18}O-enriched gas at 1100 °C for 3 h and that calculated using Eq 1

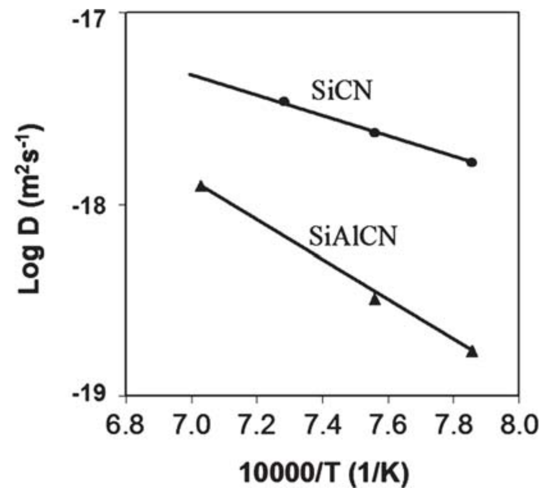

Fig. 3 Arrhenius plot of the coefficient of the network diffusion

is significant accumulation of ^{18}O isotope near the oxide-substrate interface of the SiCN (Fig. 1a), suggesting that O interstitial diffusion is the control process for the oxidation of the SiCN.[17] However, at the same annealing conditions, there is no ^{18}O accumulation near the oxide-substrate interface for the SiAlCN, while ^{18}O concentration is also not uniform across the oxide (Fig. 1b). Figure 1(c) shows the profiles of ^{18}O and ^{16}O in the oxide scales formed on the SiAlCN after annealing in ^{18}O-enriched gas at 1050 °C for 15 h. A slight accumulation of ^{18}O near the oxide-substrate interface can be observed, suggesting that the oxidation of the SiAlCN is also controlled by interstitial diffusion. The above results clearly demonstrate that the interstitial diffusion is faster than network diffusion for both silica and Al-doped silica, and is the rate-control process for the oxidation of both SiCN and SiAlCN, and the interstitial diffusion rate is much lower for the Al-doped silica (formed on the SiAlCN) than for the pure silica (formed on the SiCN).

The profiles presented in Fig. 1 can also be used to determine the network diffusivity by fitting them with proper diffusion models. To do so, raw data from SIMS was first converted to the concentration-penetration profile of ^{18}O, which can be done by dividing the ^{18}O signal by the sum of the ^{18}O and ^{16}O signals. Figure 2 shows a typical ^{18}O concentration-penetration profile obtained for the Al-containing silica. Due to the existence of the interstitialcy diffusion, the internal exchange between interstitial and network O needs to be considered for determining pure network diffusion. Kalen et al.[4] and Cawley and Boyce[18] suggested that an ^{18}O concentration profile such as that presented in Fig. 2 can be modeled to obtain pure network diffusivity by using the relation:

$$\frac{C - C_o}{C_s - C_o} = \exp[-\beta t]\left[erfc\left(\frac{x}{2\sqrt{D_n t}}\right) - 1 \right] + 1 \qquad \text{(Eq 1)}$$

where D_n is the O network diffusion coefficient to be determined, C is the tracer concentration at any given position, C_s is the tracer concentration at the surface, C_o is the natural abundance of ^{18}O (0.2%), β is the network-interstitial exchange coefficient,[4] t is the annealing time, and x is the penetration distance. It can be seen from Fig. 2 that the experimental data can be modeled very well by Eq 1.

The coefficients of network diffusion determined from concentration-penetration profiles of ^{18}O by using Eq 1 are presented in Fig. 3 for the pure silica and Al-doped silica. It can be seen that the diffusion coefficients exhibit Arrhenius dependence on temperature according to the relation:

$$D_n = D_o \exp(-Q/RT) \qquad \text{(Eq 2)}$$

where D_o is the preexponential factor and Q is the activation energy of diffusion. The calculated D_o and Q for the pure silica and Al-doped silica are reported in Table 1. The diffusion coefficients for the Al-doped silica are about an order of magnitude lower than those for the pure silica, suggesting that Al doping can also reduce the network diffusion of O. More importantly, the activation energy for the Al-doped silica is about twice that for the pure silica. The activation energy for the network diffusion contains two parts: the energy for the formation of O vacancies; and the energy for the migration of the vacancies.[19] Because the two oxides have essentially the same structures and compositions, except that the one formed from the SiAlCN contains a small amount of Al, it can be assumed that the migration energy for both oxides should be similar. Thus, the higher activation energy exhibited by the Al-doped silica is mainly due to the higher formation energy of O vacancies. This indicates that it is more difficult for O vacancies to form in Al-doped silica, suggesting that Al dopants could enhance the stability of the network O.

The resultant network-interstitial exchange coefficients β are summarized in Table 2. The data indicate that the network interstitial exchange showed a low rate, and thus are less important in the temperature range of the tests.

Table 2 Calculated β values

	$\beta \times 10^7$, s			
Material	**1000 °C**	**1050 °C**	**1100 °C**	**1150 °C**
SiCN	0.3	1.1	4.8	…
SiAlCN	11.8	12	…	12.5

Further analysis of the data reveals that the rates for the Al-containing silica are 5 to 10 times higher than those for the pure silica. It can be assumed that an exchange event can only occur when interstitial O is adjacent to a defect.[18] Because the density of the vacancies in Al-doped silica should not exceed that of pure silica (the former has higher energy of formation), the higher exchange rate exhibited by Al-doped silica must result from the longer time that the interstitial O stays within the material, which is consistent with the fact that the Al-doped silica has a lower interstitial diffusion rate.

The structure of amorphous silica can be characterized by connected rings composed of SiO_4 tetrahedra (Fig. 4a).[20] The majority of these rings are six-membered or higher.[21-23] Therefore, the interstitial diffusion of O through amorphous silica is controlled by O molecules passing through the six-membered rings.[24] According to conventional understanding, the presence of impurities can destroy the original "perfect" network structure of pure silica, which results in the formation of nonbridging O (Fig. 4b),[11] thus enhancing O diffusion. The current study, however, demonstrates that Al doping leads to a decrease in O interstitial diffusivity and thus suggests that the Al doping must either block part of the six-membered rings or significantly alternate the structure of otherwise pure silica. A previous nuclear magnetic resonance study[13] suggested that the structure of Al-doped silica is similar to that of the pure silica, and the Al atoms were not incorporated into the SiO_2 network to replace the Si atoms. Accordingly, the authors propose a new structural model for Al-doped silica in which Al sits at the center of the six-membered rings (Fig. 4c). This model can be used to explain the lower interstitial diffusivity observed in Al-doped silica. The model can also be used to explain the higher activation energy of network diffusion for Al-doped silica. Figure 4(c) shows that in this new model, Al contributes additional bond energy toward the surrounding O, which is already bonded to two Si atoms. In other words, compared with pure silica, the generation of O vacancies in the Al-doped silica requires the breaking of the extra Al–O attraction in addition to two Si–O bonds. The proposed model is a prospective one, and further characterization of the Al position in such Al-doped silica is desired to fully understand the observed phenomena.

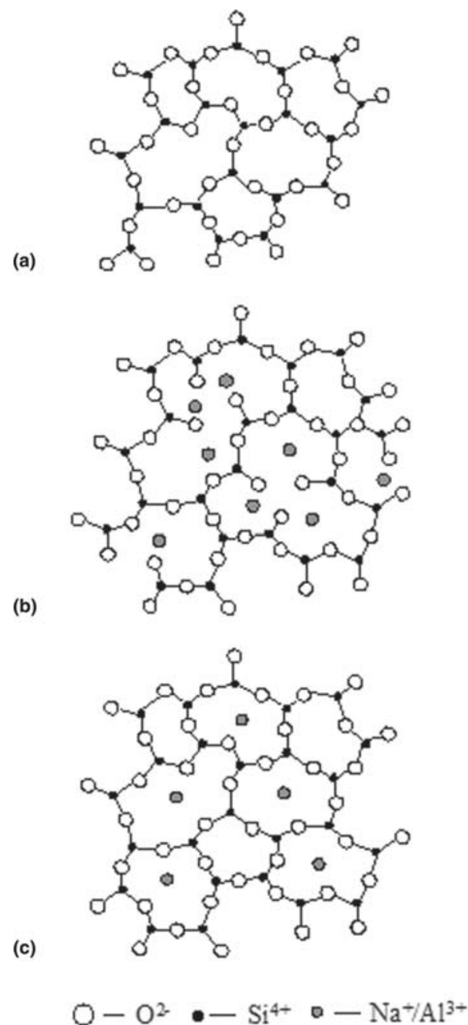

Fig. 4 A schematic diagram of the two-dimensional structures of (a) pure silica, (b) silica with impurities (conventional model), and (c) Al-doped silica (currently proposed)

4. Summary

In summary, the authors demonstrated that the rate of O diffusion through both interstitials and the network is much lower for Al-doped silica than that for pure silica. The activation energy of the network diffusion for Al-doped silica is about two times higher than that for pure silica. Based on these observations, the authors proposed a new structural model for the Al-doped silica, in which Al sits at the center of the rings composed of six SiO_4 tetrahedra.

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