Active Oxidation of SiC

Nathan S. Jacobson[a], Dwight L. Myers[b], and Bryan J. Harder[a]

[a]NASA Glenn Research Center, Cleveland, OH [b]Department of Chemistry, East Central University, Ada, OK

Microscopy of Oxidation 8, Liverpool, UK April 10-13, 2011

Contact: nathan.s.jacobson@nasa.gov

Abstract

The high temperature oxidation of silicon carbide occurs in either a passive or active mode, depending on temperature and oxygen potential.
Passive oxidation forms a protective oxide film which limits attack of the SiC:

$$SiC(s) + 3/2\ O_2(g) = SiO_2(s) + CO(g)$$

Active oxidation forms a volatile oxide and leads to extensive attack of the SiC:

$$SiC(s) + O_2(g) = SiO(g) + CO(g)$$

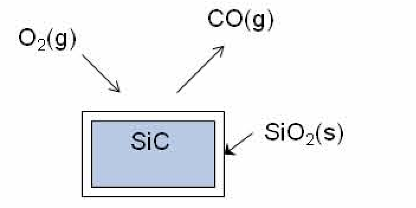
The transition points and rates of active oxidation are a major issue.

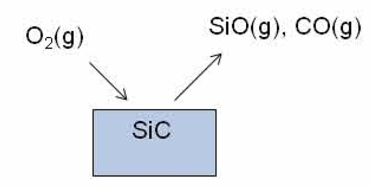
Previous studies are reviewed and the leading theories of passive/active transitions summarized. Comparisons are made to the active/passive transitions in pure Si, which are relatively well-understood. Critical questions remain about the difference between the active-to-passive transition and passive-to-active transition.

For Si, Wagner [2] points out that the active-to-passive transition is governed by the criterion for a stable Si/SiO_2 equilibria and the passive-to-active transition is governed by the decomposition of the SiO_2 film. This suggests a significant oxygen potential difference between these two transitions and our experiments confirm this. For Si, the initial stages of active oxidation are characterized by the formation of SiO(g) and further oxidation to $SiO_2(s)$ as micron-sized rods, with a distinctive morphology.

SiC shows significant differences. The active-to-passive and the passive-to-active transitions are close. The SiO_2 rods only appear as the passive film breaks down. These differences are explained in terms of the reactions at the SiC/SiO_2 interface. In order to understand the breakdown of the passive film, pre-oxidation experiments are conducted. These involve forming dense protective scales of 0.5, 1, and 2 microns and then subjecting the samples with these scales to a known active oxidation environment. Microstructural studies show that SiC/SiO_2 interfacial reactions lead to a breakdown of the scale with a distinct morphology.

Passive/Active Oxidation of SiC





Passive Oxidation [1]
$SiC + 3/2\ O_2(g) = SiO_2(c) + CO(g)$

Active Oxidation [1]
$SiC + O_2(g) = SiO(g) + CO(g)$

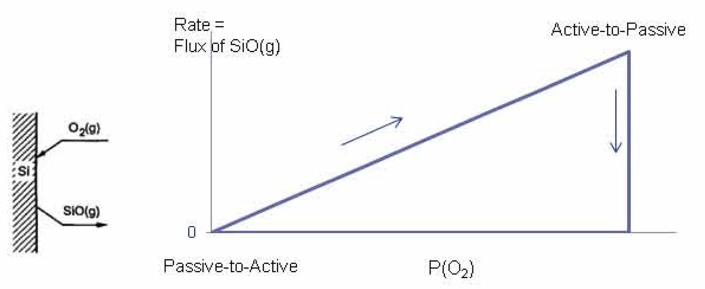
- Critical issues
  - Transitions: active ↔ passive
  - Rates of active oxidation
- Unexplored area: Focus of this study
  - Hysteresis for SiC: active to passive and passive to active
    - Breakdown of passive film

Theories of Active/Passive Transitions

Investigator	Basic Concept	Strength	Weakness
Wagner [2]	Active-to-Passive: Equilibrium between Si/SiO_2 Passive-to-Active: Decomposition of SiO_2	Accounts for hysteresis between active-to-passive and passive-to-active; thermodynamically rigorous	Does not explain SiO_2 rod formation
Singhal [3]/ Gulbransen & Jansson [4]	Extends active-to-passive equilibration condition to SiC	Thermodynamically rigorous	Unclear which SiC/SiO_2 equilibria is operative
Turkdogan [5] et al./Hinze and Graham [6]	SiO(g) forms at surface; reacts a distance away from surface to form SiO_2(smoke)	Includes mass transport, fits data	Only active-to-passive; not passive-to-active
Nickel [7]	Uses condition of equilibria between SiC/SiO_2 involving condensed phase SiO(c)	Fits data	Only active-to-passive; existence of SiO(c) controversial
Balat [8]	Simultaneous active/passive oxidation	Fits data	
Schneider [9]/Ogura [10]	Bubble formation leads to breakdown of passive scale		Describes only passive-to-active transition

Wagner: Active-to-Passive Transitions for Silicon [2]

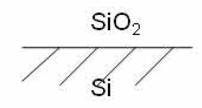
Oxygen strikes a bare Si surface, gradually increase $P(O_2)$



Generate sufficient SiO(g) from reaction (a) for stable Si/SiO_2 equilibrium reaction (b)

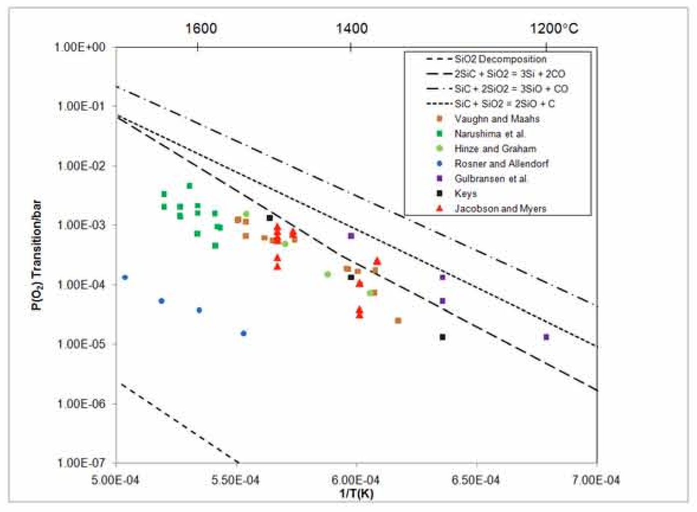
$$Si(c) + ½\ O_2(g) = SiO(g) \quad (a)$$
$$Si(c) + SiO_2(s) = 2SiO(g) \quad (b)$$

$$P_{O_2}^{transition} = \frac{1}{2}\left(\frac{D_{SiO}}{D_{O_2}}\right)^{1/2} P_{eq}(SiO)$$

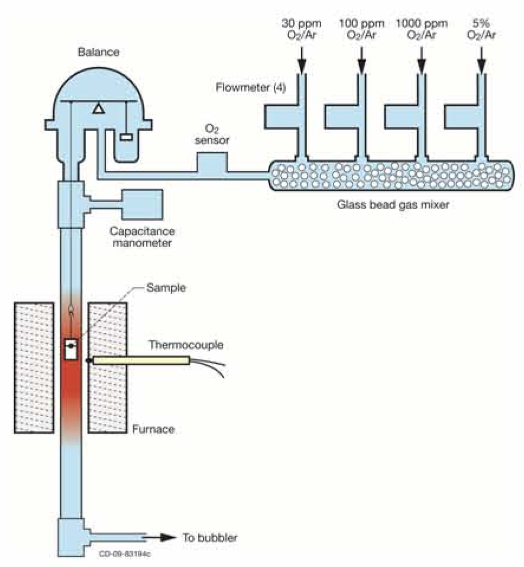


Extend to SiC

- Critical Condition for SiC/SiO_2 equilibrium [4, 6]
  - $SiC(s) + SiO_2(s) = C(s) + 2SiO(g)$
  - or $SiC(s) + 2SiO_2(s) = 3SiO(g) + CO(g)$
  - or $2SiC(s) + SiO_2(s) = 3Si(s) + 2CO(g)$
- Comparison to experimental data [6, 11-15]



Experimental Approach



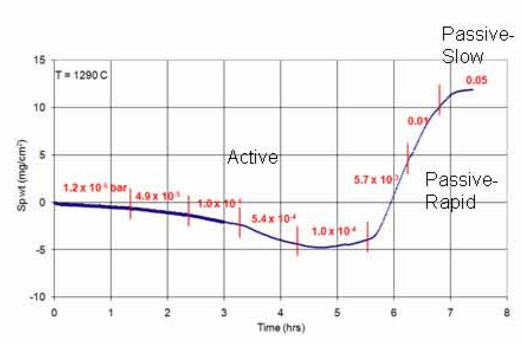
Starting Materials
- Semi-conductor grade Si and CVD SiC
- Quartz tube, hangwire; no alumina to prevent contamination [16]

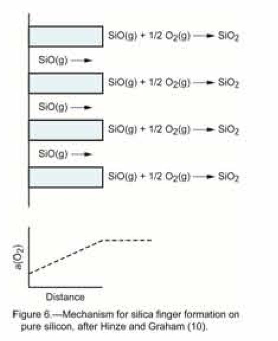
Thermogravimetric system
- Gradually increase or decrease O_2 in Ar
- Active-to-passive transition: Weight loss stops
- Passive-to-active transition: Weight loss begins

Pre-oxidation studies
- SiO_2 films grown on SiC in a clean environment [16]

Microstructural examination
- FE-SEM (Hitachi S4700)

Silicon: Active-to-Passive Transition

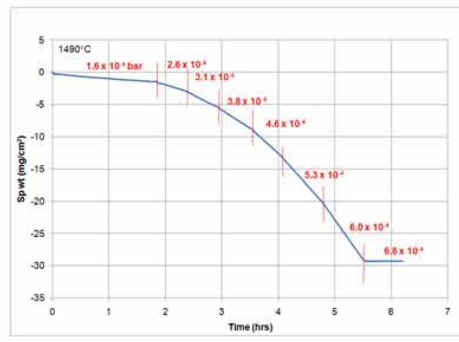




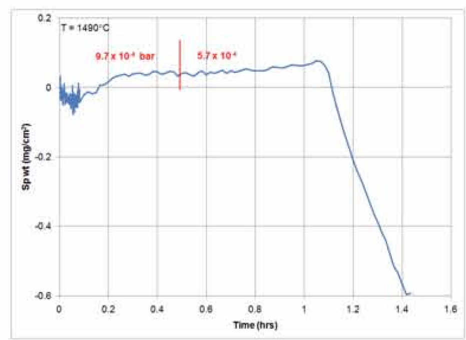
Active-to-Passive transition for silicon
- Initial rapid regime
- Rods of amorphous SiO_2
- Generated by mechanism to right
- cf Hinze and Graham [6]

Rods of SiO_2 are an important 'marker' of SiO(g) generation

SiC: Active-to-Passive and Passive-to-Active Transition



Active-to-Passive Transition
- Oxygen potential lowered until passivity reached
- Instantaneous response



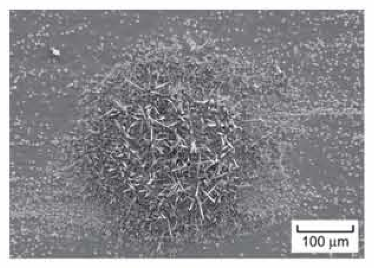
Passive-to-Active Transition
- Oxygen potential raised until active oxidation begins reached
- Time lag is significant

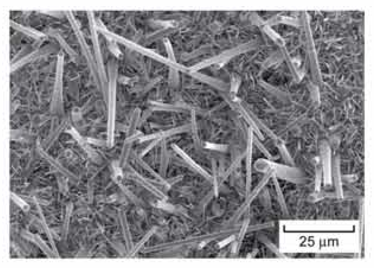
SiC: Active-to-Passive Transition

Temperature	P(trans) expt	P(trans) calc*
1490	9.63E-04	2.12E-04
1490	7.92E-04	
1390	1.05E-04	1.41E-03
1390	1.05E-04	

- Oxygen potential is gradually increased
- Initially $SiC + ½\ O_2(g) = Si\ (c) + CO(g)$
- As $P(O_2)$ is increased eventually enough CO(g) to satisfy the equilibria:
  - $2SiC(s) + SiO_2(s) = 3Si(s) + 2CO(g)$
  - *Above equilibria used to calculated P(trans)
  - Once this condition is met, a passive SiO_2 film is formed.

SiC: Passive-to-Active Transition





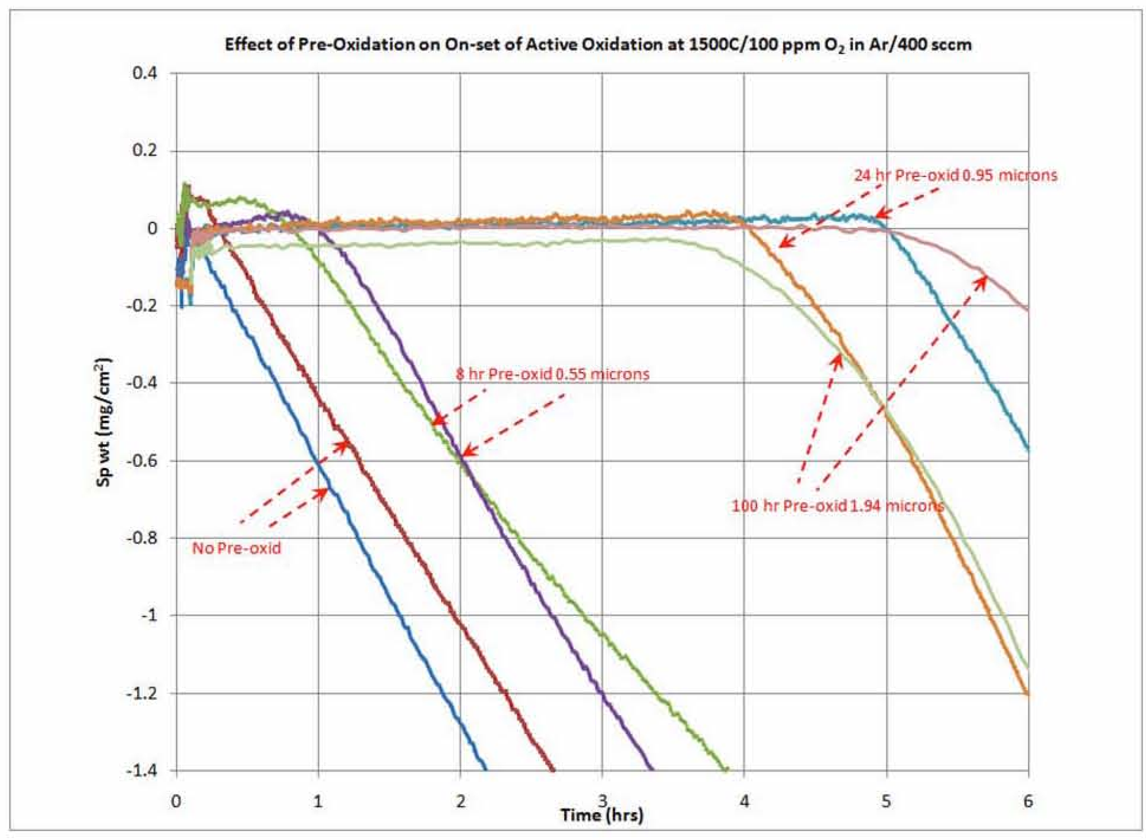
- Oxygen potential is gradually decreased
- SiC and SiO_2 react

$$SiC(s) + 2SiO_2(s) = 3SiO(g) + CO(g)$$
$$↳ SiO(g) + ½\ O_2 = SiO_2$$

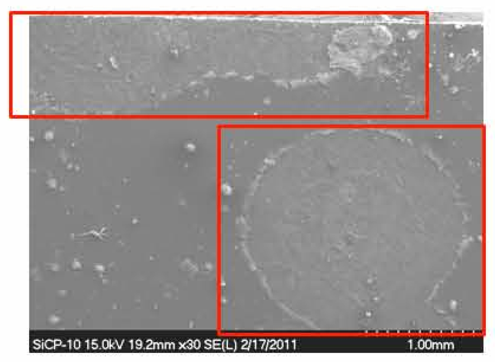
- Consumption of SiO(g) 'pulls' reaction and generates more CO(g)
- CO(g) builds up pressure and lifts and removes scale

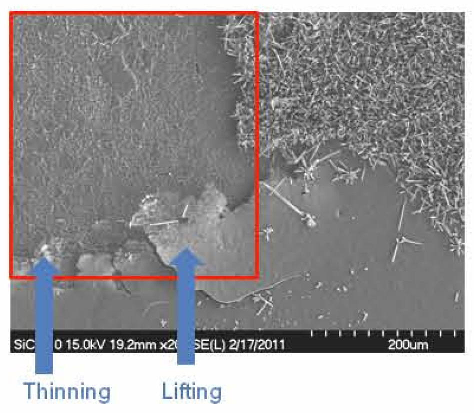
Pre-Oxidation and the Breakdown of the Passive Scale

- Experiment: Form 0.5, 1, 2 micron SiO_2 scales on CVD SiC [17]
- Expose to known active oxidation environment (100 ppm O_2-Ar/1500°C)
- Determine how the passive scale breakdown
- Gives insights into the passive-to-active transition



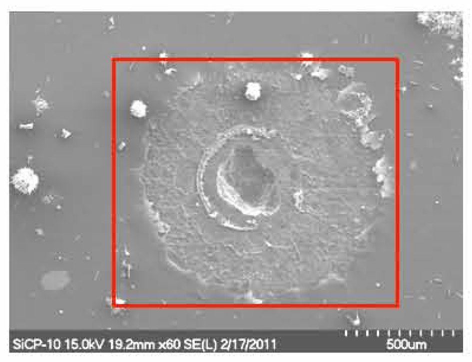
Breakdown of Passive Scale





- Regions of SiO_2 scale removed from SiC, often as circular areas
- Edges of spalled areas provide clues of mechanism
- $SiC(s) + 2SiO_2(s) = 3SiO(g) + CO(g)$
  $↳ SiO(g) + ½\ O_2 = SiO_2$
- Reaction leads to scale consumption, CO(g) generation leads to lifting of scale

Etching/Pitting of SiC



- Circular regions where SiC exposed
- Grain boundary etching
- Often large pits in center

Summary and Conclusions

- Active oxidation of SiC:
  - $SiC(s) + ½\ O_2(g) = SiO(g) + CO(g)$
- Unexplored area is the difference between the active-to-passive and passive-to-active transition for SiC
- Active-to-passive transition
  - Attain sufficient $P(O_2)$ to establish the SiC/SiO_2 equilibria
- Passive-to-active transition
  - Scale/substrate react and SiO(g) product removal 'pulls' reaction
    - $SiC(s) + 2SiO_2(s) = 3SiO(g) + CO(g)$
      $↳ SiO(g) + ½\ O_2 = SiO_2$
- Examine pre-oxidized SiC to understand breakdown of SiO_2 scale

References

1. Jacobson, N., *Corrosion of Silicon-Based Ceramics in Combustion Environments,* Journal of the American Ceramic Society, 1993. **76**(1): p. 3-28.
2. Wagner, C., *Passivity during the Oxidation of Silicon at Elevated Temperatures,* Journal of Applied Physics 1958. **29**: p. 1295-1297.
3. Singhal, S.C., *Thermodynamic Analysis of the High-Temperature Stability of Silicon Nitride and Silicon Carbide,* Ceramurgia International. **2**(3): p. 123-130.
4. Gulbransen, E.A. and Jansson, S. A., *The High-Temperature Oxidation, Reduction, and Volatilization Reactions of Silicon and Silicon Carbide,* Oxidation of Metals, 1972. **4**(3): p. 181-201.
5. Turkdogan, E.T., Grieveson, P., and Darken, L. S., *Enhancement of Diffusion-Limited Rates of Vaporization of Metals,* The Journal of Physical Chemistry, 1963. **67**(8): p. 1647-1654.
6. Hinze, J.W. and Graham, H. C., *The Active Oxidation of Si and SiC in the Viscous Gas-Flow Regime,* Journal of the Electrochemical Society, 1976. **123**(7): p. 1066-1073.
7. Nickel, K.G., *The Role of Condensed Silicon Monoxide in the Active-to-Passive Oxidation Transition of Silicon Carbide,* Journal of the European Ceramic Society, 1992. **9**(1): p. 3-8.
8. Balat, M.J.H., *Determination of the Active-to-Passive Transition in the Oxidation of Silicon Carbide in Standard and Air,* Journal of the European Ceramic Society, 1996. **16**(1): p. 55-62.
9. Schneider, B., Guette, A., Naslain, R., Cataldi, M., and Costecalde, A., *A Theoretical and Experimental Approach to the Active-to-Passive Transition in the Oxidation of Silicon Carbide*, Journal of Materials Science **33**, 535 (1998).
10. Ogura, Y. and Morimoto, T., *Mass Spectrometric Study of Oxidation of SiC in Low-Pressure Oxygen*, Journal of the Electrochemical Society **149**(4), J47 (2002).
11. Vaughn, W.L. and Maahs, H.G., *Active-to-Passive Transition in the Oxidation of Silicon Carbide and Silicon Nitride in Air,* Journal of the American Ceramic Society, 1990. **73**(6): p. 1540-1543.
12. Narushima, T., et al., *High-Temperature Active Oxidation of Chemically Vapor-Deposited Silicon Carbide in an Ar-O_2 Atmosphere,* Journal of the American Ceramic Society, 1991. **74**(10): p. 2583-2586.
13. Rosner, D.E. and H.D. Allendorf, *High-temperature Kinetics of the Oxidation and Nitridation of Pyrolytic Silicon Carbide in Dissociated Gases,* The Journal of Physical Chemistry, 1970. **74**(9): p. 1829-1839.
14. Keys, L.H., *The Oxidation of Silicon Carbide* in Properties of High Temperature Alloys with an Emphasis on Environmental Effects,1977: Electrochemical Society.
15. Jacobson, N. and Myers, D., *Active Oxidation of SiC,* Oxidation of Metals, 2010: p. 1-25.
16. Opila, E., *Influence of Alumina Reaction Tube Impurities on the Oxidation of Chemically-Vapor-Deposited Silicon Carbide,* Journal of the American Ceramic Society, 1995. **78**(4): p. 1107-1110.
17. Ogbuji, L.U.J.T. and Opila, E. J., *A Comparison of the Oxidation Kinetics of SiC and Si_3N_4,* Journal of the Electrochemical Society, 1995. **142**(3): p. 925-930.