

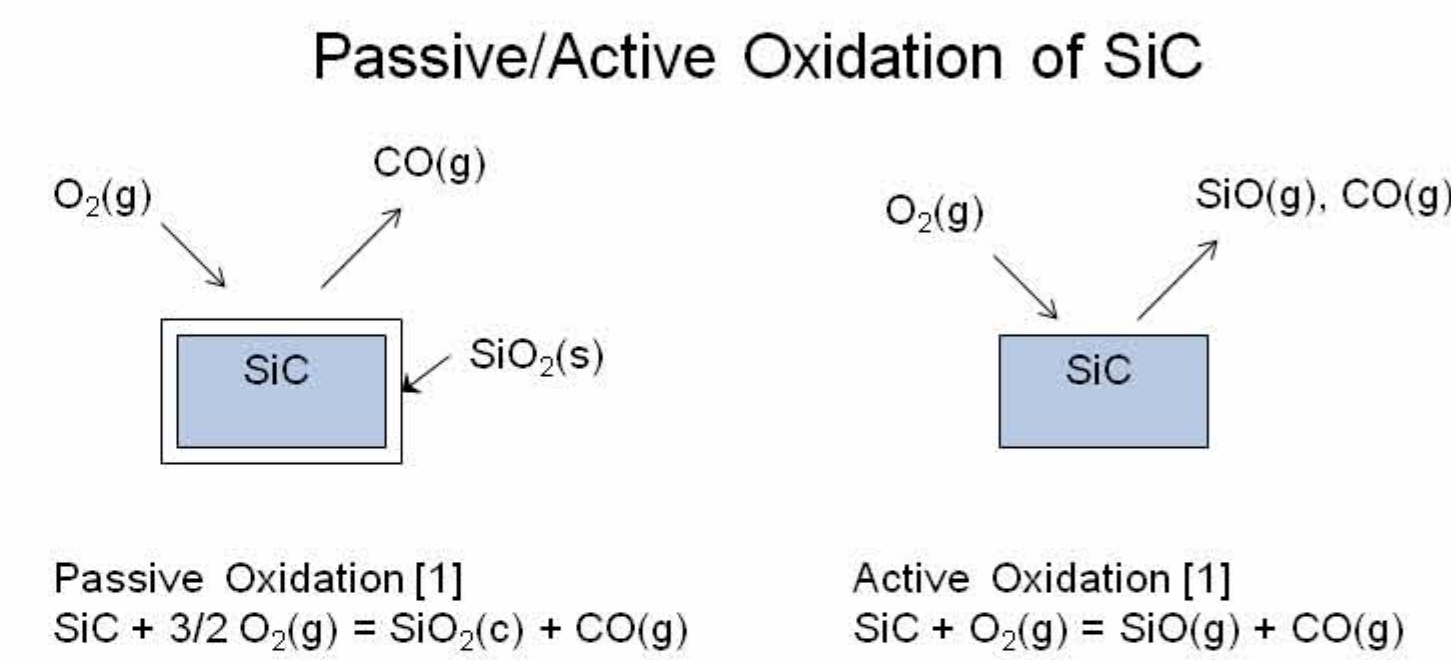
## Abstract

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:  $\text{SiC}(s) + 3/2 \text{O}_2(g) = \text{SiO}_2(s) + \text{CO}(g)$ . Active oxidation forms a volatile oxide and leads to extensive attack of the SiC:  $\text{SiC}(s) + \text{O}_2(g) = \text{SiO}(g) + \text{CO}(g)$ . 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  $\text{SiO}_2$  equilibria and the passive-to-active transition is governed by the decomposition of the  $\text{SiO}_2$  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  $\text{SiO}(g)$  and further oxidation to  $\text{SiO}_2(s)$  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  $\text{SiO}_2$  rods only appear as the passive film breaks down. These differences are explained in terms of the reactions at the SiC/SiO<sub>2</sub> 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<sub>2</sub> interfacial reactions lead to a breakdown of the scale with a distinct morphology.



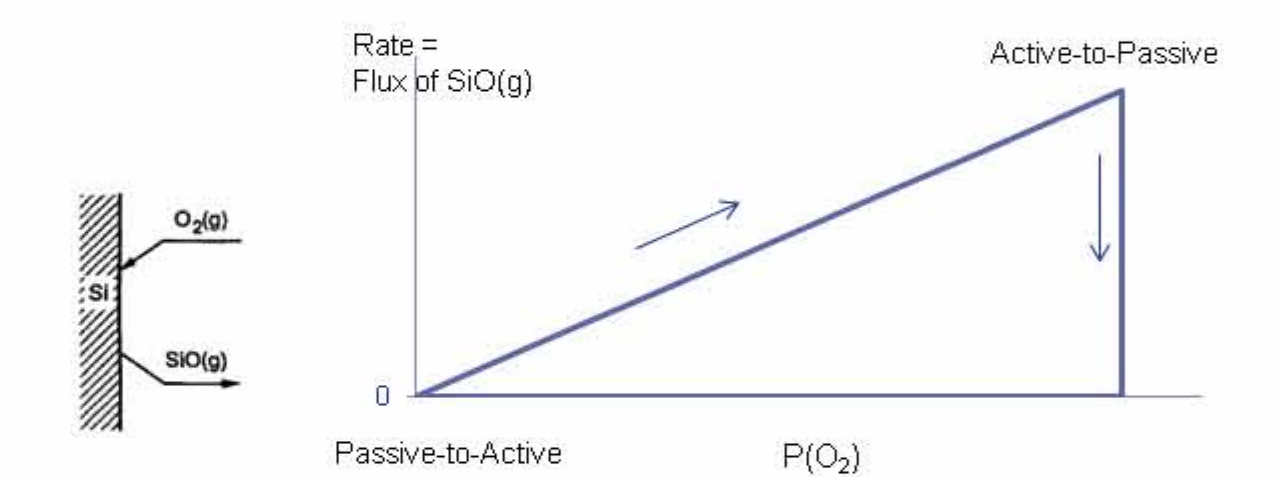
- Critical issues
  - Transitions: active ↔ passive
  - Rates of active oxidation
- Unexplored area: Focus of this study
  - Hysteresis for SiC: active to passive and passive to active
    - Breakdown of passive film

## Theories of Active/Passive Transitions

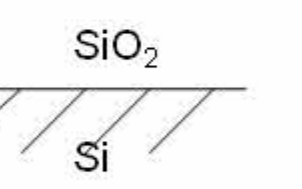
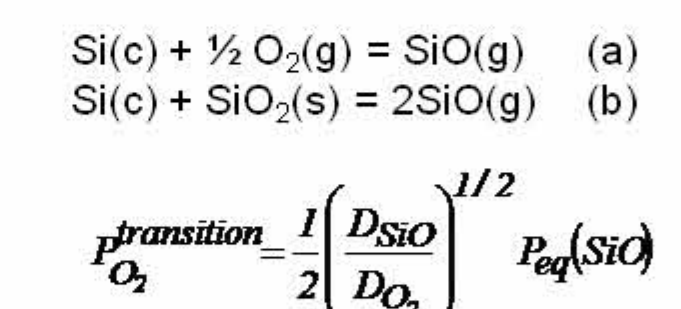
Investigator	Basic Concept	Strength	Weakness
Wagner [2]	Active-to-Passive: Equilibrium between Si/SiO <sub>2</sub> Passive-to-Active: Decomposition of SiO <sub>2</sub>	Accounts for hysteresis between active-to-passive and passive-to-active, thermodynamically rigorous	Does not explain SiC/SiO <sub>2</sub> rod formation
Singh et al [3], Gulbransen & Jansson [4]	Extends active-to-passive equilibration condition to SiC	Thermodynamically rigorous	Unclear which SiC/SiO <sub>2</sub> 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 <sub>2</sub> (smoke)	Includes mass transport, fits data	Only active-to-passive, not passive-to-active
Nickel [7]	Uses condition of equilibria between SiC/SiO <sub>2</sub> involving condensed phase SiO <sub>2</sub> (c)	Fits data	Only active-to-passive, existence of SiO <sub>2</sub> (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<sub>2</sub>)

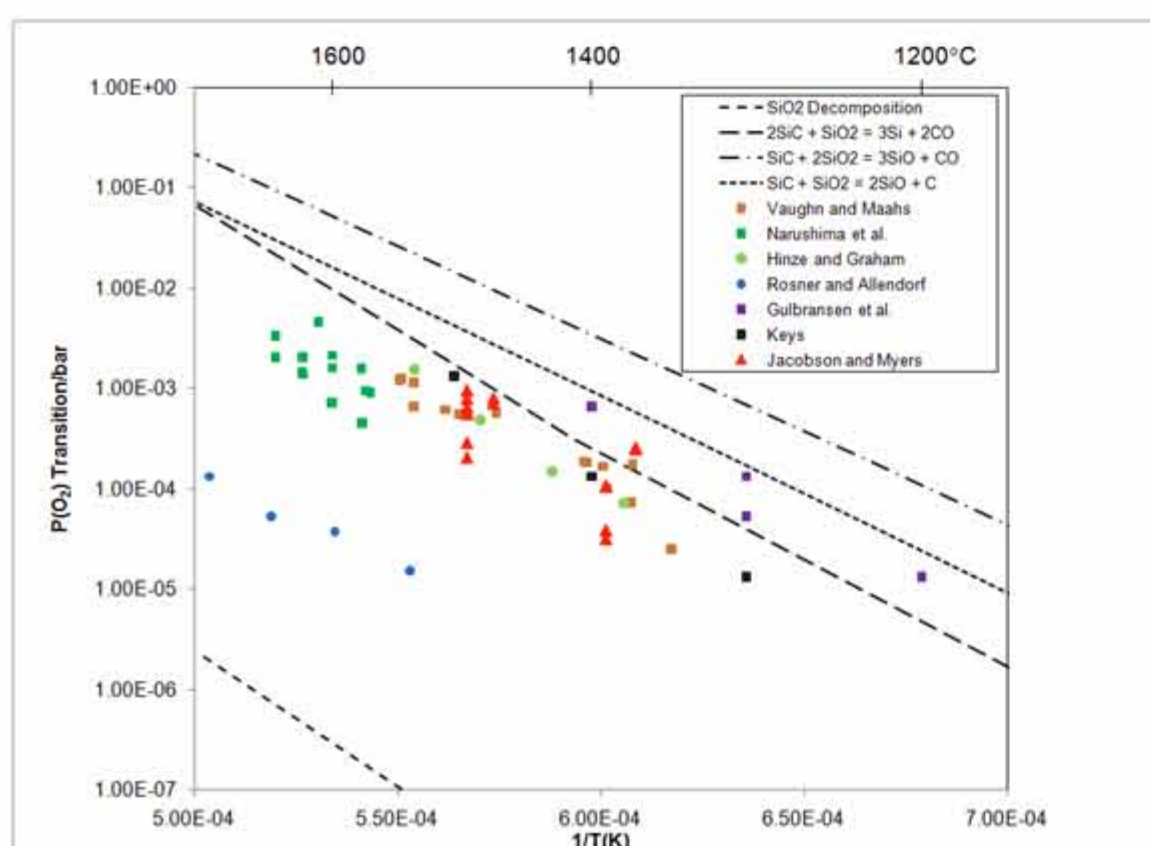


Generate sufficient SiO(g) from reaction (a) for stable Si/SiO<sub>2</sub> equilibrium reaction (b)

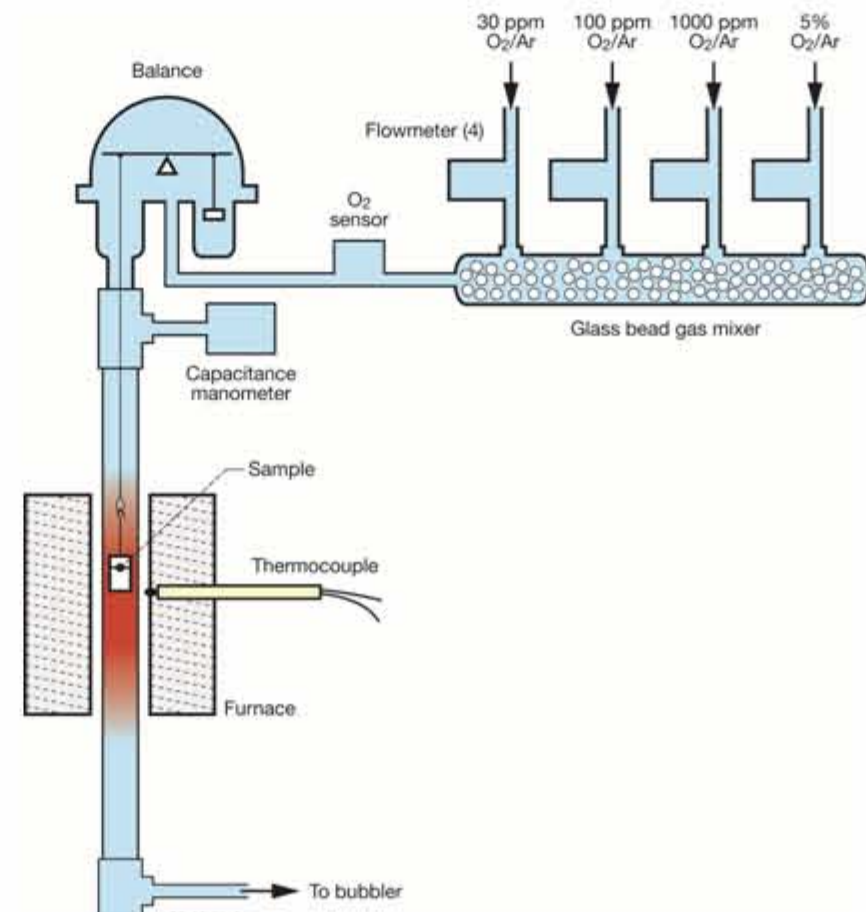


## Extend to SiC

- Critical Condition for SiC/SiO<sub>2</sub> equilibrium [4, 6]
  - $\text{SiC}(s) + \text{SiO}_2(s) = \text{C}(s) + 2\text{SiO}(g)$
  - or  $\text{SiC}(s) + 2\text{SiO}_2(s) = 3\text{SiO}(g) + \text{CO}(g)$
  - or  $2\text{SiC}(s) + \text{SiO}_2(s) = 3\text{Si}(s) + 2\text{CO}(g)$
- Comparison to experimental data [6, 11-15]



## Experimental Approach



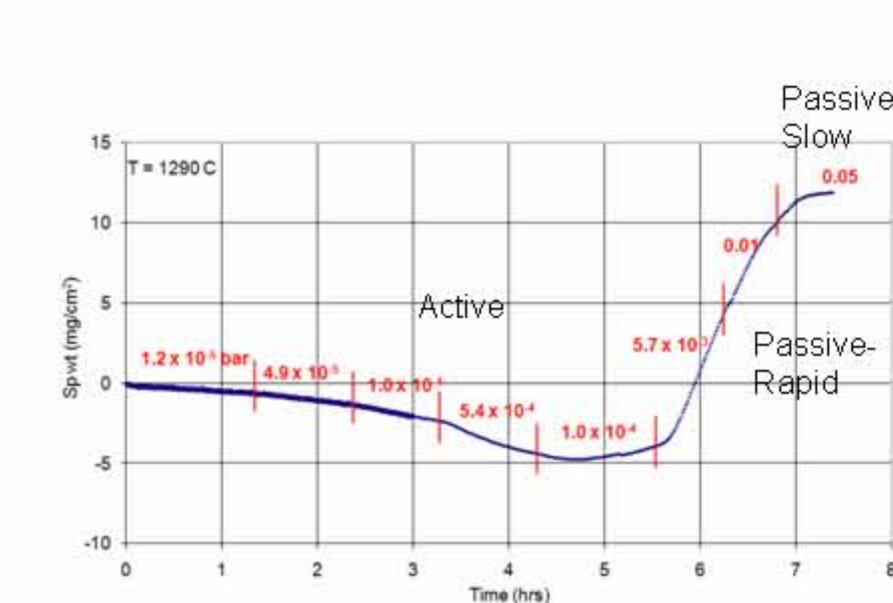
- Starting Materials
- Semi-conductor grade Si and CVD SiC
  - Quartz tube, hangwire; no alumina to prevent contamination [16]

- Thermogravimetric system
- Gradually increase or decrease O<sub>2</sub> in Ar
  - Active-to-passive transition: Weight loss stops
  - Passive-to-active transition: Weight loss begins

- Pre-oxidation studies
- SiO<sub>2</sub> films grown on SiC in a clean environment [16]

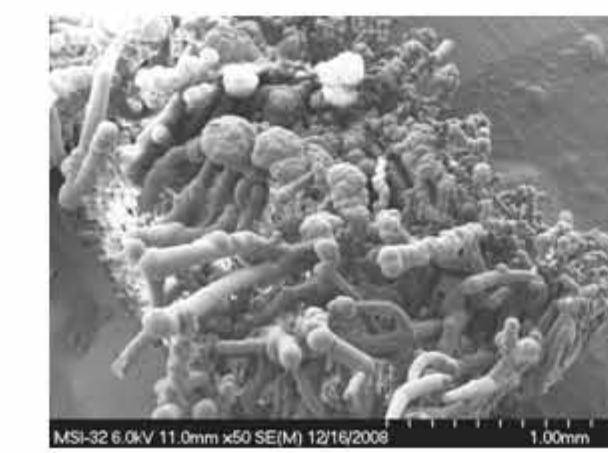
- Microstructural examination
- FE-SEM (Hitachi S4700)

## Silicon: Active-to-Passive Transition

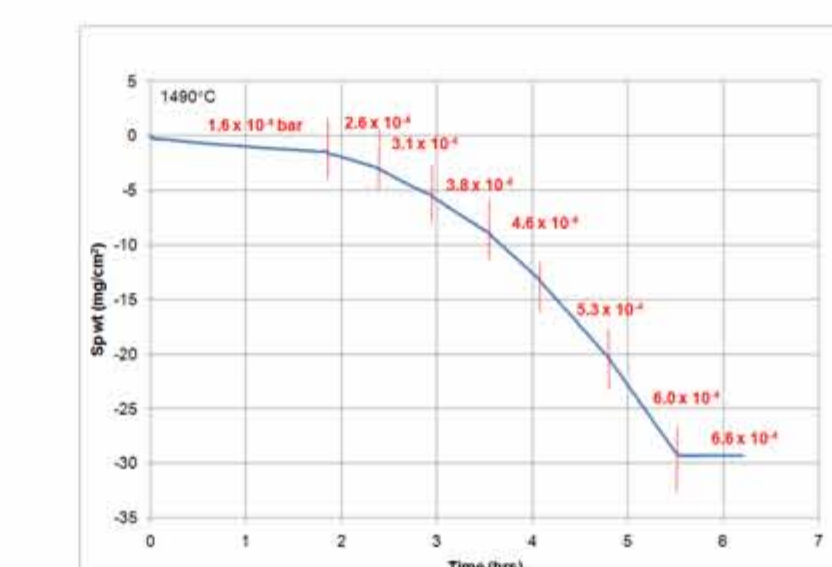


- Active-to-Passive transition for silicon
- Initial rapid regime
  - Rods of amorphous SiO<sub>2</sub>
  - Generated by mechanism to right of Hinze and Graham [6]

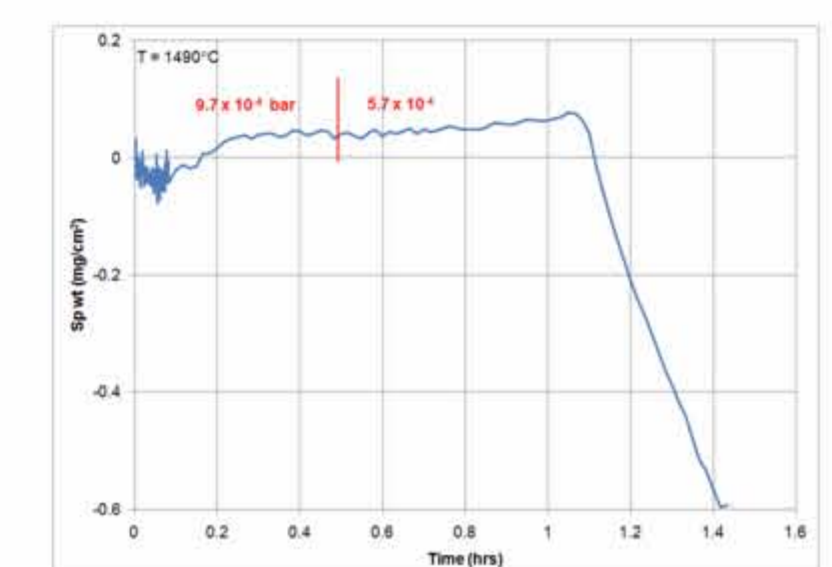
- Rods of SiO<sub>2</sub> are an important 'marker' of SiO(g) generation



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



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



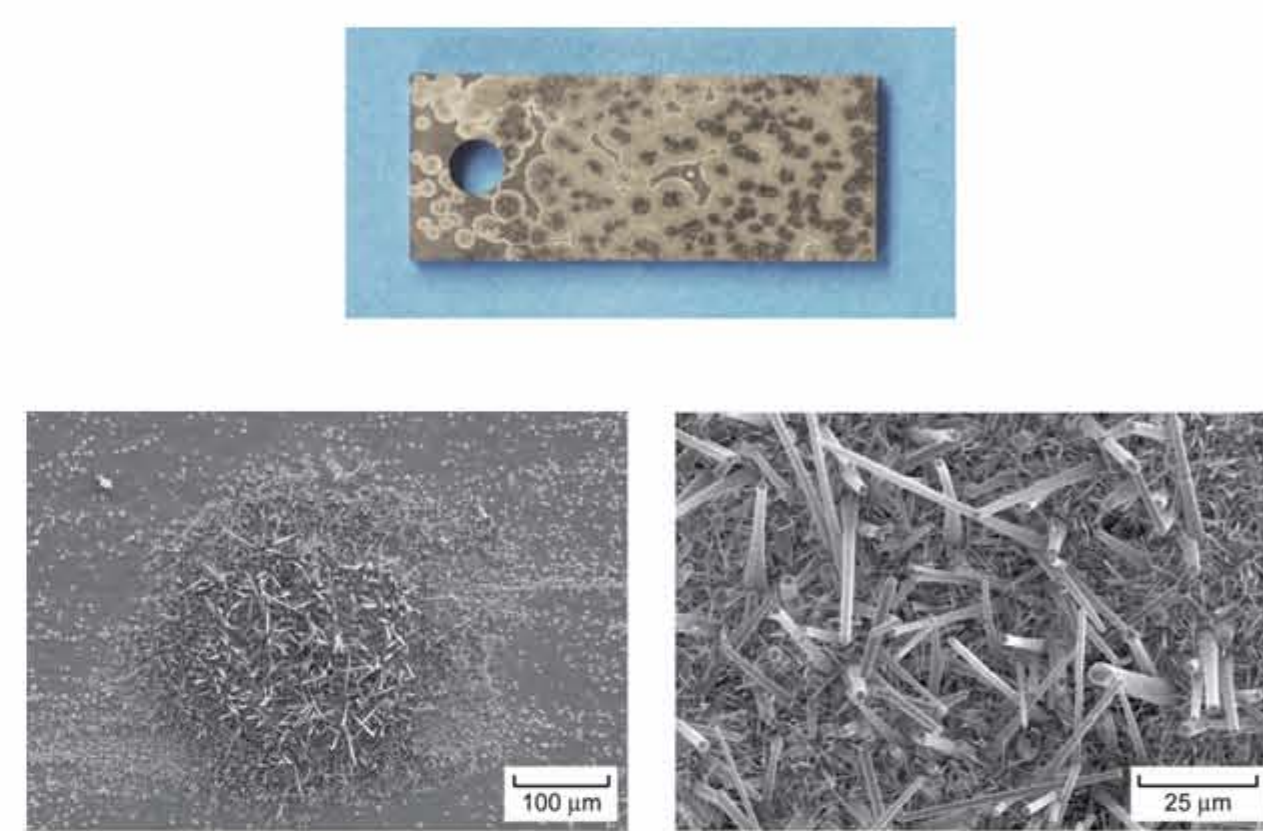
- Passive-to-Active Transition
- Oxygen potential raised until active oxidation begins reached
  - Time lag is significant

## 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  $\text{SiC} + 1/2 \text{O}_2(g) = \text{Si}(c) + \text{CO}(g)$
- As P(O<sub>2</sub>) is increased eventually enough CO(g) to satisfy the equilibria:
  - $2\text{SiC}(s) + \text{SiO}_2(s) = 3\text{Si}(s) + 2\text{CO}(g)$
  - \*Above equilibria used to calculate P(trans)
  - Once this condition is met, a passive SiO<sub>2</sub> film is formed.

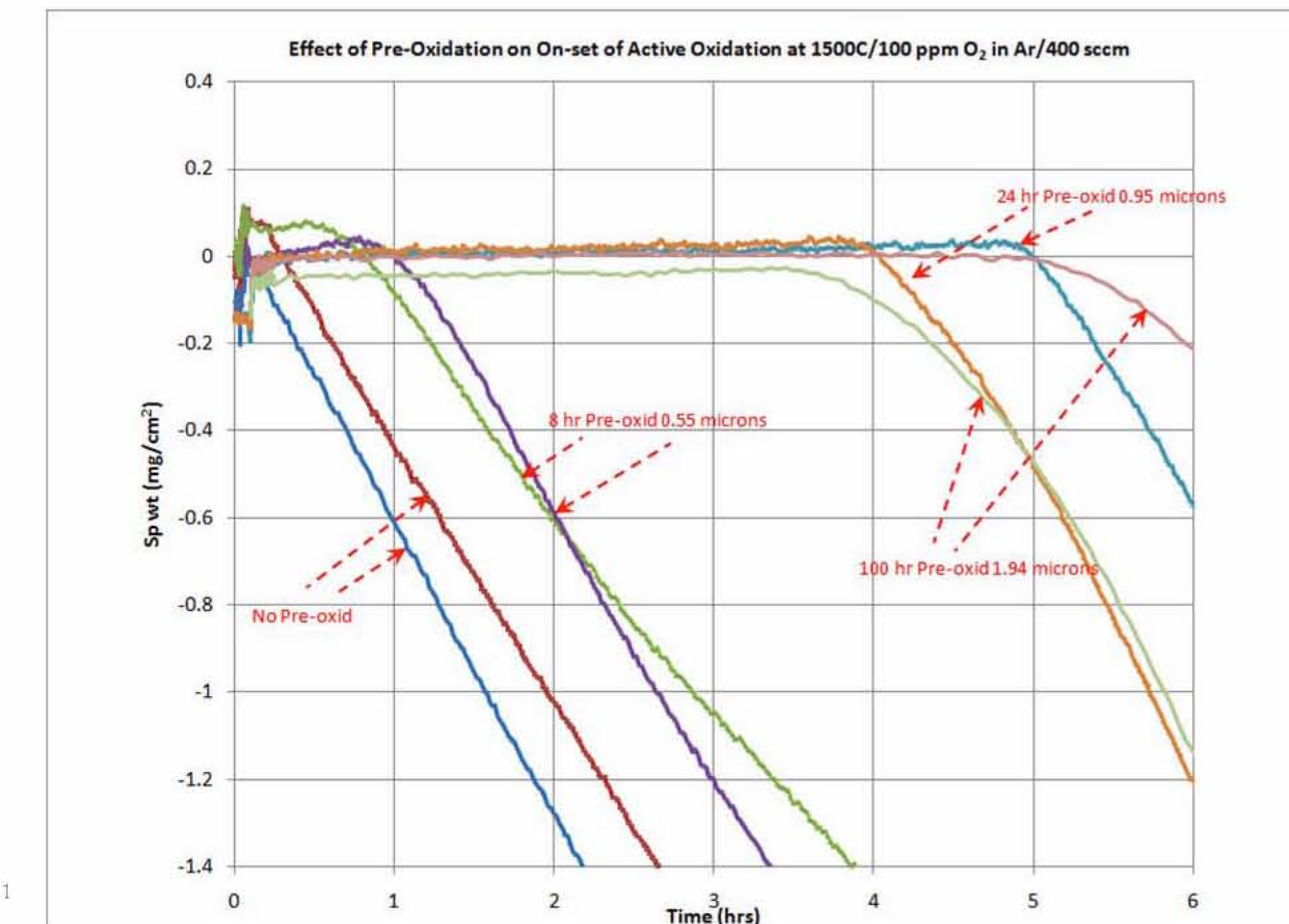
## SiC: Passive-to-Active Transition



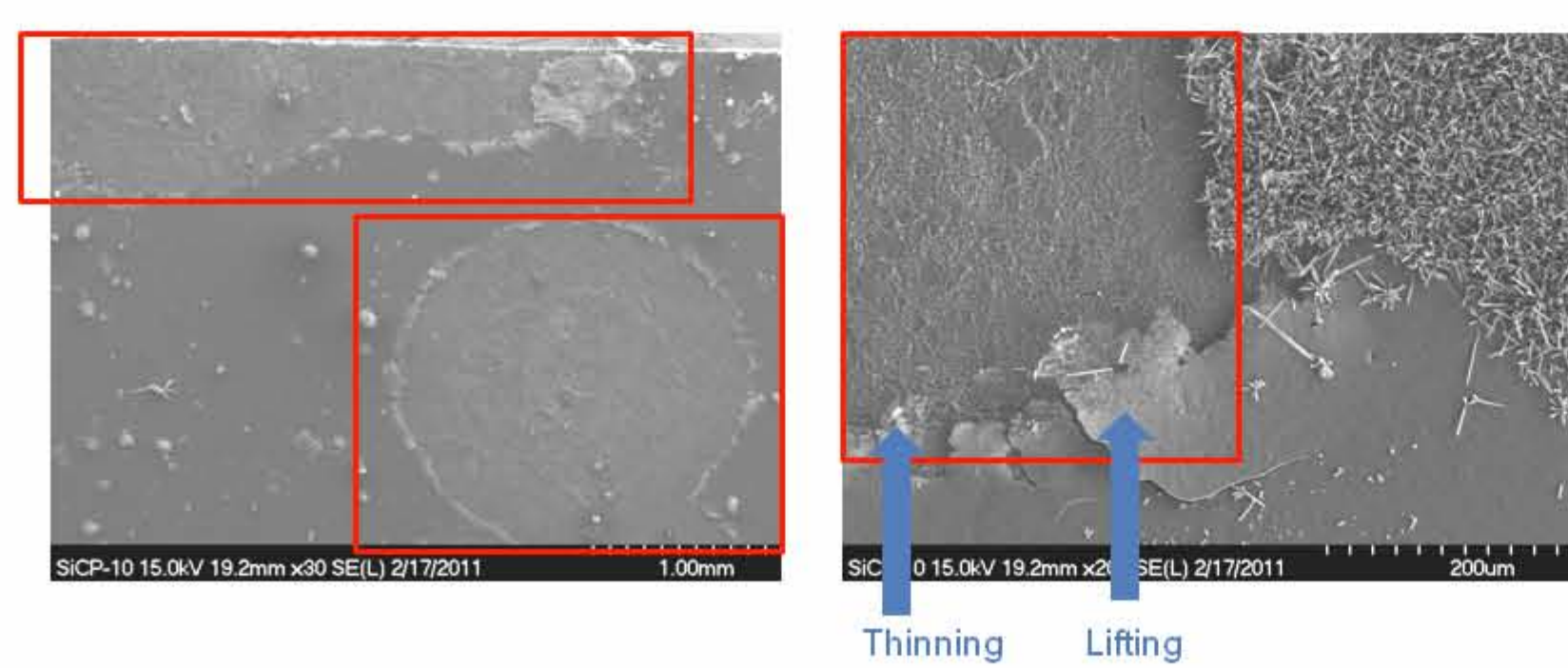
- Oxygen potential is gradually decreased
- SiC and SiO<sub>2</sub> react
  - $\text{SiC}(s) + 2\text{SiO}_2(s) = 3\text{SiO}(g) + \text{CO}(g)$
  - $\text{SiO}(g) + 1/2 \text{O}_2 = \text{SiO}_2$
- Consumption of SiO(g) 'pulls' reaction and generates more CO(g)
- CO(g) builds up pressure and lifts and removes scale

## Pre-Oxidation and the Breakdown of the Passive Scale

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

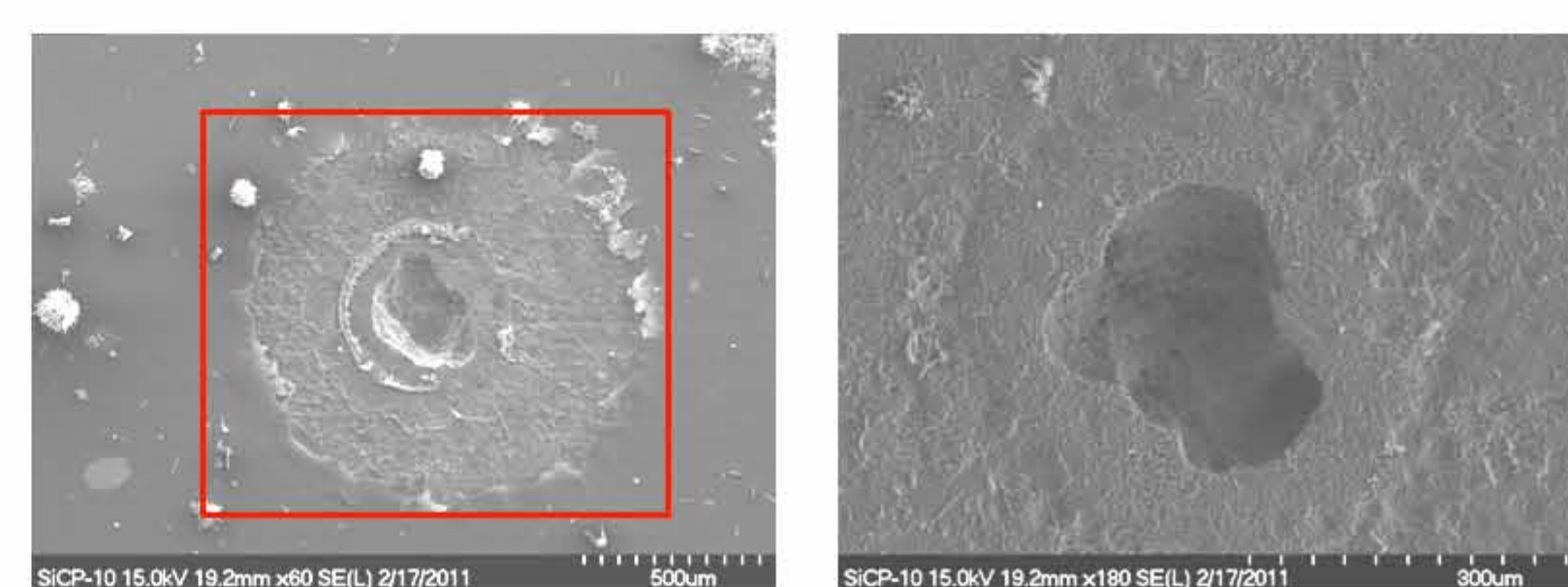


## Breakdown of Passive Scale



- Regions of SiO<sub>2</sub> scale removed from SiC, often as circular areas
- Edges of spalled areas provide clues of mechanism
- $\text{SiC}(s) + 2\text{SiO}_2(s) = 3\text{SiO}(g) + \text{CO}(g)$ 
  - $\text{SiO}(g) + 1/2 \text{O}_2 = \text{SiO}_2$
- 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:
  - $\text{SiC}(s) + 1/2 \text{O}_2(g) = \text{SiO}(g) + \text{CO}(g)$
- 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<sub>2</sub>) to establish the SiC/SiO<sub>2</sub> equilibria
- Passive-to-active transition
  - Scale/substrate react and SiO(g) product removal 'pulls' reaction
    - $\text{SiC}(s) + 2\text{SiO}_2(s) = 3\text{SiO}(g) + \text{CO}(g)$
    - $\text{SiO}(g) + 1/2 \text{O}_2 = \text{SiO}_2$
- Examine pre-oxidized SiC to understand breakdown of SiO<sub>2</sub> scale

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