The Effect of Dissociated Oxygen on the Oxidation of Si, Polycrystalline SiC, and LPCVD Si_3N_4

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Ultra-high temperature ceramic (UHTC) composites intended as sharp leading edge and control surface components on hypersonic flight vehicles will experience intense aerothermal heating in environments containing significant levels of dissociated oxygen. Atomic oxygen is generated by the dissociation of oxygen molecules in the bow shock that forms ahead of vehicle leading edges. Oxygen atoms can diffuse through the boundary layer to the surface, where they may recombine into molecular oxygen or react with the surface material(s) to form adherent or volatile oxides.

The effects of dissociated oxygen on the oxidation behavior of metal carbides, borides and nitrides are not yet well quantified. SRI International and Vanderbilt University are collaborating on research investigating the influence of oxygen dissociation on (1) the reaction rates for passive and active oxidation, (2) the boundaries between passive and active oxidation regimes, (3) the composition, morphology, and optical properties of resulting oxide layers, for UHTC composites and their constituent materials.

Here we report the results of initial oxide growth experiments on (100) p-type Si, polycrystalline SiC, and LPCVD deposited Si_3N_4 surfaces at low pressure (~3-4 Torr) and moderate temperature (~900 °C). A high-power microwave discharge was used to dissociate Ar/O_2 and Ar/N_2O gas mixtures that were then passed over samples heated in a tube furnace.

Oxide thicknesses were determined using spectroscopic ellipsometry and ion beam backscattering. Ellipsometric analysis of the silicon and silicon nitride films was very straight forward, as these systems are well characterized. Optical analysis of the polycrystalline SiC films was more of a challenge, as most of the optical studies on SiC reported in literature were performed on single crystal substrates.

Significant differences in oxide growth were seen between oxidation with and without the discharge. For example Table I presents results for oxidation of LPCVD Si_3N_4 surfaces exposed to approximately 900 °C Ar/O_2 at approximately 3.3 torr for 3 hours. The ellipsometry analyses suggest that the interface under the SiO_2 grown on Si_3N_4 roughens during the oxidation process. Table II presents results for oxidation of silicon exposed to approximately 900 °C Ar/O_2 and Ar/N_2O at approximately 4.8 torr for 3 hours. In addition to these results we will present the SiC oxidation results as well as data collected for oxidations performed in the Ar/N_2O environments.

We will conclude this presentation with a discussion of the applicability of these results to the oxidation of ultra-high temperature ceramic (UHTC) composites.

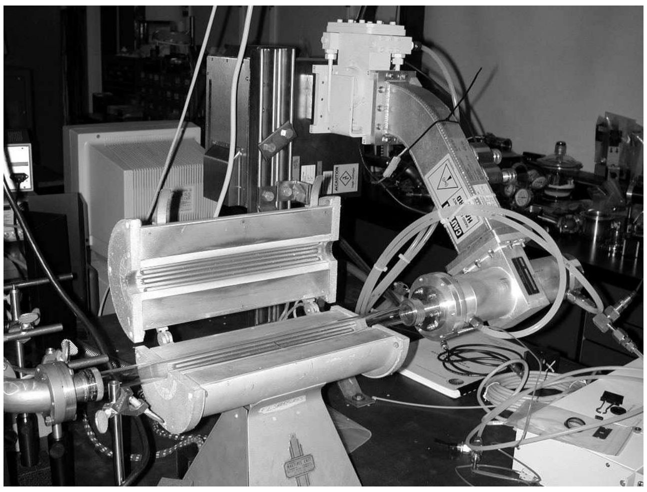

Figure 1: High power microwave discharge facility

Sample	Si_3N_4 (Å)	Interface Roughness (Å)	SiO_2 (Å)
Si_3N_4- O_2, discharge off	1393.5	38.6	14.2
Si_3N_4- O_2, discharge on	758.6	37.4	1024.6

Table I. Ellipsometry measurements of SiO_2 growth on LPCVD Si_3N_4. after 3 hour exposure at approximately 900 °C.

Sample	SiO_2 (Å)
Silicon- O_2 discharge off	65.2
Silicon- O_2 discharge on	1114.0
Silicon- N_2O discharge on	1381.4

Table II. Ellipsometry measurements of SiO_2 growth on (100) p-type silicon after 3 hours exposure at approximately 900 °C.