



## Model nucleation and growth studies of nanoscale oxide coatings suitable for modification of microcellular and nano-structured carbon

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### ABSTRACT

In this paper, a detailed study of the nucleation and growth of plasma assisted oxide coatings on model graphitic substrates has been performed. The surface chemistry and morphology of these films (as they grow on graphite) have been monitored using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). It is shown that oxide coatings start as islands having average height of 3–5 nm. The density and lateral size of these islands grow to form complete layers. Therefore complete and smooth coverage can be obtained with a film thickness in the range of a few nanometers (3–5 nm). The coating chemical composition is identical to SiO<sub>2</sub>. Detailed XPS analysis during overlayer growth reveals the presence of strong –Si–C– bonds at the graphite–coating interface. This is an important finding that can help to predict the mechanical, thermal and other functional properties of the interface. The durability of this coating at high operating temperatures has been investigated, and it is found to withstand up to 1000 °C heat treatments in argon environment.

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### 1. Introduction

Microcellular foams and nanofibers of sp<sup>2</sup> graphitic carbon (Fig. 1) have significant potential in aerospace, automotive and thermal management applications. These have been shown to be effective as core materials in multifunctional composites because of their unique thermal, mechanical and electrical properties, and their low densities [1–10].

The surface properties of carbon structures, however, present a special processing challenge for composite formation. Graphitic surfaces resist bonding, and are not easily wettable by polymeric or metallic matrix materials. This may result in low adhesion, inadequate infiltration, and porosity of the resulting composite [7]. To overcome these problems, graphitic surfaces need to be modified appropriately without compromising the desirable properties of the underlying material.

Wettability and interfacial bond strength of carbon with matrix materials can be enhanced by controlled “oxidation” of the carbon surface with treatments such as acid etching [9,11–14]. This makes the surface more hydrophilic. It also improves adhesion with many matrix materials through a combination of increased chemical bonding and enhanced mechanical interlocking due to the increased roughness of the carbon surface at the atomic scale. However, such improvements in interfacial strength are often achieved at the expense of fracture toughness and impact resistance [15,16] because some of the sp<sup>2</sup> C–C bonds are broken in the process.

Therefore, a coating that produces oxygen functional groups on the carbon structures without etching will be an attractive approach of

achieving high strength and good fracture toughness. Microwave plasma coating offers such an option. Homogeneous nanoscale surface modification, yielding a surface with the desired functional groups, can be successfully implemented in the plasma phase. This technique has the additional advantage of being effective on complex and uneven shapes, since plasma can reach intricate porous surfaces unlike many other thin film techniques such as sputtering and pulsed laser deposition.

Plasma, the fourth state of matter, [17] is a partially or fully ionized gas containing electrons, ions, and neutral atoms or molecules. From the plasma of volatile organic compounds, highly adherent and conformal coatings can be deposited with novel chemistries and physical properties [18]. The technology of plasma thin film deposition is used in several industries for a variety of applications such as a primer layer for promoting interfacial adhesion, anti-corrosion coatings, optical modifiers and diffusion membranes [19,20]. Plasma reactor designs are evolving in modern technology with enhanced capability of activating a large variety of molecular groups. This approach can alter the normal pathways through which surface modification is performed and therefore enable production of novel materials.

In the literature, plasma organosiloxanes such as hexamethyldisiloxane [(CH<sub>3</sub>)<sub>3</sub>SiOSi(CH<sub>3</sub>)<sub>3</sub>: HMDSO], tetraethoxysilane [Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>: TEOS] and chlorotrimethylsilane [Si(CH<sub>3</sub>)<sub>3</sub>Cl: CTMS] have been used for the growth of transparent silicon oxide films on electronic components [21]. Among these, HMDSO seems to be the most popular due to its high deposition rate, non-toxic nature, and a relatively high vapor pressure at normal temperature (98 mbar at 310 K) [22]. The simultaneous addition of oxygen in microwave sustained plasmas of HMDSO enables glass-like and scratch resistant coatings with good substrate adhesion [23]. The stoichiometry of the SiO<sub>x</sub> film is strongly related to plasma composition

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[18]. Increasing the oxygen flow has an appreciable effect on the silicon chemical environment. Hence, the desired surface chemistry can be obtained by optimizing the plasma parameters. Even though many research groups have investigated plasma assisted silicon oxide coatings on flat electronic substrates, there is no study of such films grown on carbon, and no discussion about their possible use in uneven and porous nanostructures. For applications of these types of films, major unanswered questions remain to be addressed, some of which are listed below:

- What are the actual bonding states of the atoms/ions at the carbon-coating interface, and within the film itself?
- How does the coating nucleate and grow on the substrate?
- What is the minimum thickness required to completely cover the carbon structures? How effective will these coatings be at the nanoscale? Most of the earlier studies dealt with micron-scale layers or larger materials. When the intended substrates are carbon nanofibers, the effectiveness of this coating at the atomic scale becomes a crucial question that needs fundamental study.
- Can oxide coatings withstand high temperature treatments customary of carbon composite fabrication?

This study is focused on addressing these questions. The primary goal of this paper is to present the chemistry and morphology of the growing overlayer using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). These analyses have been carefully performed starting from the initial stages of coating nucleation on model flat graphitic substrates all the way to complete coverage of thick overlayers. Correlation between XPS and AFM data at every step provides insight into the mechanism of nucleation and growth of these layers and interfacial bonding states between the substrate and the film. Durability and high temperature applications of these coatings have also been studied and results presented.

## 2. Experimental details

Quantitative surface analysis will require detailed study on a model flat surface. Carbon foams and nanofibers used in aerospace applications described earlier are identical to graphite [8]. Therefore, highly oriented pyrolytic graphite, (HOPG ZYH grade supplied by Molecular Imaging) was used in this study. Samples were ultrasonically cleaned using isopropyl alcohol before surface modification from plasma. A microwave plasma chamber manufactured by PlasmaTech Inc. was used for coating deposition. In the instrument, the 8 cm×16 cm rectangular microwave coupling quartz window is located on top of a 25 cm×25 cm aluminum square vacuum chamber. The low-pressure microwave (2.45 GHz) plasmas are of high chemical activity due to the high generation rate of reactive atoms or molecules [24].

Deposition of oxide coating was done in three steps:

- a. Ultra high purity O<sub>2</sub> gas (99.99%) was introduced into the plasma chamber at a flow rate of 50 ml/min, chamber pressure of 48 Pa and 225 W microwave power. Due to the high microwave frequency, carrier gas gets ionized and it cleans and activates the surface of the sample to be coated. This process was carried out for 180 s.
- b. O<sub>2</sub> carrier gas (50 ml/min, 56 Pa) was introduced into the chamber along with HMDSO (2 ml/min) at a microwave power of 250 W. This mixture was used to deposit oxide on the surface.
- c. O<sub>2</sub> carrier gas (50 ml/min, 48 Pa) was introduced into the chamber at a microwave power of 150 W for 60 s to stabilize the oxide coating.

XPS was used for the chemical characterization of plasma coatings to quantify elements present on the top few atomic layers (0.5–7.0 nm) and also to yield information related to the chemical bonding states of the elements. XPS analysis was carried out in the Kratos Axis Ultra System using monochromatic AlK<sub>α</sub> (1486.6 eV) X-rays in ultra high vacuum environment (~10<sup>-10</sup> Torr). The X-ray source was run at a power of 140 W (14 kV with a 10 mA emission current). Survey

scans (Binding energy: 0–1000 eV) were collected to identify the elements present on the sample surface and high resolution scans for the selected elements were acquired using an analyzer pass energy of 80 eV. Two scans were collected on each area, which is about 110 μm diameter (analysis spot size), and averaged to enhance the signal/noise ratio. Sample charging was minimized by using a charge neutralizer that floods the surface with low energy (2.6 eV) electron beams.

XPS peaks and their respective binding energies have been identified by using peaks taken in the same Kratos instrument on standard pure materials. The XPS data have also been verified with the values available from the open literature such as Wagner et al., 1979 [25], and Alexander et al., [18,19]. Charge-corrections were verified using the C 1s component at BE=284.5 eV corresponding to HOPG graphite. In spectra where silica film is expected, Si 2p peak at 103.2 eV and O 1s peak at 532.1 eV (SiO<sub>2</sub>) are used as additional checks. XPS analysis was performed at every step of the film growth process, starting from very small deposition times (initial stages of nucleation) to long deposition times when the overlayer is thick and unchanging.

At every step, XPS analysis was supplemented with surface morphology monitoring using intermittent contact AFM. AFM measurements were conducted using a Molecular Imaging PicoSPM II using Al-coated Si intermittent contact mode cantilevers with a nominal force constant of 42 N/m (Nanosensors). All AFM measurements were performed in air at room temperature. Microstructural images were obtained using JEOL 35 Scanning Electron Microscope, and JEOL 100CXII Transmission Electron Microscope systems.

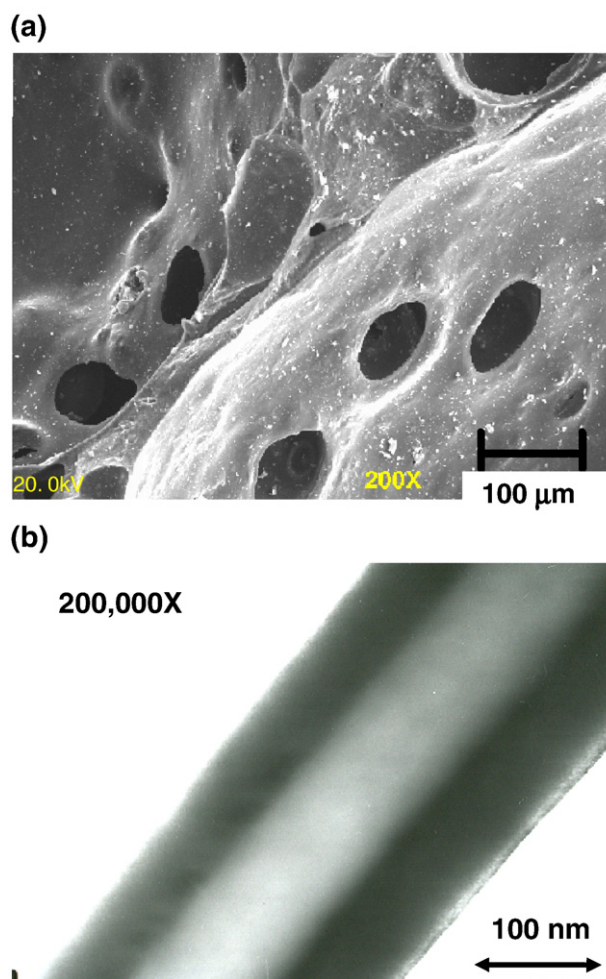


Fig. 1. (a) SEM image of microcellular carbon foam, and (b) TEM image of carbon nanofibers.

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