Low Temperature Chemical Vapor Deposition of Aluminosilicate Thin Films on Carbon Fibers

Vernal N. Richards, Jason K. Vohs, and Bradlev D. Fahlman[†]

Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859

Geoffrey L. Williams

Department of Biology, Central Michigan University, Mount Pleasant, Michigan 48859

We report the deposition of aluminum oxide and aluminosilicate thin films onto carbon fiber substrates, at temperatures of 200° and 250°C, respectively. For aluminosilicate films, the Al/Si ratio of the resultant film varied concomitantly with the composition of the liquid precursor mixture. The growth rate for the oxide films was 15–17 A/min, comparable with other methods carried out at higher temperatures. Cross-section SEM images indicate that the deposited films are conformal, following the complex topography of the carbon fiber substrate. Preliminary gas-phase IR analysis suggests that the coatings decompose the nerve agent simulant dimethyl methylphosphonate at temperatures as low as 35°C, suggesting the utility of the reported methodology for the design/fabrication of actively protective fabrics and clothing.

I. Introduction

WITH the constant threat of terrorist attacks, much attention has been focused on the development of materials that will protect both military personnel and civilians against the release of chemical and biological warfare agents. Solid metal oxides, such as aluminum oxide, have been shown to adsorb and decompose organophosphorus-based chemicals at temperatures not far removed from ambient.¹ The deposition of thin films of these materials onto substrates such as clothing fibers and fabrics would represent an intriguing utility for actively protective clothing, for both military and civilian use. For the deposition of coatings onto thermally sensitive substrates with such complex topography, it is imperative to have a low-temperature method that is still able to produce conformal thin films. The ultimate methodology would further enable one to control the stoichiometry of the growing film. To this end, we report the low-temperature deposition of conformal aluminum oxide and aluminosilicate thin films on carbon fiber substrates, with facile control over Al:Si ratios for the latter films. Our temperatures represent the lowest-reported temperatures to date, allowing other possible applications for temperature-sensitive substrates.

Common precursors used for the chemical vapor deposition (CVD) of Al_2O_3 films include $AlCl_3$,² $AlMe_3$,³ $Al(acac)_3$,⁴ and various aluminum alkoxides.⁵ Alkoxides are the precursors of choice, producing films with little carbon incorporation at low temperatures even in the absence of an oxidizing gas. For aluminosilicate films, systems utilizing one or two precursors have been used; the first single-source precursor was the monosiloxide complex, Al(OⁱPr)₂(OSiMe₃).⁶ However, the use of this precursor required temperatures exceeding 900°C in order to get films with an even distribution of aluminum and silicon. Although attempts have been made to control Al:Si ratios in aluminosilicate films, such stoichiometric control remains difficult to control, for both single-source and dual-source systems.⁷

II. Results and Discussion

Our CVD system for the growth of aluminum oxide and aluminosilicate films featured the controlled hydrolysis of watersensitive precursor liquids. To prevent extensive gas-phase reactions and a granular coating, water and precursor vapors were introduced through separate tubes, and allowed to come into contact only in the immediate vicinity of the substrate (Fig. 1). For aluminum oxide films, a volatile precursor, $[Me_2Al(^iOPr)]_2$, was used alone; for aluminosilicate films, tetraethoxysilane was added to the above aluminum-containing liquid. It should be noted that both ¹H and ¹³C NMR confirmed that the simple physical mixing of aluminum and silicon liquids did not result in reaction by-products, only a homogeneous one-phase solution.

The effective deposition temperature for aluminosilicate and alumina thin films was found to be substrate-dependent. On Si (100), the lowest temperatures yielding a homogeneous coating of aluminum oxide and aluminosilicate were 125° and 200°C, respectively (Fig. 2). However, when carbon fibers were used as substrates, no observable coating was observed at temperatures below 200° and 250°C for aluminum oxide and aluminosilicate, respectively. These values indicate that a higher temperature is required for the migration/nucleation of surface species over the complex topography of an irregular carbon fiber, relative to a silicon wafer. The increased thermal conductivity of Si (100) relative to carbon would also explain the increased migratory efficiency of intermediates at lower temperature on silicon, causing nucleation and growth of films at lower temperatures. The temperature regime used in our system is far below the reported deposition temperature (500°-600°C) for low-pressure chemical vapor deposition (LPCVD) using the above aluminum precursor alone⁸ or associated with metal acetylacetonates.^{9,10} To our knowledge, our study also represents the first use of $[Me_2Al(^iOPr)]_2$ for atmospheric-pressure chemical vapor deposition (APCVD) growth of aluminum oxide-containing films, allowing for facile industrial scale-up relative to LPCVD techniques.

The aluminosilicate films grown on the carbon fiber are conformal, perfectly following the rough terrain of the fiber surface (Fig. 3). Because of the low temperatures used for deposition, the as-deposited films are amorphous, confirmed by powder X-ray diffraction. Auger spectroscopy suggests that the alumi-

L. C. Klein-contributing editor

Manuscript No. 11255. Received August 6, 2004; approved November 9, 2004. Supported by the State of Michigan and Central Michigan University by a Research Excellence Fund award for this and continuing work. Also supported by Dendritic Nanotechnologies and the Department of Defense (Army Research Laboratory). [†]Author to whom correspondence should be addressed. e-mail: fahlm1b@cmich.edu



Fig. 1. Schematic of the chemical vapor deposition system used for deposition of aluminum oxide and aluminosilicate thin films.

num oxide films are stoichiometric Al_2O_3 . By contrast, the silicon environment in aluminosilicate films is intermediate between SiO₂ and SiO(OH)₂. Our observed growth rates for aluminum oxide (17 Å/min) and aluminosilicate (15 Å/min)



films are comparable with APCVD using metal acetylacetonate precursors.⁷

Figure 4 shows elemental dot-maps of C, O, Al, and Si concentrations for a cross-section of a coated carbon fiber. Both Al and Si are observed to completely encapsulate the fiber, indicating a high degree of surface mobility of reactive intermediates during deposition. It should be noted that a randomly intertwined tow of fibers is placed in the CVD chamber for deposition runs, rather than an individual carbon fiber. The conformality exhibited at such a low temperature will allow for facile scale-up of this procedure; a tow of fibers may be reeled through the deposition furnace at a specific rate, with coated fibers being rewound onto a new spool.

The Al:Si ratio of the deposited film was found to vary directly with the relative ratio in the precursor solution (Table I). This is counterintuitive, as the volatility of $[Me_2Al(OPr)]_2$ is much greater than Si(OEt)₄, suggesting that a solution containing both liquids would simply yield silicon-free aluminum oxide films until the Al precursor has been vaporized. This trend was only observed when the fraction of the aluminum precursor exceeded that of the silicon component. When there is an excess of the relatively involatile component corresponding to a relatively low overall solution volatility, the vapor pressure of the aluminum precursor is suppressed, resulting in less at.% Al in the growing film.



Fig. 2. Elemental dot-map of the aluminum (blue) and silicon (red) concentrations on Si (100). Shown are (a) aluminum oxide deposited at 125°C and (b) aluminosilicate grown at 200°C (2:1 Al:Si precursor). The penetration-depth intensity from the silicon substrate has been subtracted.



Fig. 3. Cross-section SEM image of a carbon fiber coated with an aluminosilicate thin film. Scale bar is 2 microns.



Fig. 4. Cross-section elemental dot-maps of a coated carbon fiber (1:1 Al:Si precursor). Shown are concentrations of (a) carbon, (b) oxygen, (c) aluminum, and (d) silicon.

In order to study the potential catalytic activity of the oxide films toward the decomposition of chemical warfare agents, the organophosphorus compound dimethyl methylphosphonate (DMMP) was used. This compound has been used as a simulant in previous studies, as it mimics the structure of a number of deadly agents. The use of the deposited oxide layer as a catalyst for the decomposition of DMMP vapor at ambient temperatures was studied using gas-phase IR spectroscopy (Fig. 5). One of the products of DMMP decomposition is methanol, indicated in IR by the presence of a strong v(O–H). Although DMMP was distilled *in vacuo* overnight and stored over molecular sieves,

 Table I.
 Aluminum/Silicon Ratios of Precursor and Deposited

 Film[†]

Al:Si precursor ratio	Al:Si film ratio
0.85	0.46
1.00	1.06
1.30	1.23
2.00	1.74
2.50	2.32

 $^{\dagger}Deposition$ temperature = 250°C; flow rates: H2O = 10 mL/min and precursor = 40 mL/min.

there is still a trace amount of methanol that is inherent in the liquid from its synthesis. This corresponds to the observation of a v(O-H) peak from the vaporization of DMMP in the presence of an uncoated fiber (Fig. 5(a)). It should be noted that the intensity of this peak is identical for the blank experiment when no fiber is present in the gas IR cell. However, at temperatures $> 35^{\circ}$ C there is a marked increase in the concentration of gasphase methanol that is present in the cell when a coated fiber is present, relative to uncoated carbon fiber. It is especially noteworthy that there was no observable difference in the low-temperature decomposition behavior between aluminum oxide and aluminosilicate-coated fibers, or for fibers with varying film thicknesses. This suggests that both films possess a similar concentration of surface hydroxyl groups, which are proposed to be influential in the decomposition pathway.^{11,12} The low deposition temperatures used in our system are most desirable for such catalytic applications, as the low crystallinity as well as copious surface defects and -OH moieties provide increased sites for adsorption/decomposition of gaseous organophosphorus agents. We are continuing our work in this area by examining other metal oxide films, as well as more sensitive surface analysis techniques to determine the decomposition mechanism and effectiveness of the deposited films.

III. Experimental Procedure

Trimethylaluminum, tetraethoxysilane (Strem Chemicals, Inc., Newburyport, MA), and aluminum isopropoxide (Aldrich, St. Louis, MO) were purchased and used without further purifica-



Fig. 5. Gas-phase IR spectrum of (a) an uncoated carbon fiber exposed to dimethyl methylphosphonate (DMMP) vapor and (b) an aluminosilicatecoated carbon fiber exposed to DMMP vapor.

To prepare the aluminum precursor, an amount of aluminum isopropoxide (11.73 g, 575 mmol) and trimethylaluminum (8.273 g, 114.9 mmol) were weighed into separate Schlenk flasks inside the glove box. The trimethylaluminum was subsequently transferred to the flask containing the aluminum isopropoxide powder via cannula at -78° C. The reactants were left to stir for 24 h, after which the product was separated from the remaining solid by distillation. ¹H NMR (300 MHz, C_6D_6 , δ): -0.6 6H CH₃-Al, 1.1 6H CH(CH₃)₂, 3.9 1H CH(CH₃)₂: ¹³C NMR (300 MHz, C₆D₆, δ): 3.0, 25.3, 66.9.

In order to minimize vapor-phase mixing, the precursor and water vapor were carried into the CVD chamber through separate lines. A tow of carbon fibers (ca. 10-20 cm in length) was rinsed with acetone and dried prior to use. Silicon wafers were cleaned prior to use by dipping in a 10% solution of HF, followed by rinsing with distilled water and air drying. Before the precursor was allowed to enter the CVD chamber, the substrate was placed at the base of the quartz tube, and the system was purged with argon until the desired reaction temperature was reached. Initial trials were run at a reaction temperature of 500°C, and the temperature was gradually reduced in subsequent trials as to ascertain the lowest temperature required for deposition. Trials with varying substrate positioning and precursor flow rates were run to determine the precursors along with the water vapor introduced at flow rates of 40 and 10 mL/ min, respectively. The flow was stopped and the furnace turned off after 1.5 h for all trials. Characterization of thin films on silicon wafers and carbon fibers was performed using a JEOL JSM-840A scanning electron microscope (JEOL USA, Peabody, MA) equipped with a WinEDS detector, capable of detecting elements \geq B. Film thickness measurements were obtained using a Filmetrics F20 film thickness analyzer (Filmetrics, Inc, San Diego, CA).

Acknowledgment

We give special thanks to Dr. Donald Tomalia for his continuing support and many fruitful discussions related to this and other research projects currently in progress.

References

¹V. N. Sheinker and M. B. Mitchell, "Quantitative Study of the Decomposition of Dimethyl Methylphosphonate (DMMP) on Metal Oxides at Room Temperature and Above," Chem. Mater., 14 [3] 1257-68 (2002), and references therein.

B. Lux, H. Colombier, H. Altena, and K. Sternberg, "Preparation of Alumina Coatings by Chemical Vapour Deposition," Thin Sol. Films, 138 [1] 49-64 (1986).

³M. D. Groner, F. H. Fabreguette, J. W. Elam, and S. M. George, "Low-Temperature Al2O3 Atomic Layer Deposition," Chem. Mater., 16 [4] 639-45 (2004).

⁴O. B. Ajayi, M. S. Akanni, J. N. Lambi, H. D. Burrow, O. Osasona, and B. P. Podor, "Preparation and Optical Characterization of Pyrolytically Deposited Thin Films of Some Metal Oxides," Thin Sol. Films, 138 [1] 91-5 (1986).

⁵S. Blittersdorf, N. Bahlawane, K. Kohse-Höinghaus, B. Atakan, and J. Müller, "CVD of Al2O3 Thin Films Using Aluminum Tri-isopropoxide," Chem. Vapor Depos., 9 [4] 194-8 (2003). ⁶F. Chaput, F. A. Lecomte, A. Dauger, and J. P. Boilot, "Preparation and

Structure of Aluminosilicate Aerogels," Chem. Mater. 1 [2] 199-201 (1989).

A. R. Barron, "Chemical Vapor Deposition of Insulating Thin Films," in The CVD of Nonmetals, Edited by W. S. Rees Jr. VCH, Weinheim, Germany, 1996.

⁸W. Koh, S.-J. Ku, and Y. Kim, "Chemical Vapor Deposition of Al₂O₃ Films Using Highly Volatile Single Sources," Thin Sol. Films, 304 [1-2] 222-4 (1997).

⁹B. D. Fahlman and A. R. Barron, "CVD of Chromium-Doped Alumina 'Ruby' Thin Films," Chem. Vapor Depos., 7 [2] 62-6 (2001).

¹⁰B. D. Fahlman and A. R. Barron, "Substituent Effects on the Volatility of Metal B-Diketonates," Adv. Mater. Opt. Electron., 10 [3-5] 223-32 (2000).

¹¹M. K. Templeton and W. H. Weinberg, "Adsorption and Decomposition of Dimethyl Methylphosphonate on an Aluminum Oxide Surface," J. Am. Chem. Soc., 107 [1] 97-108 (1985).

¹²M. K. Templeton and W. H. Weinberg, "Decomposition of Phosphonate Esters Adsorbed on Aluminum Oxide," J. Am. Chem. Soc., 107 [4] 774-9 (1985).