PRF#: 59048-DNI5
Project Title: Patterned Coatings for Responsive Surface Cleaning
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2019 Progress Report Narrative

Primary Motivation and Goals. Chemical vapor deposition (CVD) processes offer coating technologies for a wide range of materials and applications (separation membranes, biomedical devices, textiles, etc.). A significant advantage of CVD methods is that they can deposit conformal thin films, which is critical for coating performance but becomes a limitation for patterning surface chemistry. Methods for creating chemical patterns require lithography techniques limiting the type of materials that can be utilized due to concerns regarding degradation, dissolution, and contamination. The primary goals of this project are to (1) establish a mechanism for *in situ* patterning of vapor-phase deposition and (2) apply patterned coatings to develop self-cleaning surfaces.

Focus of Effort this Past Year. The first year of this project was spent training the graduate student on the custom-designed CVD chamber and performing systematic studies on the influence of temperature gradients on vapor-phase deposition. We use an initiated chemical vapor deposition (iCVD) technique as a model system to pattern vapor-phase deposition (**Figure 1**). The iCVD method produces functional polymeric coatings via free-radical polymerization on the sample surface. Deposition conditions (pressure, flowrates, substrate temperature, and filament temperature) determine the composition, thickness, molecular weight, and coverage of iCVD polymer coatings. Our system consists of a 10” x 10” x 2” pancake reactor with a temperature-controlled stage, automated pressure controller, and in situ interferometer. Connected to the chamber are six independent inlet lines for inert carrier gas, initiator, and monomers. The graduate student training on the iCVD system consisted of learning the kinetics of the chemical reactions in the system, understanding how the kinetics are influenced by the deposition conditions, and technical training on how each component functions and the associated maintenance. Training activities produced a comprehensive list of baseline deposition conditions for *12* polymer coatings that can be applied to this project. After completing iCVD training, systematic studies were performed to probe how temperature gradients can be used to pattern monomer adsorption and polymerization. The central aim is to establish a range of deposition conditions, or system configurations, that *do not* result in polymerization in order to ultimately produce patterned coatings.

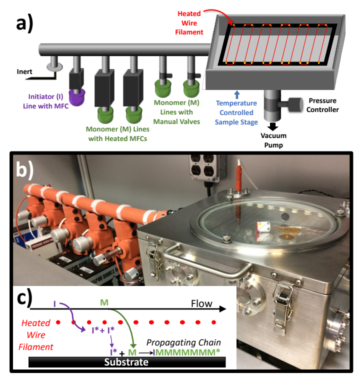
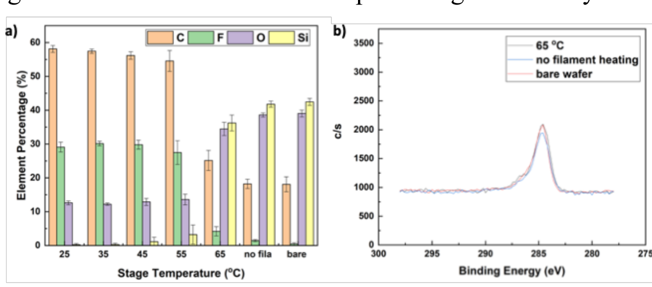


Figure 1. a) Schematic and b) photo of the Bradley group custom iCVD system. c) Illustration of the deposition process.

Summary of Results

Effect of Substrate Temperature on Deposition. To investigate the role of substrate temperature on deposition kinetics, we used poly(pentafluorophenyl methacrylate) (PPFM) as the model polymer because the fluorine content would enable facile characterization of surface composition by x-ray photoelectron spectroscopy (XPS). Depositions of PPFM were performed at stage temperatures varying from 25 to 65°C; in these experiments the samples had a uniform temperature to evaluate the effect of absolute temperature independent of local gradients. The substrate temperature influences the amount of monomer adsorbed to the substrate surface which is described in the iCVD process by the ratio of the monomer partial pressure (P_m) to the monomer saturation pressure (P_{sat}). Increasing the substrate temperature from 25 to 65°C, keeping all other conditions constant, resulted in a decrease in P_m/P_{sat} from 0.17 to 0.03 and a corresponding decrease in the deposition rate from 15$\pm$2 to 0 nm/min. Achieving no deposition (rate = 0 nm/min) is the primary goal to establish conditions for patterning. XPS analysis confirmed no deposition at 65°C

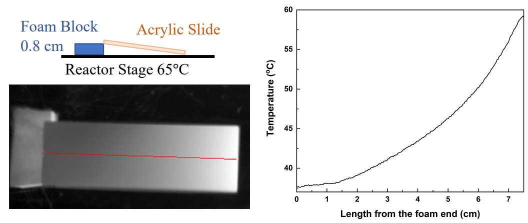
Figure 2. XPS (a) atomic compositions and (b-c) high resolution C1s spectra of PPFM depositions onto silicon wafers at a range of substrate temperatures compared to an uncoated silicon wafer.



because the atomic composition and high resolution C1s spectrum are identical to an uncoated silicon substrate (detecting primarily carbon contamination), while all depositions at lower substrate temperatures exhibit the expected atomic composition and spectrum for PPFM (**Figure 2**).

Exploring Patterning using Temperature Gradients. We initially proposed to utilize differences in substrate temperature to locally pattern iCVD deposition. Design and implementation of a device based on thermoelectric coolers is underway. Preliminary studies established a temperature gradient by placing rectangular samples in a tilted configuration with one end in contact with the hot stage (65°C) and the other end lifted on a foam block (**Figure 3**). For acrylic slides, a continuous temperature gradient of ~3°C/cm can be maintained using a foam block with a height of 0.8 cm; the overall temperature variation and local gradients are dependent on the height of the foam block. Temperature gradients across substrates are highly dependent on the thermal conductivity. We have been *un*successful in establishing any significant temperature gradients on inorganic substrates.

Figure 3. Temperature gradient established across an acrylic slide with one side in contact with the hot stage and the other lifted on a foam block.



Exploring an Alternative Patterning Approach. Our examination of temperature gradients reveals the need for sophisticated devices to control local temperature. The original plan was to develop microfluidic devices to establish and maintain temperature gradients during deposition. In an effort to simplify the system and make it compatible with both organic and inorganic substrates, we are currently exploring utilizing disordered nanoparticle (NP) packings to locally pattern polymer coatings through capillary condensation of vapor-phase precursors in the pores of the particle packings. Such NP packings can be patterned with micron-sized features using soft lithography that is compatible with roll-to-roll processing; this technology was developed by a colleague at UMass Amherst, James Watkins. Preliminary experiments to test this new direction were done by depositing poly(hydroxyethyl methacrylate) (PHEMA) at room temperature and pressure onto bare silicon wafers and silicon wafers containing ~120 nm thick particle packings comprised of 8 nm TiO_2 NPs (**Figure 4**). The experimental set-up consisted of a closed glass Petri dish containing the samples and individual vials (0.3 mL) of HEMA monomer and photoinitiator. Monomer and initiator are expected to condense in the pores of the NP packings that was then polymerized by exposure to UV light (300 W, 30 minutes). For the bare silicon wafer, ellipsometry detected no PHEMA deposition and the water contact angle was unchanged after deposition. For the NP packings, PHEMA deposition was confirmed by a decrease in the water contact angle from 69.09±3.87° to 48.56±2.17° and a slight increase in the refractive index from 1.73 to 1.76. *We believe these results motivate a change in research direction to explore the use of NP packings, instead of temperature gradients, to locally pattern vapor-phase deposition.*

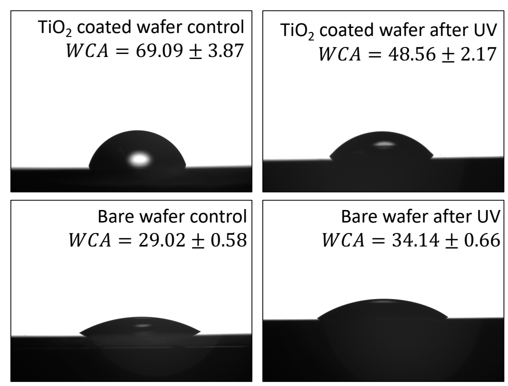


Figure 4. Comparison of water contact angles for PHEMA deposition onto TiO_2 NP packings and bare silicon wafer controls.

Impact on PI Career Development. This project has nucleated a novel research area for the PI. Results motivate incorporating physical chemistry associated with confined volumes in NP packings that will further expand the expertise of the group. In addition, the foundation of this project in patterning polymer coatings has initiated new collaborations incorporating iCVD patterned coatings into electronic devices (collaboration with James Watkins). Lastly, based on the themes of this project, the PI co-organized a symposium at the 2019 National Conference of the American Institute of Chemical Engineers which will provide a networking opportunity for academic and industrial professionals working in thin films and confinement.

Impact on Graduate Student Academic Development. Research activities related to this project have accelerated the academic development of the graduate student. Starting with training on the basic operation of iCVD, the graduate student has expanded technical skills in polymer characterization (XPS, contact angles, profilometry) and system design (temperature gradients and NP packings). Through these research activities the graduate student is becoming independent in both experimental design and management of collaborative activities.