Induced wetting of polytetrafluoroethylene by atomic layer deposition for application of aqueous-based nanoparticle inks

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ABSTRACT

Atomic layer deposition of aluminum oxide is shown to control the surface energy and wetting properties of polytetrafluoroethylene (PTFE) films and membranes. Independent of deposition temperature, gradual and abrupt wetting transitions were observed for PTFE films and membranes, respectively. To assess the enhanced compatibility of treated PTFE substrates with nanoparticle inks, drop casting and inkjet printing of silver nanoparticle solutions are performed and analyzed by optical microscopy and time of flight secondary ion mass spectroscopy. Untreated PTFE substrates showed poor compatibility with the nanoparticle inks, drying in a coffee ring pattern, whereas aluminum oxide treated PTFE substrates exhibited uniform silver nanoparticle distribution after drying.

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1. Introduction

Polytetrafluoroethylene is an inert fluorocarbon polymer that finds practical use in applications such as gaskets, lubricants, and insulating materials. Due to its higher thermal and electrical stability as compared to polyethylene (PE), PTFE has received interest in applications including filtration where it is often desirable to wet PTFE surfaces for compatibility with particular chemical or biological solutions [1] such as those pertaining to waste water treatment facilities [2,3]. From an electronics stand-point, PTFE is well suited as a substrate for flexible sensors [4], supercapacitors [5], fuel cells [6], and aerospace devices [7]. To meet the demands of high throughput processing, aqueous inks containing inorganic particles are used to pattern functionalized regions on the surface of polymer [8,9]. However, many of these aqueous-based processes are not compatible with PTFE due to its hydrophobic nature. As these inks dry, a characteristic coffee-ring pattern forms resulting in a nonuniform distribution of the inorganic material [10]. In addition, line patterns are inaccessible and methods such as lamination are required for producing patterns on a PTFE substrate.

To enhance the compatibility between hydrophobic surfaces and aqueous inks, surface modifications have been explored including wet chemical [11] and plasma methods [12]. These methods have been successful in PTFE modification, but rely on cleavage of the C–F and C–C bonds in order to introduce polar moieties or intermediates for subsequent chemical modification. Vapor phase materials growth methods such as atomic layer deposition (ALD) have also been shown to create nanoscale inorganic coatings on polymer surfaces, thereby reducing the surface energy and inducing a wetting state. ALD is a material processing technique in which ceramic coatings are formed by sequentially introducing a set of reactants to a surface. The self-limiting nature of the reaction on the surface results in a nanoscale control of the thickness. Due to the availability of material growth of many ALD chemistries at low temperatures ($< 150\ ^\circ C$), ALD has shown application onto organic polymer substrates [13,14]. Hyde et al. examined ALD growth of aluminum oxide (Al_2O_3) onto polypropylene substrates, resulting in a wetting transition from hydrophobic to hydrophilic after sufficient ALD cycles were performed [15]. The delay in observed wetting transition is attributed to a nucleation and growth process for the Al_2O_3 thin film. This transition was observed only at low temperatures, in which diffusion of the ALD vapor precursors into the polymer is limited [16]. While ALD processing of alumina on PTFE has been demonstrated to result in decrease in hydrophobic character [2,17], the influence of PTFE morphology and effects of low ALD processing temperature on observed wetting transitions has not been examined. Moreover, this work shows the ability of ALD surface modifications to enhance the compatibility of aqueous-based nanoparticle printing techniques on PTFE.

2. Experimental

Polytetrafluoroethylene (PTFE) film and membrane substrates (5 μm pore size) were purchased from Fluoro Plastics Inc. and EMD Millipore, respectively, and were used as received. Silver nanoparticles (100 nm average diameter, 10 mg/mL in ethanol) were provided

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by Blue Nano Inc. ALD of Al_2O_3 was performed in a custom-fabricated viscous flow tube reactor using co-reactants of trimethylaluminum (TMA) (98%, Strem Chemicals Inc.) and H_2O (Sigma-Aldrich, BCP grade). The ALD cycling consisted of a TMA dose, N_2 purge, H_2O dose, and a N_2 purge with respective times of 0.2–30–0.2–45 s. Ultra-high purity N_2 (Machine Welders) used as the carrier gas for TMA and H_2O dosing was further purified using a nickel catalyst filter (Gate-Keeper®, Entegris Inc., < 10 parts per trillion impurity). The flow rate of N_2 was used to maintain a constant pressure of 1 Torr in the reactor during deposition. The temperature within the reactor was maintained between 60 and 120 °C, resulting in a Al_2O_3 growth rate of ∼1.2–1.4 Å/cycle as measured by spectroscopic ellipsometry from deposition onto planar silicon substrates.

Static water contact angle (WCA) evaluation was performed with a Future Digital Scientific Corp. (OCA-20) goniometer using 4 μL droplets of deionized H_2O placed and averaging at least three separate regions of the PTFE film and membrane samples (∼3 cm × 4 cm).

Inkjet printing of silver nanoparticle (AgNP) solutions was performed using a drop-on-demand inkjet printing system (Microfab Inc., Jet Drive 3) mounted onto an X–Y gantry stage. The diameter of the printing orifice was 80 μm, and the distance between the print head and the substrate was maintained between 1–2 mm. Solutions of AgNP were diluted to a concentration of 1 mg/mL in ethanol. Inkjet printed droplets were approximately 50–70 μm, as measured using high magnification imaging at the printing orifice. Dropcasting of an AgNP solution was performed using ∼0.2 mL of solution in a disposable syringe. Analysis of AgNP uniformity after drying was performed using optical microscopy and TOF-SIMS elemental mapping using Bi^+ and Cs^+ ion sources. (ION TOF TOF-SIMS 5).

3. Results and discussion

PTFE wetting Al_2O_3 ALD treatments: The WCA of PTFE films and membranes before and after Al_2O_3 ALD treatment at 60, 90, and 120 °C are shown in Fig. 1. Prior to Al_2O_3 ALD, PTFE films and membranes were hydrophobic, having WCA of 122° and 139°, respectively. For PTFE films (Fig. 1a), a linear decrease in the WCA is observed with increasing Al_2O_3 ALD cycles. Only after 100 cycles, does the WCA < 90°. Furthermore, Al_2O_3 deposition within the temperature examined has a negligible effect on the wetting transition. In contrast, PTFE membranes showed an abrupt wetting transition from hydrophobic to completely wetting (WCA=0°) after ∼80 Al_2O_3 ALD cycles. For both films and membranes, an increase in the substrate surface energy of ∼50 dynes/cm is observed. The difference in the nature of the wetting transition between the PTFE film and membrane is due to the surface morphology of the two substrates. PTFE films are largely planar in nature with sub-micron surface roughness visible using optical microscopy. In contrast, PTFE membranes are comprised entirely of interconnected pores similar to a sponge or a dense nonwoven fabric, which introduces capillary forces that enhance the absorption beyond that of the films [18]. The membranes also allow for the moisture to wick into the material, whereas films only allow for water transport across the surface [19].

Prior examination of ALD Al_2O_3 growth on PTFE at high temperatures (> 150 °C) has shown a reduced effect on hydrophobicity [2], as a result of nodular surface growth similar to what has been observed on polypropylene at higher processing temperatures [16]. Therefore, it is useful to examine the growth mechanisms of PTFE and polypropylene due to their subtle differences. Alumina deposition onto inert polypropylene follows an island-like nucleation mechanism as a result of there being no reactive sites for TMA interaction [16]. Only at low deposition
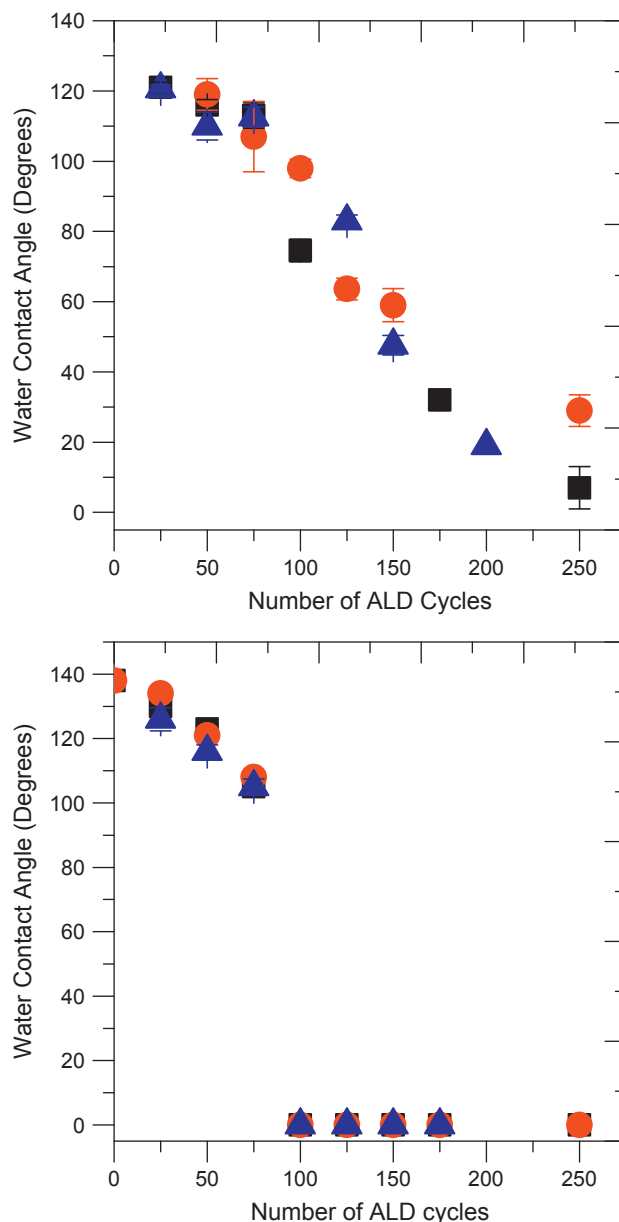

Fig. 1. Water contact angle of PTFE films (top) and membranes (bottom) after Al_2O_3 ALD at 60 (■), 90 (●), and 120(▲) °C.

temperatures is a conformal Al_2O_3 film deposited onto polypropylene due to minimal thermal expansion of the polymer. At higher deposition temperatures (> 90 °C), a nanoscale roughness is observed that induces a metastable Cassi–Baxter state. Although PTFE is a highly inert polymer similar to polypropylene, Lee et al. have demonstrated that ALD precursors such as TMA can interact directly with the PTFE, forming a hybrid (organic–inorganic) material based on interchain bonds between neighboring polymer chains [20]. Similar nucleation behavior exhibited on nylon-6 has shown a bi-layer structure with a hybrid organic–inorganic layer beneath an ALD thin film residing on the surface [16]. At lower temperatures, ALD growth on PTFE shows a conformal surface modification as expected since the diffusion of the precursor as well as the reaction kinetics between the polymer and precursor is reduced. At higher ALD temperature growth on PTFE, a pronounced nodular growth mechanism is observed, resulting in enhanced nanoscale surface roughness and hydrophobicity. This nodular growth is likely due to the unreacted precursor diffused into the polymer escaping and reacting with the water