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Wetting properties induced in nano-composite POSS-MA polymer films by atomic layer deposited oxides

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Due to their unique properties, nano-composite polyhedral oligomeric silsesquioxane (POSS) copolymer films are attractive for various applications. Here we show that their natural hydrophobic character can become hydrophilic when the films are modified by a thin oxide layer, up to 8 nm thick, prepared using atomic layer deposition. A proper choice of the deposition temperature and thickness of the oxide layer are required to achieve this goal. Unlike other polymeric systems, a marked transition to a hydrophilic state is observed with oxide layers deposited at increasing temperatures up to the glass transition temperature ($\sim 110^\circ\text{C}$) of the POSS copolymer film. The hydrophilic state is monitored through the water contact angle of the POSS film. Infrared absorbance spectra indicate that, in hydrophilic samples, the integral of peaks corresponding to surface Al–O (hydrophilic) is significantly larger than that of peaks linked to hydrophobic species. © 2012 American Vacuum Society. [DOI: 10.1116/1.3639134]

I. INTRODUCTION

Poly[(propylmethacryl-heptaisobutyl-polyhedral oligomeric silsesquioxane)-co-(methylmethacrylate)] (POSS-MA) films are interesting for microfluidics¹ and as dental restorative materials,² among other technologies. This type of nano-composite hybrid offers simultaneously attractive properties characteristic of organic and inorganic materials.¹ However, the surface properties need to be modified to tailor wettability, biofouling, and electro-osmotic flow characteristics in a manner which is stable with time; thus useful for applications. Previous studies have shown that the wettability of POSS-MA films can be improved by using oxygen plasma treatments.¹ Here we show that thin atomic layer deposited (ALD) oxide layers on POSS-MA films can also increase the surface wettability, i.e., lower the water contact angle (WCA). Improved wettability is effectively achieved when the ALD oxide coatings are prepared at increasing growth temperatures up to the glass transition temperature (T_g) of the polymer. We correlate this finding with the behavior in the infrared (IR) absorbance spectra of the POSS-MA and oxide

peaks, and compare the results to those reported for other polymer-based film systems.

Coatings fabricated using ALD are known to enable surface modifications.^{3–14} However, only a few studies are devoted to investigating the effects of ALD number of cycles and growth temperature on WCA.^{3,4,9} On polymeric materials most of the attention is devoted to describing ALD coating nucleation.⁴ A systematic study of the effects of growth temperature and ALD oxide layer thickness was performed on polymer fibers by Hyde *et al.*,³ but the wettability trends are poorly understood in planar polymeric films. Surface wetting studies of ALD films on planar spin-coated polymer films are limited. One recent study by Spagnola *et al.*⁹ investigated ALD-induced surface modifications of polydimethylsiloxane (PDMS) films on silicon.

The purpose of this work is (1) to investigate the effects of ALD Al_2O_3 layers on the wettability of spin-coated POSS-MA films on silicon and (2) to correlate the WCA of ALD oxide coated POSS-MA films with the thickness and growth temperature of the thin amorphous ALD Al_2O_3 layers. By integrating the characteristic peaks in IR absorbance spectra of POSS-MA films on silicon, we find a correlation between the IR absorption of the characteristic peaks of Al_2O_3 and

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FIG. 1. Structure of the POSS-MA polymer.

POSS-MA, and the corresponding WCA. The analysis method used here could be employed to examine the effects of ALD oxides on the wettability of other polymeric systems. The structure of the POSS-MA polymer is shown in Fig. 1.

II. EXPERIMENT

The POSS-MA copolymer, in a composition of 45 wt. % POSS, was dissolved in a CHCl_3 solution, as described elsewhere,¹ and spun-cast onto H-terminated Si(100). The silicon substrates were prepared by immersion for 30 s in a 1:10 ratio of $\text{HF}:\text{H}_2\text{O}$ solution, followed by a 60 s rinse in de-ionized (DI) water and blown dry in nitrogen flux. The spin-casting deposition process took place at 1000 rotations per minute (rpm) to form polymer films about 29 nm thick.¹ The POSS-MA film thickness was measured using a variable-angle spectroscopic ellipsometer (J. A. Woollam, Co.) and fitted assuming the polymer to be transparent with a refractive index of ~ 1.5 . Subsequently, the POSS-MA films were coated with amorphous Al_2O_3 layers in the custom-made horizontal hot wall viscous flow ALD reactor described below.

The ALD reactor consists of a 1-1/2 in. stainless steel tube, 24 in. long, whose central part (the reaction zone) is placed in a Lindberg Blue tube furnace capable to heat up to 1100 °C. Stainless steel lines carry the metal organic precursors, water vapor, and argon gas into the reaction zone through a feedthrough. The argon gas, stored in a tank, is purified from water vapor via a Drierite gas purifier before passing through a mass flow controller (Brooks – 5850E). The flux is governed by the relative pressure difference in the reactor. The argon gas acts as purging and precursor carrier gas. Its flux is governed by the mass flow controller. During the deposition process, the pressure in the reactor is set around 350 mTorr through the argon gas flux. The metal organic (trimethylaluminum precursor (TMA) 98%, Strem

Chemicals) and the oxygen precursor (DI water) are stored in appropriate containers kept at room temperature. The DI water level is controlled through a glass window in the stainless steel cell. The stainless steel lines that carry the precursors in the reaction zone are kept at about 75 °C using heating tapes (Omegalux, TP FG STD). The load lock and the pressure gauge (MKS Baratron type E28B) are placed in the reactor on the opposite side of the precursor lines. The pressure gauge is a capacitance manometer effective between 1 mTorr and atmospheric pressure. The reactor is maintained in low vacuum by a rotary vane pump (Adixen Pascal Series SD) lubricated with oil. The base pressure in the reactor is ~ 3 mTorr. A gate valve (Humphrey 410-20 solenoid valve) separates the reactor from the pump, and a standard oil mist eliminator (Adixen OME 25 S) protects the pump from the by-products of the ALD reactions. The cyclic opening and closing of the pneumatic valves (Swagelok ALD valves), providing the precursor supply in the reaction zone, is automated through a computer program (Labview 8.5).

For the ALD process, TMA was used as the aluminum source, and DI water as the oxygen source. The deposition temperature was calibrated with a thermocouple (Keithley 2000), and set at 40, 60, 90, and 115 °C for the experiment described in this work. The temperature 115 °C is above the T_g of the 45% in weight POSS-MA films, estimated to be ~ 110 °C.¹⁵ In each ALD cycle, the samples were exposed to TMA and DI water for 1 s. Metal organic precursor and DI water pulses were followed by 40 and 50 s purges in argon, respectively. Long purge times were utilized to facilitate the elimination of residual precursor and reaction by-products at the low deposition temperatures used in the ALD processes. On silicon, the Al_2O_3 film growth rate is ~ 0.13 nm/cycle, as determined by ellipsometry on films between 5 and 30 nm thick at 90 and 60 °C. The vibrational species in coated and uncoated POSS-MA films were studied using transmission Fourier transform IR spectroscopy (FTIR) at 0° incidence angle with a Bruker Vertex 70 IR spectrometer purged with nitrogen. The spectra, acquired with 4 cm^{-1} resolution, are shown in absorbance, i.e., $-\log_{10}(\text{transmittance})$ versus wave-number (cm^{-1}). The peaks were integrated using the OPUS spectroscopy software. The WCA of the coated and uncoated POSS-MA surfaces were measured using static contact angle with DI water, utilizing a custom-fabricated tool described elsewhere.¹ To eliminate possible effects of laboratory air exposure, the POSS-MA films on silicon were transferred to low vacuum (~ 500 mTorr) storage within ~ 10 min after being removed from the ALD reactor. The samples were sealed in a sample box (Entegris) of fluorine-based material, and packaged in a plastic bag. Air was then extracted using a conventional hermetic food packaging machine.¹⁶ The WCA data were collected under laboratory air conditions after the ALD-coated samples had been stored under vacuum for ~ 24 h. The samples were exposed to air in total for 15 min before, during and after WCA measurement. The water droplet was allowed to stabilize for ~ 60 s on the surface of the sample, after which three data points were collected, averaged, and the standard deviation was determined.

Scanning electron micrographs (SEM) of the ALD coatings on the POSS-MA films were acquired with a FEI Phenom microscope, which analyzes backscattered electrons and operates at a 5 kV accelerating voltage.

Composition depth profiles of selected samples were acquired using a Riber LAS-3000 x-ray photoelectron (XPS) spectrometer with a MAC2 analyzer. The Mg anode x-ray source of the instrument was operated at 12 kV, 15 mA, with a spot size of 1 mm². The takeoff angle is approximately 75° from the surface. Energy calibration was established by referencing to adventitious carbon (C 1s line at 285.0 eV binding energy). The system is equipped with an Ar⁺ gun used for surface cleaning and depth profiles. The Ar⁺ ions are accelerated to 5 keV and are able to typically remove material at a rate of ~0.2 nm/min.

III. RESULTS AND DISCUSSION

Figure 2 exhibits the WCA measured on POSS-MA films on silicon after coating with ALD Al₂O₃ at 115, 90, 60, and 40 °C with 5, 20, 40, and 60 ALD cycles (0.65, 2.6, 5.2, and 7.8 nm on silicon, respectively). The standard deviations on the WCA values are reported. All POSS-MA films coated with ALD Al₂O₃ in the 115 to 40 °C temperature range exhibit a decrease in WCA with increasing number of ALD cycles and temperature. Only the WCA for the POSS-MA film coated at 90 °C with 5 ALD cycles is slightly higher (~111°) than that of the samples coated at 115, 60, and 40 °C. The horizontal line represents the WCA for an uncoated POSS-MA film.

Figure 3 illustrates the IR absorbance spectra of ALD Al₂O₃ coated POSS-MA films on silicon measured one day after they were coated with 5, 20, 40, and 60 cycles of ALD Al₂O₃ at 90 °C. The peak at about 700 cm⁻¹ is related to the Al-O bond in amorphous Al₂O₃ layers.¹⁷ The Al-O bonds are the polar components on the surface of the ALD oxide coated POSS-MA films,^{12,13} and are responsible for the film's hydrophilic character. The hydrophilic hydroxyl (OH) groups between 4000 and 3000 cm⁻¹ appear after the POSS-MA films are coated with the ALD oxide layer. The peak in the 1200–1050 cm⁻¹ range is attributed to Si-O-Si bonds,^{18–20} which are also hydrophilic. The assignment is

FIG. 2. (Color online) Water contact angle (WCA) of ALD Al₂O₃-coated POSS-MA films on silicon measured the day after they were coated at 115, 90, 60, and 40 °C with 5, 20, 40, and 60 ALD Al₂O₃ cycles. The horizontal line represents the WCA value for an uncoated POSS-MA film.

FIG. 3. (Color online) Transmission absorbance FTIR spectra of a POSS-MA film on silicon the day after they were coated with 5, 20, 40, and 60 cycles of ALD Al₂O₃ at 90 °C. The characteristic peaks of the Al₂O₃ layer (Al-O (Ref. 17)) and the POSS-MA film (Si-O-Si (Refs. 18–20, C=O (Refs. 20–22), and CH₃-CH₂ (Refs. 18, 23)) are labeled. The hydroxyl-(OH) groups between 4000 and 3000 cm⁻¹ appear after the ALD coating process is performed.

justified because of the presence of polar Si-O-Si bonds in the POSS-MA cage.¹ The peak in the 1760–1650 cm⁻¹ range is related to the polar C=O bond. This bond is present in poly(methyl methacrylate) (PMMA) backbone,^{21,22} which is the co-polymer in POSS-MA. The peaks in the 3050–2850 cm⁻¹ range are associated with C-H stretches in CH₃ and CH₂.^{18,23} These peaks can be correlated with the nonpolar isobutyl hydrocarbon groups present in the POSS cage and PMMA backbone. These CH₃-CH₂ groups determine the natural hydrophobic state (large WCA) of these polymeric films as-deposited,^{1,24} and hide the hydrophilic Si-O-Si bonds. It is noticeable that, as the number of ALD cycles increases, the Si-O-Si and CH₃-CH₂ peaks do not change significantly, whereas an increase in the Al-O peaks intensity is clearly observed. Similar trends are found in the IR absorbance spectra of ALD Al₂O₃ coated POSS-MA films on silicon measured one day after they were coated with the same number of ALD cycles at 115, 60, and 40 °C.

Figure 4 exhibits the ratio between the integral in IR absorbance spectra of the Al-O and CH₃-CH₂ peaks of ALD Al₂O₃-coated POSS-MA films on silicon measured the day after they were coated at 115, 90, 60, and 40 °C with 5, 20,

FIG. 4. (Color online) Ratio between the Al-O and the CH₃-CH₂ peaks in FTIR absorbance spectra of ALD Al₂O₃-coated POSS-MA films on silicon measured the day after they were coated at 115, 90, 60, and 40 °C with 5, 20, 40, and 60 ALD cycles of Al₂O₃.

FIG. 5. (Color online) Transmission absorbance FTIR spectra of a POSS-MA film on silicon after they were heated at 115 °C for a time interval corresponding to 5, 20, 40, and 60 ALD cycles, i.e., 8, 31, 62, and 92 min, respectively. The four panels focus on the spectra in the whole middle IR region (a), around the Si–O–Si (b), the C=O, and the CH₃–CH₂ (d) peaks.

40, and 60 ALD Al₂O₃ cycles. The Al–O/CH₃–CH₂ ratio was obtained after background subtraction, and describes the relative trends of the hydrophilic and hydrophobic components of the ALD Al₂O₃ coated POSS-MA films. The Al–O/CH₃–CH₂ ratio slightly increases with increasing number of ALD cycles, and this ratio is especially steep for the POSS-MA film coated at 115 °C. This trend causes a decrease in the WCA, which is observed to be nearly independent of coating temperature between ~40 and 115 °C. We note that previous studies of ALD on hydrophobic polypropylene films³ show a transition from hydrophobic to hydrophilic surface wetting that occurs when the surface is coated with ALD Al₂O₃, but the extent of the transition depends on the temperature of the ALD coating step. For coatings performed at low temperatures (~60 °C), the surface becomes hydrophilic with WCA < 30°, whereas, after coating at ~90–100 °C, the WCA remains larger than 60° even after 200 ALD cycles.³

Figure 5 illustrates the transmission absorbance FTIR spectra of a POSS-MA film on silicon after they were heated at 115 °C for a time interval corresponding to 5, 20, 40, and 60 ALD cycles, i.e., 8, 31, 62, and 92 min, respectively. Panel 5(a) pictures the transmission absorbance FTIR spectra in a large wavenumber range (400–4000 cm⁻¹). Panels 5(b) and 5(c) show no significant changes in the Si–O–Si and C=O peak regions upon heating at 115 °C. Panel 5(d), focusing around the CH₃–CH₂ region, indicates that some of these vibrations slightly blue shift upon heating the POSS-MA films near T_g. Blue shifts of the hydrocarbon groups, due to polymer backbone modifications, were also found in polypropylene as a consequence of the ALD process.²⁵

Figure 6 shows the SEM micrograph of a POSS-MA films on silicon coated with an ALD Al₂O₃ layer deposited 115 °C

with 60 cycles. The sample surface looks smooth and the dark features correspond to cracks.

Figure 7 reports the results of the XPS depth profile analysis. The depth profiles were investigated in samples coated with an ALD Al₂O₃ layer at 115 °C, where the highest probability exists, among the conditions investigated, to promote the diffusion of atomic species in the POSS-MA polymer film. Panel (b) shows the survey scans. The POSS-MA films on silicon coated with an ALD Al₂O₃ layer deposited 115 °C with 60 cycles is analyzed down to a depth of approximately

FIG. 6. Scanning electron micrograph of an ALD Al₂O₃-coated POSS-MA films on silicon. The Al₂O₃ coating was deposited at 115 °C with 60 cycles.

FIG. 7. (Color online) (a) Schematics of the two samples whose compositional profile was measured by XPS. (b) XPS survey scans of the POSS-MA films on silicon coated with ALD Al_2O_3 layers deposited at 115°C with 60 cycles after sputtering for 10 min, and five cycles after sputtering for 15 min. Counts per second (CPS) are reported on the vertical axis. An offset of 3×10^4 CPS was given to the samples coated with 5 cycles of ALD Al_2O_3 to make its features more clearly distinguishable. The more significant atomic species are labeled. (c) Atomic percentage (%) vs sputter time (in minutes) for the POSS-MA films on silicon coated with ALD Al_2O_3 layers deposited at 115°C with 60 (empty symbols) and 5 cycles (full symbols). The more significant atomic species are labeled.

2 nm. The atomic species are those present in the Al_2O_3 layer. No silicon from the POSS cage is revealed. The small amount of argon present in the spectrum is due to the sputtering ions used for the depth profile. The POSS-MA films on silicon coated with an ALD Al_2O_3 layer deposited 115°C with five cycles were analyzed down to a depth of approximately 3 nm. The amount of aluminum in the spectrum is at a low level, but the silicon from the POSS cage is significant. Panel (c) reports the atomic percentages versus sputter time (or depth in the sample; 5 min sputter time corresponds to a depth of ~ 1 nm). The empty symbols, corresponding to the

POSS-MA films on silicon coated with an ALD Al_2O_3 layer deposited 115°C with 60 cycles, illustrate the typical concentration of atomic species in the Al_2O_3 layer. The amount of all species (Al $2p$, O $1s$, C $1s$), except Si $2p$, decreases with depth in the POSS-MA films on silicon coated with an ALD Al_2O_3 layer deposited 115°C with 5 cycles, i.e. about 1 nm (full symbols). The increase in the amount of Si $2p$ is due to the increased penetration of the analysis into the POSS cage. The presence of Al below the surface Al_2O_3 layer and the decrease of the Al $2p$ with depth may be ascribed to difficulty in uniformly removing a polycrystalline metal layer by the Ar^+ ions used for the analysis.

IV. DISCUSSION

Our data clearly indicate that, with increasing ALD oxide growth temperature and number of cycles, the WCA of ALD oxide coated-POSS-MA films decreases, and the samples transition to a hydrophilic state. To single out the factors that drive the POSS-MA films to overcome their natural hydrophobic state, we observe, in Fig. 3, that the amount of Al-O bonds increases with number of ALD cycles. We further observe in Fig. 3 that the amount of chemical species in the POSS-MA (Si-O-Si, C=O, and $\text{CH}_3\text{-CH}_2$) are affected neither by the number of ALD cycles nor by the growth temperature. As a consequence, the Al-O/ $\text{CH}_3\text{-CH}_2$ peak area ratio increases with increasing number of ALD cycles because of the increase in the amount of Al-O and $\text{Al}(\text{OH})_3$ bonds. Therefore we consider the Al_2O_3 layer to supply the hydrophilic component to the POSS-MA films on silicon, in agreement with other authors (e.g., Refs. 12 and 13). In addition, we further conclude that the relative amount of the hydrophilic and the hydrophobic components determines the degree of wettability of the coated POSS-MA films.

The transition to the hydrophilic state of the POSS-MA film coated with an ALD Al_2O_3 layer near the T_g (110°C) of the 45 wt. % POSS-MA films, as shown in Figs. 2 and 4, is distinct. The reasons for this behavior might reside in the changes occurring in the POSS-MA films after heating at 115°C , as illustrated in Fig. 5. The blue shift of the frequencies of the $\text{CH}_3\text{-CH}_2$ vibrations upon heating the POSS-MA films near T_g might also lead to the observed changes in WCA, and contribute to the WCA and the Al-O/ $\text{CH}_3\text{-CH}_2$ values.

As mentioned above, Hyde *et al.*³ found that planar polypropylene films coated with ALD Al_2O_3 are more hydrophilic as the ALD oxide growth temperature decreases. This result is opposite to the trend shown in Fig. 2. Using FTIR and *in situ* quartz crystal microgravimetry, respectively, Lee *et al.*²⁶ and Spagnola *et al.*²⁵ demonstrated that, on polypropylene, growth rate and mass uptake of ALD Al_2O_3 from TMA and DI water increase with increasing growth temperature from 40 to 100°C with fixed number of cycles.^{25,26} Therefore, the decrease in WCA with increasing growth temperature found by Hyde *et al.*³ cannot be linked only to the amount of Al-O. Indeed, Spagnola *et al.*²⁵ also demonstrated enhanced diffusion of precursor into polypropylene with increasing growth temperature. The lack of Al-O bonds on

the polypropylene surface at higher temperatures might therefore lead to the large WCA values of polypropylene films coated with ALD Al_2O_3 above 60 °C. On the contrary, the low WCA values of ALD Al_2O_3 coated POSS-MA films suggest that the Al_2O_3 film resides mostly on the surface of the POSS-MA film, and that little or no precursor diffusion occurs in the film with increasing temperature. The presence of cracks on the surface of ALD Al_2O_3 coated POSS-MA films in scanning electron micrographs (SEM) in Fig. 6 supports this conclusion.²⁵ The XPS depth profiles in Fig. 7(c) indicate that the Al_2O_3 forms primarily on the top surface of the POSS-MA film. Indeed, the revealed atomic % of Al 2p in the profile of the spectrum of the POSS-MA films on silicon coated with an ALD Al_2O_3 layer deposited 115 °C with 5 cycles after sputtering is probably due to nonuniform sputtering of the Al_2O_3 layer.

V. CONCLUSIONS

We have examined nano-composite POSS copolymer films on silicon coated with Al_2O_3 layers obtained using atomic layer deposition in a range of number of ALD cycles, and growth temperatures up to the glass transition temperature of the polymeric film. The Al_2O_3 layers grow on the surface of the POSS copolymer films. Varying the deposition conditions of the thin oxide layers, up to 8 nm thick, enables changing the wettability, and, thus, the water contact angle of the planar nano-composite POSS copolymer films. The Al–O/CH₃–CH₂ ratio, measured by integrating the peaks in infrared absorbance spectra, allows a good qualitative prediction of the water contact angle behavior. The comparison of the trends in the Al–O/CH₃–CH₂ ratios with those of water contact angle suggests that the balance between the surface hydrophilic and hydrophobic groups plays a crucial role in determining the wettability of the coated nano-composite POSS copolymer films. These results could be exploited for using nano-composite POSS films in microfluidics. We also believe that the correlation between water contact angle and infrared absorbance peaks could be successfully applied to examine the trends in wettability in other polymeric film systems processed via atomic layer deposition.

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