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Area Selective Molecular Layer Deposition of Polyurea Films

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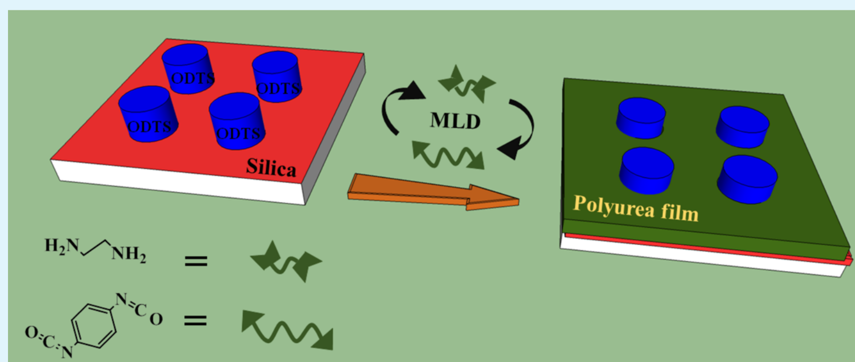
Supporting Information



ABSTRACT: Patterned organic thin films with submicrometer features are of great importance in applications such as nanoelectronics and optoelectronics. We present here a new approach for creating patterned organic films using area selective molecular layer deposition (MLD). MLD is a technique that allows for conformal deposition of nanoscale organic thin films with exceptional control over vertical thickness and composition. By expanding the technique to allow for area selective MLD, lateral patterning of the film can be achieved. In this work, polyurea thin films were deposited by alternating pulses of 1,4-phenylenediisocyanate (PDIC) and ethylenediamine (ED) in a layer-by-layer fashion with a linear growth rate of 5.3 Å/cycle. Studies were carried out to determine whether self-assembled monolayer (SAM) formed from octadecyltrichlorosilane (ODTS) could block MLD on silicon substrates. Results show that the MLD process is impeded by the SAM. To test lateral patterning in MLD, SAMs were patterned onto silicon substrates using two different approaches. In one approach, SiO_2-coated Si(100) substrates were patterned with an ODTS SAM by soft lithography in a well-controlled environment. In the second approach, patterned ODTS SAM was formed on H−Si/SiO_2 patterned wafers by employing the chemically selective adsorption of ODTS on SiO_2 over H−Si. Auger electron spectroscopy results revealed that the polyurea film is deposited predominantly on the ODTS-free regions of both patterned substrates, indicating sufficient blocking of MLD by the ODTS SAM layer to replicate the pattern. The method we describe here offers a novel approach for fabricating high quality, three-dimensional organic structures.

KEYWORDS: *molecular layer deposition (MLD), organic thin film, polyurea, self-assembled monolayer, microcontact printing, patterned organic structures*

■ INTRODUCTION

Molecular layer deposition (MLD) has increasingly garnered attention as a powerful technique for fabricating high quality organic films.[1,2] Similar to atomic layer deposition (ALD), the self-saturating reactions between organic precursors and the substrate surface in MLD enable nanometer-scale control over the coating thickness. The deposited layer's thickness is precisely controllable based on the number of MLD cycles. Conformal coating on high surface area substrates[3] and compositional control[4] of organic films by MLD have been previously shown. Nonetheless, MLD can provide for thickness control only in the vertical direction. Area selective MLD (AS-MLD) would offer the addition of lateral control of the organic film, creating patterns of micro- or nanoscale 3D organic structures.

Because of the similar process between MLD and ALD, the strategies used for area selective ALD (AS-ALD) could potentially be applied for AS-MLD. In AS-ALD, specific areas of the surface are chemically modified with chemical agents. Self-assembled monolayers (SAMs) have been commonly used to achieve the surface modification. SAMs are molecular assemblies spontaneously formed by the chemical adsorption of the active precursor molecules onto a substrate surface.[5] Specifically on the SiO_2 surface, organosilane precursors are typically chosen to form SAMs due primarily to the strong covalent linkage between the headgroup of these precursors and surface silanol (-Si−OH) groups. For area selective deposition, SAMs typically act as a resist layer, preventing nucleation and growth at the surface. SAMs have been shown in the literature to effectively block the growth of several

Received: October 2, 2013
Accepted: November 14, 2013
Published: November 14, 2013

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inorganic films.[6−12] However, there are, to the best of our knowledge, no reports on the use of SAMs to prevent deposition of organic films deposited by MLD.

In this study, we demonstrate the use of octadecyltrichlorosilane (ODTS) SAMs as a resist layer for area selective polyurea MLD. Polyurea was chosen because of its high thermal stability[3,4] and its potential application in lithography.[13,14] Polyurea films are made from the coupling reaction between 1,4-phenylene diisocyanate (PDIC) and ethylenediamine (ED) dosed from the vapor phase. Results from ellipsometry, water contact angle measurement, Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) all confirm the ability of ODTS SAMs to block polyurea MLD. Patterns of ODTS SAMs were created both by micro contact printing and by use of H−Si/SiO_2 patterned wafers. After polyurea MLD, 3D micro structures were observed. These results offer a new approach for making 3D organic structures with high spatial resolution.

■ EXPERIMENTAL SECTION

All reagents, unless otherwise noted, were purchased from Sigma-Aldrich and used without further purification.

Si (100) substrates, with a layer of native oxide around 36 Å thick, were cleaned with piranha solution (7:3 ratio of concentrated sulfuric acid and 30% hydrogen peroxide) for 15 min, rinsed with deionized water and then blown dried with compressed air. If they were not immediately used after the cleaning process, samples were typically stored in deionized water. SAM formation on blanket substrates was performed inside a dry, air-purged glovebox by dipping cleaned wafers into a 10 mM solution of octadecyltrichlorosilane (ODTS) in dry toluene over a period of more than 24 h, unless otherwise specified. Once SAM formation was completed, samples were then rinsed with copious amount of toluene, acetone, and chloroform, respectively, to remove unreacted molecules of ODTS from the SiO_2 surface. If samples were not immediately used for MLD deposition, they were kept in a container inside a dry air-purged glovebox. We found that the water contact angle of samples stored in this container for a period of weeks was similar to that of the freshly prepared samples, indicating a high stability of ODTS SAMs on SiO_2 substrates.

Patterned ODTS SAM substrates were prepared by two distinct methods: one via soft lithography and the other through patterned H−Si/SiO_2 substrates. The preparation of patterns via microcontact printing followed the standard procedures that were formerly described.[15] Briefly, a Si master that has features of micrometer-scale squares was used for the PDMS stamp preparation. Prior to inking, the PDMS stamp was exposed to UV-ozone for 5 min to fully generate an −OH rich surface. Subsequently, the hydrophilic PDMS was inked with ODTS solution for 1 min and then stamped onto cleaned SiO_2 for 15 min. Light external pressure was applied during the stamping process to ensure a complete grafting of ODTS on the SiO_2 surface.

H-terminated Si (H−Si)/SiO_2 patterned substrates were generously donated from the Pruitt lab at Stanford University. This pattern was fabricated by typical thermal oxide growth and conventional photolithography. The thickness of thermally grown SiO_2 in this pattern is approximately 1 μm. Prior to SAM formation, the patterned substrate was quickly dipped into a 1% HF solution for 15 s to remove the native oxide and create H-termination on the Si surface regions. We note that this quick etching process does not fully remove the thick thermal oxide layer on the pattern, leaving those regions as SiO_2. ODTS SAM formation on these patterned substrates was performed in a similar fashion to blanket Si substrates.

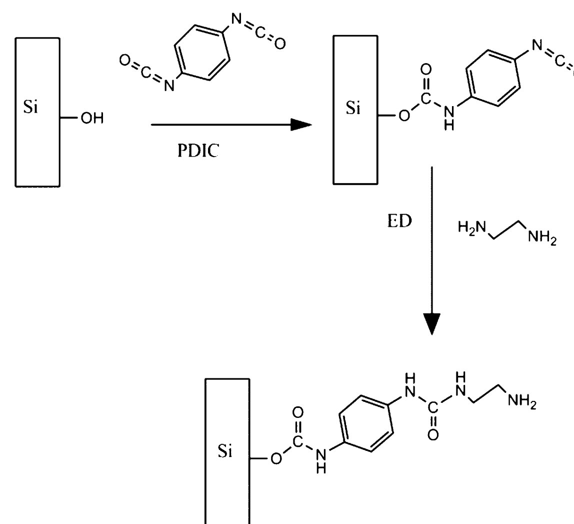
After SAM formation, substrates were loaded into a custom-made hot wall flow reactor which is connected to a rotary vane pump with a base pressure below 10 mTorr for MLD deposition. MLD precursors and nitrogen purge gas were introduced to the chamber via manual valves. A container of PDIC, which is solid at room temperature, was submerged in a temperature-controlled silicone oil bath at 50 °C. To enhance the pressure of PDIC inside the reactor when dosing, the reactor was isolated from the pump while backfilled with PDIC vapor. A bubbler of ED, which is a volatile liquid precursor, was kept at room temperature. During the ED pulse, the valve between reactor and ED was closed once the pressure of ED reached 1 Torr. All MLD films were deposited at room temperature. One MLD cycle consists of a 4 min pulse of PDIC, followed by a 2 min nitrogen purge, then a 2 min dose of ED, and subsequently purged by 4 min pulse of nitrogen. MLD cycles were repeated until the desired thickness was reached. Samples were removed from the chamber for ex situ characterization and analysis.

Water contact angle measurements were used to analyze the hydrophobicity of the surface. One microliter of deionized water (Millipore) was brought into contact with the samples to analyze the wettability of the films on the surfaces. FTIR spectroscopy (Thermo Nicolet 6700 FTIR spectrometer) was employed to analyze the chemical bonding of the films on the substrates. Spectra were taken with 200 scans at 4 cm^{-1} resolution with a piranha-cleaned Si wafer as a background. A Gaertner Scientific Corp. L116C He−Ne laser ellipsometer with 632.8 nm light was used for ellipsometry measurements. Thickness was measured in at least 3 different spots on each sample to ensure the uniformity of the film. XPS was performed on a PHI 5000 Versaprobe spectrometer, using Al Kα radiation (1486.6 eV) as the excitation source. Survey scans were collected to measure the elemental composition of each sample using an energy step of 1 eV. Atomic force microscopy (AFM) was carried out on a Park System XE-70 in a noncontact mode with a scan size of 100 × 100 μm. Auger electron spectroscopy (AES) mapping on patterned substrates was performed on a PHI 700 Scanning Auger Nanoprobe.

■ RESULTS AND DISCUSSIONS

Scheme 1 represents the proposed mechanism for the polyurea MLD film growth on a SiO_2 surface. A procedure to deposit polyurea MLD films has been formerly described.[4] Here, we slightly modified the method by depositing PDIC on the SiO_2 surface without pretreating the surface with 3-aminopropyltriethoxysilane (APTES). Based on ellipsometry, we found that the growth rate of the polyurea MLD film was not significantly altered by the absence of APTES pretreatment. As shown in Figure 1, a linear relationship between the film thickness and the number of MLD cycle was observed. The measured growth rate is 5.3 Å/cycle, slightly higher than previously reported

Scheme 1. Chemical Reaction of Polyurea Film Growth on a SiO_2 Surface



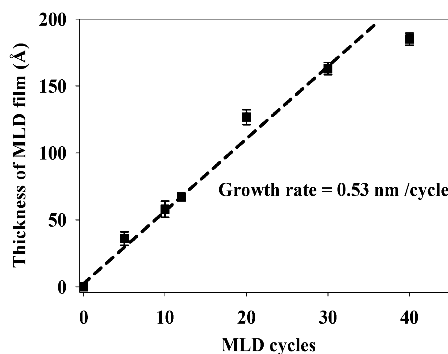


Figure 1. Plot of the thickness of polyurea MLD film as a function of number of MLD cycles.

value.[4] Nonetheless, the apparent growth of polyurea directly on the SiO_2 surface confirms the hypothesis that a nucleation step of this polyurea MLD procedure involves a coupling reaction between −OH groups on the SiO_2 surface and the isocyanate functional groups on PDIC molecules. This was further verified by experiments showing that when cleaned SiO_2 substrates were exposed to a half cycle of PDIC vapor only, the substrates became more hydrophobic and exhibited N signal in XPS, indicating PDIC attachment on the SiO_2 surface.

The atomic composition of a 20 cycle polyurea MLD film (ca. 11 nm thick) was analyzed by XPS, as shown in Figure 2.

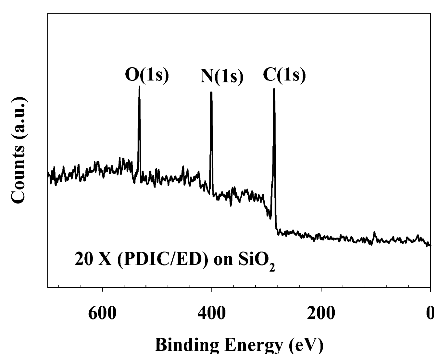


Figure 2. X-ray photoelectron spectroscopy survey scan of 20 cycles of PDIC/ED MLD film.

The ratio between C:N:O is equal to 5.5:2.0:1.2, close to the theoretical value of 5:2:1. The small differences between the experimental result and expected values may arise from adventitious carbon that contaminated the sample from ex situ analysis, and a small signal from the underlying SiO_2 substrate.

The chemical bonding in the MLD film was measured by FTIR spectroscopy. Figure 3 illustrates an FTIR spectrum of a 30 cycle polyurea MLD film (ca. 16 nm thick) on a SiO_2 surface. The most significant peaks that confirm the urea coupling reaction on this film are ν(C=O) at 1651 cm^{-1}, and δ(N−H) at 1510 cm^{-1}, ascribable to characteristic amide I and amide II modes of urea.[16−18] The surface morphology of the polyurea MLD films was additionally analyzed by AFM. We found that a film thickness of about 5 nm (9 cycles) has an RMS roughness of 0.3 nm, conveying a rather smooth MLD film covered on top of the SiO_2 surface.

We first evaluated the ability of an ODTS SAM to block polyurea MLD on blanket SiO_2 substrates. The procedures for achieving high quality ODTS SAMs on SiO_2 were previously

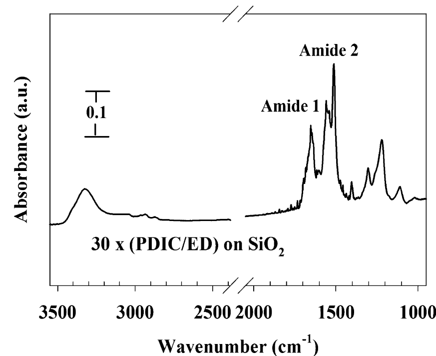


Figure 3. FTIR spectrum of film as deposited by 30 cycles of PDIC/ED MLD.

described.[15,19] Following the formation of the ODTS SAM, ellipsometry, water contact angle goniometry and FTIR spectroscopy were utilized to probe its quality. We found that the thickness of ODTS on SiO_2 increased with SAM formation time until reaching a plateau at 26 Å, in good agreement with previous reports in the literature.[5,12,20] The water contact angle followed a similar trend to that observed in ellipsometry, approaching a value of 110° at developing times longer than 6 h (see Supporting Information). Although the results from both of these measurements suggest that a well-packed SAM is formed at times less than 6 h, FTIR measurement (see below) reveals that a longer dipping time is needed for a good quality SAM.

Synder et al.[21] reported that the peak position of $\nu_{as}(CH_2)$ in crystalline hydrocarbons appears at 2917 cm^{-1} but for a liquid-like hydrocarbon, the position shifts to higher wavenumbers, appearing at 2928 cm^{-1}. Figure 4 illustrates the antisymmetric

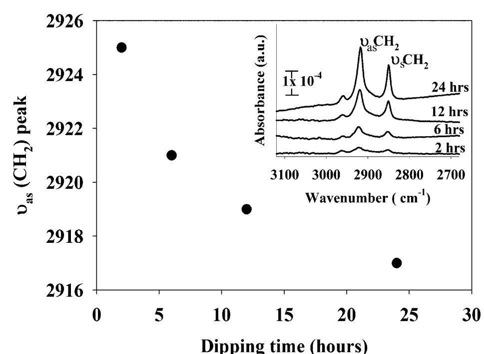


Figure 4. CH_2 asymmetric stretching peak position as a function of dipping time of ODTS SAM. (Inset) Typical FTIR spectra of ODTS on SiO_2 surface at various dipping times.

C−H stretching peak position of ODTS SAM on SiO_2 as a function of SAM dipping time. The inset shows an escalation of peak intensity as the dipping time increases. It is evident from Figure 4 that the peak position shifts toward lower wavenumbers as the dipping time increases and reaches a value of 2917 cm^{-1} once the dipping time is longer than 24 h. This implies that the packing structure of the SAM was crystalline-like, or densely packed, at this SAM formation time.

After formation of densely packed ODTS SAMs (prepared with a dipping time of 48 h), substrates were subsequently processed with polyurea MLD to test the ability of the SAM to prevent deposition. Figure 5a shows a comparison of MLD thickness, as measured by ellipsometry, on clean SiO_2 and on

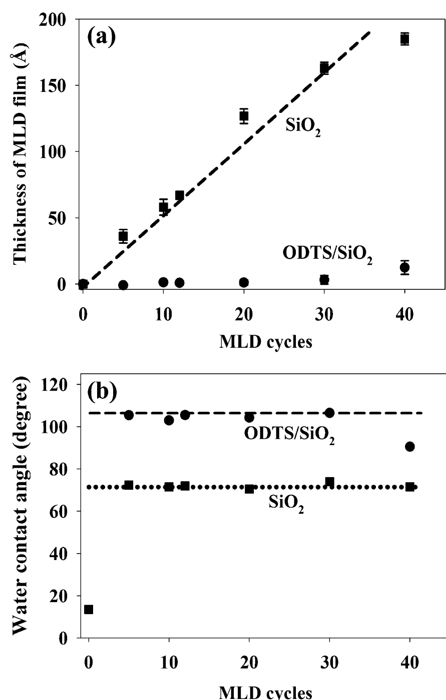


Figure 5. (a) Plot of thickness of polyurea MLD films as a function of MLD cycles on SiO_2 (square) and ODTS SAM-coated SiO_2 (circle); (b) plot of water contact angle of the organic film as a function of MLD cycles on SiO_2 (square) and ODTS SAM-coated SiO_2 (circle). Note the dashed line and dotted line indicate the expected water contact angle of an ODTS film and a polyurea MLD film, respectively.[5,12,20]

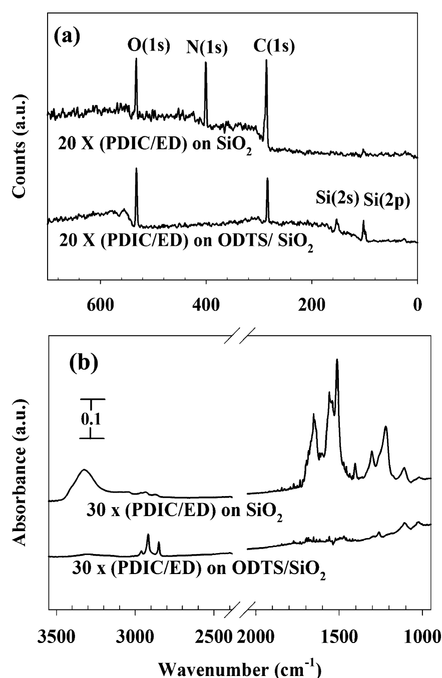


Figure 6. Comparison of (a) XPS spectra and (b) FTIR spectra of polyurea MLD on SiO_2 and ODTS-coated SiO_2.

ODTS SAM-coated SiO_2. We note that the thickness of the ODTS SAM previously grown on the SiO_2 surfaces (around 26 Å) has been subtracted from the film thicknesses of the ODTS-coated SiO_2 substrates, so that the thicknesses reported in Figure 5a represent just that of the MLD film. A negligible increase in film thickness on the ODTS-coated SiO_2 samples was observed up until 30 cycles of MLD, suggesting adequate blocking of polyurea MLD by the SAM. The water contact angle further provides evidence of MLD blocking by the ODTS SAM. Figure 5b shows that the water contact angle of the organic film on ODTS-coated SiO_2 after MLD deposition remains close to the expected value of an ODTS SAM on SiO_2 (ca. 110°), whereas the water contact angle for a polyurea MLD film is about 72°. We note that at 40 MLD cycles, an increase in film thickness becomes apparent. The increased film thickness was measured at 11 Å, roughly 6% of the thickness of the film without ODTS blocking. At this number of MLD cycles, the substrate also becomes less hydrophobic, as evidenced by the lower water contact angle. This result may suggest an upper limit to the ability of an ODTS SAM to block polyurea MLD.

The ability of the ODTS SAM to block deposition was further tested by XPS and FTIR spectroscopy. Figure 6a shows a comparison of XPS spectra taken after 20 cycles of MLD on SiO_2 and on an ODTS-coated SiO_2 substrate. As evidenced by the absence of a N peak on the ODTS-coated SiO_2 sample, we conclude that polyurea MLD was effectively blocked by the ODTS SAM. Further fine scan XPS measurements on this substrate revealed no N signal (see Supporting Information), confirming the MLD blocking ability by the ODTS SAM. In addition, the characteristic IR peaks of polyurea were not observed on ODTS-coated SiO_2 after MLD, as seen in Figure 6b. This provides another indication that the growth of polyurea is hampered by the ODTS SAM. We propose that the ODTS SAM prevents MLD through the following mechanism: first, the silane head groups of the SAM react with and eliminate many of the free surface OH groups at the SiO_2 surface; second, by forming a densely packed film on the SiO_2 surface, the ODTS SAM prevents PDIC from reaching the surface of SiO_2 and reacting with any remaining active sites (−OH groups). As a result, polyurea films were not observed on the ODTS-coated SiO_2 substrates.

Once the ability to block polyurea MLD by ODTS SAM was confirmed on the blanket substrates, patterned ODTS SAM were created on SiO_2 substrates to test the AS-MLD process. Microcontact printing was initially used to create such patterns by inking PDMS stamps with ODTS solution, which was later transferred to the SiO_2 substrates. Samples were then brought into a MLD reactor and subsequently deposited with 12 cycles of MLD (ca. 60 Å). Figure 7 panels a and c show SEM images of the patterned organic film after MLD deposition. These patterns were created from a PDMS stamp based on two different masters: one with square features of 500 μm on a side and the others with square features of 2−4 μm on a side. The PDMS stamp used in Figure 7a contained a grid pattern, whereas the stamp used in Figure 7c had the opposite pattern, that is, contained protruding squares. It is apparent that the patterns were effectively transferred from the stamp to the surface of SiO_2. The brighter areas in the SEM images correspond to the regions covered with ODTS.

Nitrogen Auger electron mapping, which was acquired by plotting N intensity as a function of beam position on the patterns, provides strong proof of the AS-MLD result. The maps show the relative elemental distributions (peak intensity) as a pixel intensity. In other words, the greater the Auger peak intensity, the brighter the pixel value. The bright regions in Figure 7 panels b and d represent the presence of N (or polyurea), while the dark areas indicate an absence of N. The

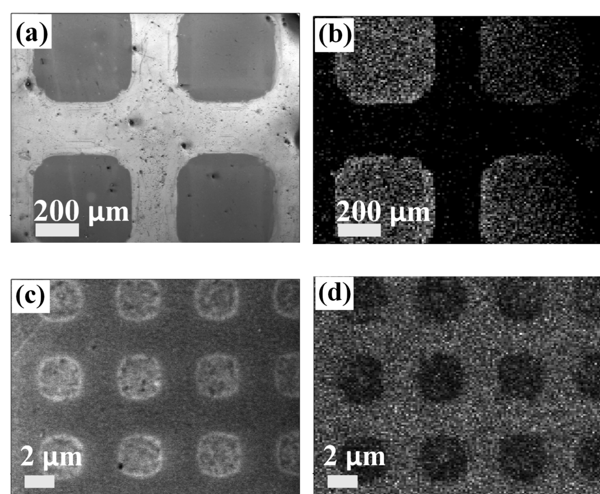


Figure 7. SEM and scanning Auger analysis of patterned SiO_2 substrates after 12 cycles of polyurea MLD. Panels (a) and (c) show the SEM images of patterned ODTS on SiO_2 after MLD; the brighter areas are where ODTS was stamped. Panels (b) and (d) show N Auger electron maps of micro patterned grid structures of panels (a) and (c) after MLD. Note that the scale bar in panels (a) and (b) is 200 μm; in panels (c) and (d) it is 2 μm.

images reveal that polyurea MLD is predominantly deposited on the ODTS-free regions, demonstrating, to some degree, selective MLD deposition at the patterned SiO_2 surface. Although we have demonstrated that pattern transfer of the polyurea MLD film can be achieved by microcontact printing, we note that the selectivity is only modest. Small defects are noticeable within the patterns. In addition, when an AES survey scan was performed in the area where ODTS was stamped, a small N peak was observed (data not shown). The low selectivity obtained from micro contact printing can be partially explained by the relatively short SAM formation time (~15 min) instead of the 48 h SAM formation as we used for the blanket SiO_2.

In an effort to improve the selectivity of polyurea MLD, we explored a second approach to create ODTS SAM-patterned substrates. Previous reports on AS-ALD of HfO_2 achieved by selective surface modification of a patterned H−Si/SiO_2 substrate demonstrated higher deposition selectivity over microcontact printing.[22] The surface modification on this pattern relies on the intrinsic chemical selectivity of adsorption of ODTS on SiO_2 over H−Si. As a result, only the SiO_2 region is covered by ODTS and the H−Si surface is left intact. After HfO_2 ALD, the deposition occurred solely on the H−Si regions. To test the suitability of this process for MLD, we initially carried out a study to determine the growth properties of polyurea MLD on the H−Si surface (see Supporting Information). Interestingly, the growth rate of MLD, as measured by ellipsometry, on an H−Si surface is similar to what we observe on a SiO_2 surface, suggesting that MLD naturally deposits on both H−Si and SiO_2 equally well. We note that the nucleation process of polyurea MLD on the H−Si surface is not yet fully understood, and further experiments will be conducted to address this issue.

The preparation of the ODTS SAM on this patterned substrate was similar to that of the blanket SiO_2 surface. After formation of the SAM on the patterned substrates, the samples were then transferred to the MLD reactor where 12 cycles of MLD (ca. 60 Å) of polyurea were deposited for AS-MLD testing. Figure 8a shows an SEM image of the test structure. The brighter areas [area 2] represent the thick thermal oxide

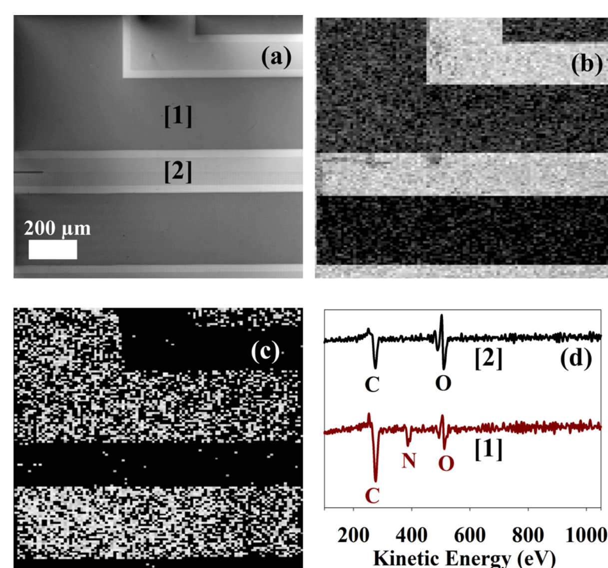


Figure 8. AES analysis on a patterned SiO_2/Si structure after the area-selective polyurea MLD process by selective surface attachment: (a) SEM; (b) C Auger electron elemental mapping after SAM deposition; (c) N Auger electron elemental mapping after polyurea MLD; (d) survey Auger scan for areas 1 and 2 on test structure.

covered with ODTS, while the darker regions [area 1] represent H−Si. Figure 8b shows C Auger electron mapping of the test structure after ODTS SAM formation prior to MLD. Clearly, the C signal was predominantly observed on the SiO_2 areas, indicating that the ODTS SAM was selectively adsorbed on the SiO_2 surface. The fainter signal of C in the Si−H regions likely arises from adventitious carbon picked up during the ex situ analysis. Figure 8c shows N Auger electron mapping of the same structure after deposition of polyurea MLD. It is evident that polyurea selectively deposited on the H−Si regions and not on ODTS-coated SiO_2. In Figure 8d, an AES survey scan on the OTDS-coated SiO_2 region [area 2] also reveals no significant N in this region, whereas a N signal was noticeably observed in the H−Si region [area 1]. We note that the very small nitrogen signal observed on the ODTS-coated SiO_2 is likely due to defects in the ODTS SAM that allow trace MLD to occur. Current investigations are being carried out to improve the selectivity of MLD by exploring other types of SAMs, substrates, and routes for selective SAM removal without damaging the MLD film.

The results we describe here indicate that AS-MLD provides an excellent approach for achieving high spatial resolution of 3D polyurea structures. By combining AS-MLD with finer masks, the potential of scaling down these 3D organic structures to the nanometer-scale is likely possible. We foresee that this novel method of fabricating high resolution 3D organic structures could be potentially useful for several applications requiring precise spatial control over organic materials.

CONCLUSIONS

In this work, we carried out a study to demonstrate AS-MLD of polyurea thin films. We chose the ODTS SAM as a resist layer to prevent polyurea growth. The conditions and methods to achieve and characterize a well-packed ODTS SAM, capable of

sufficiently blocking MLD growth, were presented. Patterns of ODTS on SiO_2 were created by soft lithography and on H−Si/SiO_2 patterned structures. After polyurea MLD on both types of patterns, we found that polyurea MLD selectively deposited on the ODTS-free regions, creating well-defined 3D polyurea microstructures. The method we presented here offers a new route to create excellent spatial resolution of 3D organic structures.

■ ASSOCIATED CONTENT

Supporting Information

Plots of thickness of ODTS and water contact angle as a function of dipping time; XPS spectrum of polyurea grown on ODTS-coated SiO_2 and the high resolution scan of nitrogen; a plot of thickness of MLD as a function of cycles on surfaces of SiO_2, H−Si, and Si_xN_y. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge financial support from Intel Corporation for this work. We thank Dr. Rami Hourani and Dr. James M. Blackwell for their scientific suggestions and helpful discussions.

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