

Improving Area-Selective Molecular Layer Deposition by Selective SAM Removal

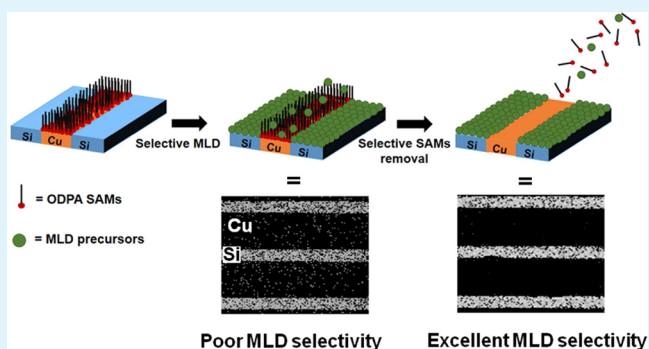
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S Supporting Information

ABSTRACT: Area selective molecular layer deposition (MLD) is a promising technique for achieving micro- or nanoscale patterned organic structures. However, this technique still faces challenges in attaining high selectivity, especially at large MLD cycle numbers. Here, we illustrate a new strategy for achieving high quality patterns in selective film deposition on patterned Cu/Si substrates. We employed the intrinsically selective adsorption of an octadecylphosphonic acid self-assembled monolayer (SAM) on Cu over Si surfaces to selectively create a resist layer only on Cu. MLD was then performed on the patterns to deposit organic films predominantly on the Si surface, with only small amounts growing on the Cu regions. A negative potential bias was subsequently applied to the pattern to selectively desorb the layer of SAMs electrochemically from the Cu surface while preserving the MLD films on Si. Selectivity could be enhanced up to 30-fold after this treatment.

KEYWORDS: molecular layer deposition (MLD), organic thin film, self-assembled monolayer, reductive SAM desorption, patterned organic structures, selective deposition



INTRODUCTION

Recently, there has been increasing interest in employing organic thin films for different applications in micro- and nanoelectronics, such as sensors,^{1,2} electronic paper,³ and light-emitting transistors.⁴ Several strategies have been utilized to accurately deposit high-quality organic films or structures on the substrates of interest.^{5–9} Among them, molecular layer deposition (MLD) has emerged as an outstanding tool to achieve high-quality organic thin films, especially on the small, intricate features found in microelectronics.^{10–16} The self-saturating reactions between organic precursors and the substrate surface in MLD allow for nanometer-scale control over the film thickness. In addition, when coupled with area-selective MLD (AS-MLD), three-dimensional micro- or nanoscale organic structures can be formed by precise deposition of material only in the areas needed.¹⁷

Area selective deposition is typically performed by forming a thin layer of densely packed SAMs to mask specific areas of the substrate.^{18,19} These SAMs behave as resist layers, ideally preventing deposition on the surface. The ability of each SAM to block the deposition varies greatly, depending on both the properties of the SAM (e.g., tail chain length, molecular packing density) and the precursors involved in the film deposition.^{18,20,21} Recently, we reported the use of octadecylphosphonic acid (ODPA) self-assembled monolayers as a resist layer to block both atomic layer deposition (ALD) and MLD on the

surface of Cu.²² This type of SAM binds strongly to the oxide layer of several metals (e.g., Ti,^{23,24} Al,^{25,26} and Cu²⁷) through metal–O–P bonds but does not bind well to SiO₂, possibly due to a much higher energetic barrier for adsorption on SiO₂.²⁸ As a result, when a Cu/Si pattern (in which both the Cu and Si are covered with native oxides) is exposed to an ODPA solution, ODPA SAMs will selectively form on the Cu surface. Subsequently, with this approach, we can selectively deposit both inorganic films from ALD and polymer films from MLD on a Si surface while leaving the surface of Cu intact.

An example of AS-MLD using a phosphonic acid SAM is shown in Figure 1. The figure displays both a scanning electron microscope (SEM) image and N Auger electron map of an ODPA-modified Cu/Si patterned substrate after 12 cycles of polyurea MLD (ca. 60 Å). The images clearly reveal that polyurea predominantly deposits by MLD on the Si (ODPA-free) regions. However, some N signal is still observed on the Cu surface—indicating only moderate selective deposition on this patterned substrate by MLD. In fact, although using SAMs to prevent ALD can be a challenge at high cycle numbers, recent studies suggest that selective deposition is even more difficult for MLD.²² We believe that the blocking ability in AS-

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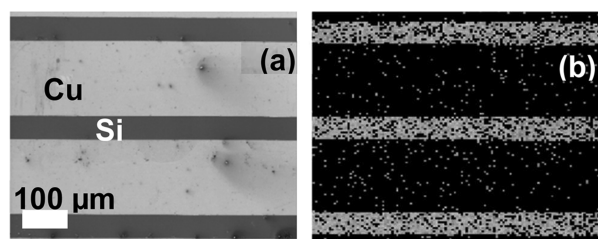


Figure 1. (a) SEM image and (b) N Auger mapping analysis of patterned Cu/Si substrate after 12 cycles of polyurea MLD. The map shows the relative elemental distribution as pixel intensity: the greater the Auger peak intensity, the brighter the pixel value. The bright regions in panel b represents the presence of N (from polyurea) while the dark areas indicate the absence of N.

MLD is typically limited by deposition occurring on or within the SAMs, and more studies are being carried out to better understand this issue.

By recognizing that the loss of selectivity originates from the onset of MLD onto the SAMs at the Cu surface, one may expect the selectivity to be significantly enhanced if the SAM layer and the associated ALD or MLD film are selectively removed from the Cu without altering the properties of the deposited film on the Si surface, as illustrated schematically in Figure 2.

Several routes to remove SAMs from the surface of metals have been reported,^{29–32} but one approach that seems particularly promising is the removal of SAMs by reductive SAMs desorption.^{33–36} The mechanism of this relatively mild electrochemical process (i.e., milder compared to chemical reduction by a strong reducing agent) involves a single-electron reduction of the adsorbed SAMs on the electrode surface to form soluble species in the electrolyte. It has been shown that the reductive SAM desorption potential depends on the type of the electrode, the SAM headgroup, and the SAM chain length. Generally, longer SAMs require a more negative potential for desorption.^{33,34,37}

In this report, we employ the selective removal strategy of ODPA SAMs on the Cu surface by reductive SAM desorption and explore whether this approach can improve selectivity in AS-MLD. We have chosen polyurea MLD as a representative system due to the potential application of these films in lithography^{10,11,13,15} and our recent success in AS-MLD with this same chemical system at low cycle numbers.^{17,22} We find a dramatic improvement in the selectivity between the Cu and Si surfaces after applying a reductive potential, without destroying the integrity of the deposited film on the dielectric surface of Si.

We note that while our focus here is aimed toward improving the selectivity of polyurea MLD, we believe that this approach can be extended to other layer-by-layer deposition processes on different metal/dielectric patterns.

EXPERIMENTAL METHODS

Unless otherwise specified, all reagents were purchased from Sigma-Aldrich and used as received without further purification.

Cu films, obtained from collaborators, were deposited by sputtering onto silicon wafers using an argon-based plasma and had a thickness of a few hundred nanometers. High temperature postsputter annealing of Cu substrates was carried out to enable recrystallization and improve film quality. The surface roughness of the Cu substrates measured with atomic force microscopy was less than 1 nm (root-mean-square (rms): 0.8 nm). 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 dry with compressed air. If they were not immediately used after the cleaning process, samples were stored in deionized water until use. [Caution: Piranha solution is potentially explosive and extremely energetic. Direct exposure to the solution can cause a severe burn. Specific safety training is required prior to handling this solution.]

Prior to SAM formation, Cu and Si substrates were sonicated in ethanol and acetone for 10 min to remove organic contamination, dried with nitrogen, and then subjected to 15 min of UV/ozone for the final cleaning. After cleaning, samples were immediately immersed into 1 mM t-butanolic solution of ODPA for 48 h, unless otherwise specified. The SAM solution was slightly heated to a temperature of 30 °C on a hot plate during SAM growth to prevent the solidification of t-butanol. For control studies, SAMs of dodecylphosphonic acid (DPA) and butylphosphonic acid (BPA) were formed by a similar procedure. All the SAMs used in this experiment were tested with electrochemical impedance spectroscopy (EIS) to ensure that they were well-packed on the Cu surface.²² After SAM formation was completed, samples were rinsed thoroughly with pure methanol and dried with compressed air. If not immediately transferred to the reactor for MLD or ALD deposition, samples were kept in a sealed container and stored inside a dry air-purged glovebox. The water contact angle of these SAMs after weeks of dry storage was similar to that of freshly prepared SAMs, suggesting rather stable ODPA SAMs on the surface of Cu. Patterned Cu on Si substrates, received from the collaborator, were prepared via conventional lithography. The thickness of Cu lines on this pattern was around 20 μm. The cleaning procedures and SAM formation on the patterned substrates were similar to those on Cu blanket materials.

After SAM formation was complete, substrates were transferred into the reactor for MLD processes. The detailed procedures for growing polyurea MLD films were previously described.^{14,15,17} For ZnO ALD study, films were deposited in a Gemstar 6 reactor (Arradance Inc.) by using a published procedure.²² After film deposition, samples were removed from the reactors for ex situ characterization and analysis.

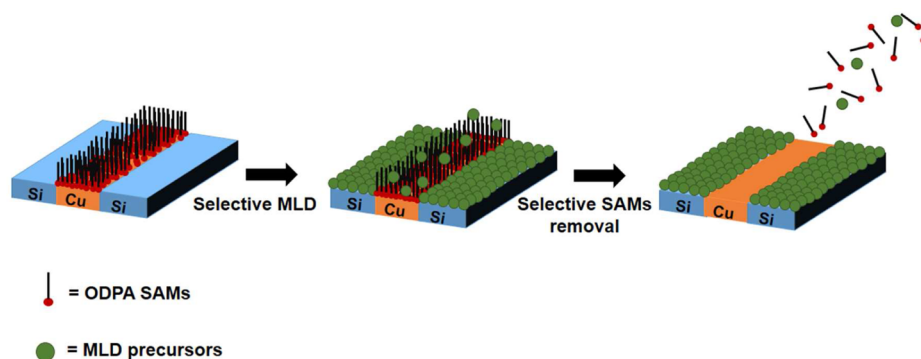


Figure 2. Proposed strategy to improve selectivity for AS-MLD on Cu/Si patterns by incorporating selective SAM removal after MLD.

Static water contact angle (WCA) measurements were made with an FTA 200 instrument. Deionized water (1 μL ; Millipore) was brought into contact with the samples to analyze the wettability of the films on the surfaces. All electrochemical measurements were made on a SP200 potentiostat equipped with a 1 MHz frequency analyzer. A three-electrode setup was used by employing Cu that has ODPA adsorbed on it as a working electrode, platinum wire as a counter electrode, and Ag/AgCl in saturated KCl(aq) as a reference. All electrochemistry experiments were performed with a solution containing 0.1 M of LiClO_4 in dry methanol. A potential range of +100 mV to -1000 mV vs the Ag/AgCl reference electrode was used to conduct cyclic voltammogram experiments. The potential was initially scanned in the negative direction with a scan rate of 10 mV/s. EIS measurements were performed without applying a bias to the working electrode.

Film thickness was measured on an Alpha-SE ellipsometer by J. A. Woollam Co. with a spectral range from 380 nm to 900 nm at three different angles of incidence (65° , 70° and 75°) and with the polarizer set to 45° . Thicknesses were measured on the silicon wafers at least 3 spots to test the uniformity of the film. Fourier-transform infrared (FTIR) spectroscopy (Thermo Nicolet 6700 FTIR spectrometer) was employed to analyze the chemical bonding of the film at the substrate. Spectra were taken with 200 scans at 4 cm^{-1} resolution with a piranha-cleaned Si wafer as a background. Elemental composition of the film was determined through X-ray photoelectron spectroscopy (XPS) on a PHI VersaProbe Scanning XPS Microprobe with Al $K\alpha$ radiation of 1486 eV. The X-ray beam diameter was 200 μm with 42 W power. Atomic force microscopy (AFM) was performed on a Park System XE-70 in a noncontact mode with a scan size of $100 \times 100\ \mu\text{m}$. Auger electron mapping on patterned substrates was performed on a PHI 700 Scanning Auger Nanoprobe.

RESULTS AND DISCUSSION

In order to improve AS-MLD by the process illustrated in Figure 2, the SAMs and any MLD film bound to the SAMs must be removed from the Cu regions of the surface. The removal of ODPA SAMs from the Cu surface was initially tested on blanket Cu substrates. Figure 3a shows representative cyclic voltammograms of an ODPA-treated Cu electrode. The cathodic current was observed at a potential of approximately -0.6 V vs Ag/AgCl corresponding to a reductive desorption potential of ODPA SAMs from the Cu surface. Shorter phosphonic acid SAMs on Cu were also investigated, and the reductive desorption potential was found to decrease with decreasing SAM chain length (see Supporting Information), consistent with literature reports.^{34,37} Subsequent scans following the first cathodic polarization of the electrodes revealed no noticeable current, suggesting near-complete removal of the ODPA SAM from the electrode surface.

Water contact angle, Bode phase angle measurements from EIS, and XPS confirmed the removal of the SAM at cathodic potentials. After the first scan, the water contact angle of the electrode dropped from nearly 110° , associated with the hydrophobic SAM tail, to around 35° , which correlated with a hydrophilic Cu surface (inset to Figure 3a). Figure 3b shows the Bode phase plot of the ODPA-treated Cu before and after applied voltage. The Bode phase angle at 0.1 Hz, which correlates to the time scale that ions interact with the electrode surface,³⁸ falls from nearly 90° to $\sim 40^\circ$, indicating a lack of a capacitance feature (associated with the SAM) on the electrode. The Bode phase plot of the ODPA-treated Cu electrode after applied voltage also resembles the bare Cu electrode, another indication that the SAM was stripped off the surface of electrode. Moreover, high resolution XPS fine scans on the Cu electrode after voltage was applied to the electrode (Figure 3c) reveals no P signal from the ODPA SAM.

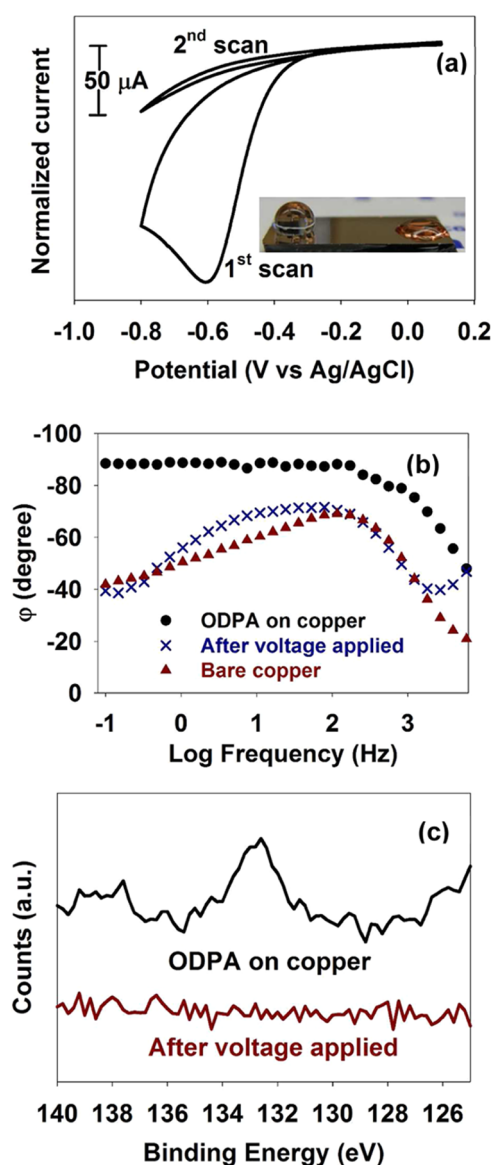


Figure 3. (a) Typical cyclic voltammograms of a Cu electrode coated with ODPA SAMs collected with sweep rate of 10 mV/s. The inset shows a photograph of water droplets on the Cu electrode after application of a negative bias. Note that the right side of the electrode was submerged in the electrochemical bath while the left side was not. (b) Impedance Bode phase spectra of ODPA on Cu electrode (black circle), ODPA on Cu electrode after applied voltage (blue cross), and bare Cu electrode (red triangle). (c) High resolution X-ray photoelectron spectra of P $2p_{3/2}$ peak of ODPA on Cu electrode before (black line) and after applied voltage (red line).

To test whether SAM removal could improve the overall selectivity in AS-MLD, we carried out the reductive SAM desorption process on the ODPA-treated Cu blanket substrates after MLD. Figure 4 shows a comparison of the film properties of the Cu surface before and after a negative bias was applied to the film. First, we examine the results before the electrochemical treatment. The water contact angle of ODPA-treated Cu surface is close to 110° (dashed horizontal black line on the graph). The water contact angle of ODPA-treated Cu subjected to a low number of MLD cycles (less than 12 cycles) remains unchanged from 110° . However, by 12 MLD cycles (ca. 6 nm), a decrease in the water contact angle is observed and it

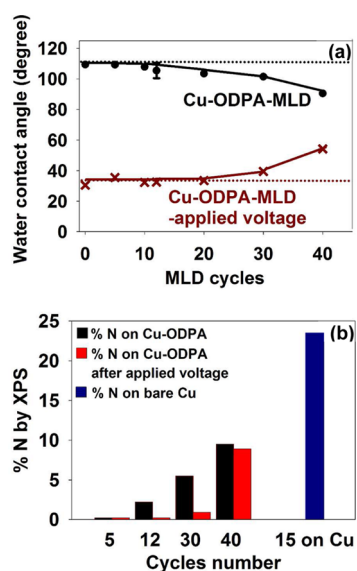


Figure 4. (a) Plot of water contact angle of the organic film as a function of MLD cycles on Cu/ODPA before (black circle) and after (red cross) applied voltage. The dotted black line and dotted red line indicate the expected water contact angle of an ODPA film and a Cu electrode, respectively. (b) The %N detected by XPS on Cu/ODPA before and after applied voltage. The blue bar represents the %N detected by XPS on a bare Cu blanket after 15 cycles of MLD with no SAM layer.

continues decreasing as the number of MLD cycles increases. The expected water contact angle of the pure MLD film is $\sim 73^\circ$.¹⁷ The downward trend in WCA toward values approaching 73° therefore suggests that some polyurea is deposited on the ODPA resist on Cu at high cycle numbers. XPS analysis also confirms that ODPA does not completely prevent MLD at a high number of cycles. The %N, which is correlated to the amount of polyurea on the surface, increases as a function of MLD cycle (Figure 4b), in good agreement with the water contact angle measurement. All these results indicate an upper limit of the selectivity at 12 cycles (ca. 6 nm) from the SAMs alone.

After both WCA and XPS measurements, the same set of samples was subsequently charged with a negative bias in the electrolyte solution and both WCA and %N were remeasured. As demonstrated by the bottom plot of Figure 4a, a significant drop in the water contact angle was seen after the electrochemical treatment for samples containing low MLD cycles (fewer than 20 cycles), reaching a value close to that of a bare Cu electrode ($\sim 35^\circ$). This behavior is consistent with removal of the ODPA SAM layer from the Cu surface. XPS analysis on the same samples (Figure 4b) also reveals that the %N notably decreases, especially for samples with 30 MLD cycles or fewer. Note that the sample with 5 MLD cycles does not show much change because the selectivity from the SAM alone is already large. The decrease in %N indicates that applying a negative bias not only strips the ODPA SAM from the surface of Cu but also removes the polyurea film which had deposited on the ODPA SAM. If the %N from XPS is used as an approximate measure of selectivity, these results suggest that up to 30 times increase in selectivity at 12 MLD cycles can be achieved after the electrochemical treatment.

At higher MLD cycles, however, the removal is less successful, as evident by the WCA and %N data. We speculate that the inability to fully remove the SAM and MLD film in

these cases is a consequence of a thicker MLD film deposited on the ODPA SAM at higher cycle numbers. In these cases, the direct removal of the SAM from the Cu surface is likely difficult because the overcoating MLD film has limited solubility in the polar solvent (methanol) we are employing and does not allow the SAM to release from the surface. Attempts to use less polar solvents (e.g., acetonitrile, tetrahydrofuran and acetone) were hampered by the finite solubility of the ODPA SAMs, resulting in no SAMs removal from the surface of Cu. It is possible that other solvents or more aggressive processes may be able to remove thicker MLD films by releasing the underlying SAM and also that other MLD chemistries may be even more susceptible to release. Nonetheless, the current method we present here can successfully extend the process of area selective deposition on a Cu surface for up to 20–30 cycles (ca. 10.6–15.9 nm) of polyurea MLD.

With an established method of improving the effectiveness of the SAM resist on the blanket Cu surface in hand, we next applied the approach to patterned Si substrates consisting of Cu lines. A patterned substrate allows us to further test improvement of the selectivity in AS-MLD. After complete SAM formation on the patterned substrates, the samples were exposed to 12 cycles of polyurea MLD and the resulting nitrogen elemental distribution was probed by AES. Figure 5a

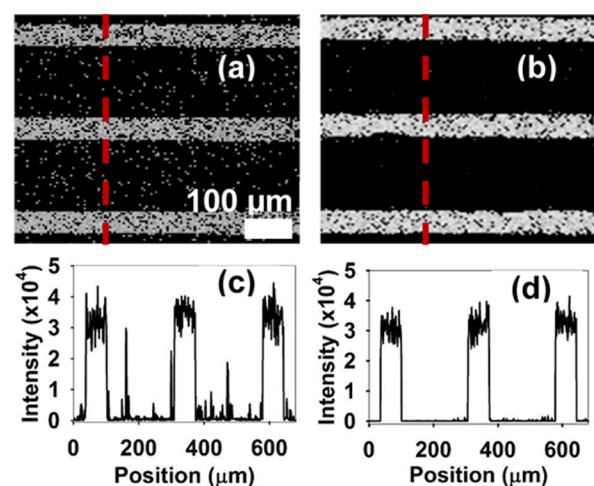


Figure 5. N Auger mapping analysis of patterned ODPA-Cu/Si substrate following 12 polyurea MLD cycles (a) before applied voltage and (b) after applied voltage. Panels c and d represent N line scans along the dashed line of samples a and b, respectively.

shows the N Auger electron mapping of this test structure, with results similar to those shown in Figure 1b. After the image in Figure 5a was collected, the pattern was then negatively biased in the electrochemical cell and re-examined. The result is shown in Figure 5b. A remarkably better selectivity is observed after the potential was applied to the test structure. N line scans on both structures (dashed line) also confirm a greater contrast of N signal between Cu and Si regions after the applied negative bias (Figure 5c and d).

After the applied negative bias, the integrity of the MLD film on the Si was confirmed by Fourier transform infrared (FTIR) spectroscopy, ellipsometry, and WCA measurements carried out on blanket Si surfaces. The thickness of the polyurea film before electrochemical treatment was 62.5 and 60.6 Å after treatment. A slight thickness loss is within the error range of our measurements, especially for organic films. The hydro-

phlicity of the film, as measured by the water contact angle, was not altered (73° both before and after treatment). In addition, the chemical bonding of the film was also not changed by such a treatment (see Supporting Information). Similar measurements were performed for film thicknesses both greater and less than 60 Å and no significant thickness loss was observed. This result shows that the process can selectively remove a partially deposited MLD film from the Cu regions of a pattern without disturbing the desired MLD film on the Si regions. Further, to demonstrate the versatility of this method, we performed a similar experiment for AS-ALD of a ZnO film. An improvement in selectivity of about 5 times, approximated from the AES Zn signal in a line scan, was found on the patterned substrate after the applied voltage for this system (see Supporting Information). From these results, we have shown that the route presented here can complement traditional area-selective deposition approaches to achieve high selectivity for various applications requiring high spatial resolution.

CONCLUSIONS

We demonstrate a new route to improve the selectivity for area selective layer-by-layer deposition on metal/dielectrics patterns. By applying a negative bias to the substrate under electrochemical conditions, ODPAs SAMs can be successfully removed from the metal surface. This in turn leads to the removal of any MLD film that adventitiously deposits on the SAM—for polyurea films deposited with up to 20–30 MLD cycles—without impacting the MLD film attached to the Si surfaces. Hence, this combined approach coupling SAM blocking layers with reductive SAM desorption via an applied negative potential yields excellent selectivity between metal/dielectric surfaces. This process can easily be extended to a variety of systems.

ASSOCIATED CONTENT

Supporting Information

Cyclic voltammograms of phosphonic acids SAMs; FTIR spectra of polyurea MLD on SiO₂ before and after applied voltage; Zn Auger mapping on Cu/Si patterns. 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.

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