

A versatile approach to selective and inexpensive copper patterns using polyelectrolyte multilayer coatings

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Abstract

Versatile, highly selective, and inexpensive metal patterning techniques on various substrates are demanded for current research in microelectronic device fabrications. We present a new process for creating highly selective and cost-effective copper patterns that can be plated on virtually any substrate including plastics by combining polyelectrolyte multilayer (PEM) coatings, microcontact printing, and electroless deposition. Optical microscope, atomic force microscopy and energy dispersive X-ray spectroscopy were used to show the resulting copper structures exclusively plated where the patterned catalyst was electrostatically bound to the PEM coated surfaces. The copper plating rate was measured using a quartz crystal microbalance. The unpatterned polyelectrolyte surfaces are still active and can be used with additional processing to create complicated three dimensional metal architectures or even bimetallic patterns.

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1. Introduction

Flexible substrates and inexpensive metal patterning techniques with high selectivity have been the focus of current research in displays, radio frequency identification (RFID) transponders, sensors and other nano- and microelectronic device fabrication [1–3]. Recently, many techniques have been developed to pattern metals on surfaces [4–10]. Most of these techniques are surface-specific, when the substrates are changed these techniques fail to function properly. A more general and versatile approach to patterning metals is demanded for current and rapidly changing microelectronic applications. Photolithography based top-down methods are the standard industrial patterning technique in microelectronics. However, this process is an expensive step in device fabrication, limits the functionality of substrates and other materials, and has an inability to work with curved substrates or the complex 3D structures needed for new electronic devices [1,11,12]. Microcontact printing (μ CP), a soft lithographic patterning technique, combined with polyelec-

trolyte multilayer (PEM) coatings offers a multitude of cost-effective routes for creating functional three dimensional structures on plastic and other flexible substrates [13]. Electroless deposition (ELD) is a convenient, inexpensive metal plating technique that works on nano- or micrometer sized objects and can be used to selectively plate metal onto 2D and 3D structures [14–16]. The combination of PEM coatings, μ CP, and ELD can provide a more economical approach for microelectronic fabrication on a wider range of substrates including plastic and flexible substrates.

PEM coatings created by alternate adsorption of oppositely charged poly-ion molecules were first introduced by Decher [17]. Layer-by-layer (LBL) assembly has been used to create ultra thin functional films on planar and 3D substrates. Incorporation of nano- and micron scale materials into multilayer assemblies alter surface [18], optical [19], mechanical [20] or other properties which have material applications [21–23]. μ CP is excellent for high throughput large area patterning with micron and submicron feature sizes. Poly(dimethylsiloxane) (PDMS) stamps were first used to create patterns of thiols on gold [24], and silanes on silica [25]. Many other functional materials including *m-d*-poly(ethylene glycol) acid [26], polymers [27,28], polyelectrolyte aggregates [29] and dendrimers

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[30] have been patterned onto PEM coated substrates. LBL assembly on PDMS stamps and subsequent μ CP was used to create 3D structures of PEM and bionanocomposite arrays with excellent selectivity [31,32].

μ CP and ELD have been used together to create selective metal patterns which are less expensive to produce than patterns created by conventional photolithography [4–10]. By using μ CP and ELD, numerous devices can be fabricated from a single photolithographic step; however devices produced solely from photolithography require the expensive photolithographic step to be repeated once per device. Metal patterns have been created from the electroless deposition of copper, silver, gold, nickel and cobalt patterns, typically on silica substrates with palladium based catalysts. ELD catalysts do not strongly adhere to the substrate so an adhesion layer is required. To overcome this obstacle a silane self-assembled monolayer (SAM) has been used as the adhesive layer [4–6]. Substrates with patterned catalyst are created by directly stamping the catalyst or via an indirect method such as patterning the adhesion layer. Other ELD adhesion layers include phosphine-phosphonic acids [7] titanium [8] and poly(amidoamine) dendrimers [9,10]. While these adhesion layers are effective, they are limited because they form substrate specific bonds that are not interchangeable like electrostatic charges. Additionally our method is more versatile because the chemical functional groups of the polyelectrolyte adhesion layer can be changed and other materials can easily be added to the multilayers to optimize the system.

LBL assembly of PEMs has been combined with ELD to make selective nickel patterns on glass and plastic substrates coated with PEMs [33,34]. This method uses PEMs as the adhesion layer between the substrate and the deposited nickel. Ink-jet printing was used to pattern a polyelectrolyte ink onto a PEM surface resulting in plus/minus patterned regions. Then, directed self-assembly was used to selectively adsorb an ionic palladium catalyst onto the plus/minus patterned surface using electrostatic interactions. This approach is limited by the ink-jet printing resolution which is at best 20 μ m [12], while μ CP is reported to have a much finer resolution, 30 nm [35]. In addition, the directed self-assembly of charged catalysts onto functionally patterned surfaces often led to poor selectivity of metal patterns on surfaces [15].

We present a new process for creating versatile and selective copper patterns by combining PEM coatings, μ CP, and ELD. For the first time μ CP was used to pattern a charged palladium catalyst onto oppositely charged PEM coated substrates. PEMs, unlike silanes and thiols, can be stably coated onto virtually any substrate including hydrophobic polymer surfaces [13]. This results in a highly selective electrostatically bound charged palladium ion complex on the PEM coated substrates. The substrate was then placed into an ELD bath where copper selectively plated only at the catalyzed regions. Our system which involves PEMs as the stable adhesion layer is more versatile, economical and works over a larger range of substrates than previous approaches. The combination of PEMs and μ CP allows the control of 3D features on the micron and submicron scale. Using our process it was possible to create stable and selective copper patterns with nanometer dimensions on flexible substrates, which can result in lower

fabrication costs to produce flexible display electronic circuits, sensors, RFID transponders, and other nano- or microelectronic devices.

2. Experimental details

2.1. Substrate preparation

To demonstrate the versatile and selective metal patterning process on virtually any surface type, hydrophilic glass and hydrophobic polystyrene substrates were selected. Glass microscope slides (Corning Glass Works, Corning, New York) were sonicated with a Branson ultrasonic cleaner (Branson Ultrasonics Corporation, Danbury, CT) for 20 min in an Alconox (Alconox Inc., New York, NY) solution followed by 10 min of sonication in water. The slides were then blown dry with nitrogen and plasma cleaned (Harrick Scientific Corporation, Broadway Ossining, NY) with oxygen at ~ 13.3 Pa for 10 min. Before use, polystyrene microscope slides (Nalge Nunc International, Rochester NY) and flexible polyester transparency films (3M, St. Paul, MN) were plasma treated under the same conditions for 10 min. A Carl Zeiss slide stainer equipped with a custom-designed ultra sonication bath (Advanced Sonic Processing, Oxford, CT) was used to mechanically coat the substrates with PEMs [36]. The glass and plastic slides were dipped into a 0.02 M solution of positively charged poly(diallyldimethylammonium chloride) (PDAC, Aldrich, Mw $\sim 70,000$) for 20 min followed by washing. Next the slides were dipped into a 0.02 M solution of negatively charged sulfonated poly(styrene), sodium salt (SPS, Aldrich, Mw $\sim 150,000$) followed by washing, which creates one bilayer. Both polyelectrolyte concentrations are based on the repeat unit of the polymer and each solution contained 0.1 M NaCl. The dipping process was repeated to form multilayers. Typically 10.5 bilayers of PDAC and SPS, written as (PDAC/SPS)_{10.5} were used to coat the substrates. The final half layer means that the outer surface is PDAC. Deionized (DI) water from a Barnstead Nanopure Diamond (Barnstead International, Dubuque, IA) purification system with a resistance of >18.2 M Ω -cm was used for all aqueous solutions.

2.2. Microcontact printing

A Sylgard 184 elastomer kit (Dow Corning, Midland, MI) was used to create PDMS stamps which were used for μ CP [24]. These stamps were created by pouring the prepolymer and initiator (10:1 mass ratio) on top of a fluorosilane treated patterned silicon master and cured in an oven overnight at 60 $^{\circ}$ C. The masters were prepared in the Microsystems Technology Lab at the Massachusetts Institute of Technology and consisted of lines with widths from 1 to 10 μ m. The silane treatment allowed for easy separation between the master and the cured PDMS. The stamps were cut to size and washed with soap and water before use. Before stamping, the PDMS stamps were oxygen plasma cleaned for one minute to make their surface hydrophilic. The PDMS stamps were soaked for 20 min in a freshly prepared 5 mM aqueous solution of the palladium catalyst, sodium tetrachloropalladate (II) (Na₂[PdCl₄], Strem

Chemicals, Newburyport, MA). The stamps were removed from the ink solution, blown dry using nitrogen and brought into conformal contact with the PEM surface for five minutes. Then they were removed and the patterned samples were rinsed with flowing DI water. Since the catalyst ink solution has an unadjusted pH of 3.0, the rinse water pH was lowered to 3.0 by adding a small amount of 1.0 M hydrochloric acid (HCl).

2.3. Electroless deposition bath

Copper was selectively plated onto the previously deposited catalyst regions in a previously optimized electroless bath [37]. The electroless bath contained 0.032 M cupric sulfate (J.T. Baker, Phillipsburg, NJ), 0.040 M 1,5,8,12-tetraazadodecane (Fisher Scientific, Pittsburgh, PA), 0.300 M triethanolamine (Fisher Scientific), 0.067 M dimethylamine borane (DMAB, Aldrich Chemical, Milwaukee, WI) and 300 mg/mL 2,2' dipyridyl (Aldrich) in DI water. The copper bath was used at a temperature of 50 °C (± 2.0) and the pH was adjusted to 9.0 (± 0.1) by adding a small amount of 1.0 M HCl.

2.4. Colloidal adsorption

To show that the unpatterned surface was still functional (i.e. charged) and available for further modification or processing after metal deposition, colloidal particles were deposited onto the PDAC regions of the surface. A 0.5 wt.% colloidal solution of 4 μm carboxylated polystyrene particles (Interfacial Dynamics Corp., Portland, OR) was gently dropped on the surface of a copper patterned glass slide and incubated for three hours. The particle coated substrates were then washed carefully with DI water and blown dry using nitrogen.

2.5. Quartz crystal microbalance crystal preparation

Gold coated quartz crystal microbalance (QCM) crystals (5 MHz, Maxtek, Inc., Santa Fe Springs, CA) were cleaned in fresh piranha solution (7:3 concentrated sulfuric acid; 30% hydrogen peroxide) for 20 s, rinsed with copious amount of water

and blown dry with nitrogen. The crystals were then immersed into an ethanol solution containing 5 mM 16-mercaptohexadecanoic acid (Aldrich) for 30 min, copiously rinsed with ethanol and blown dry with nitrogen. Then multilayers, (PDAC/SPS)_{10,5}, were deposited onto the QCM crystal as described previously. A 30 s immersion into a freshly prepared 5 mM aqueous palladium catalyst solution followed by a DI water rinse was used to catalyze the crystals before electroless deposition.

2.6. Characterization

Optical micrograph images were taken using a Nikon Eclipse ME600 microscope equipped with a digital camera. Atomic force microscope (AFM) images were collected in tapping mode using a Nanoscope IV multimode scope from Digital Instruments. An environmental scanning electron microscope (SEM, model 2020, Electro Scan) equipped with a LaB₆ filament and operated at 20 kV with a water vapor environment in the sample chamber was used to obtain SEM images. Energy dispersive X-ray spectroscopy (EDXS) spectra were obtained using a Link ISIS system (Oxford Instruments). Metal plating rates were measured using a research QCM (Maxtek, Inc.) and accompanying computer program.

3. Results and discussion

Fig. 1 shows the overall scheme of the fabrication process. With the addition of only a few polyelectrolyte bilayers the surface properties of a substrate can be completely changed to have either a positive or negative charge [13]. With this in mind, 10.5 bilayers of positively charged PDAC and negatively charged SPS, (PDAC/SPS)_{10,5}, were fabricated on glass and plastic substrates to create an outer surface with properties that are independent from the original substrate. These PEMs have a positively charged surface and a total thickness of ~ 30 nm [26]. An oxygen plasma treated PDMS stamp was soaked in a freshly prepared aqueous 5 mM ink solution that contains negatively charged palladium ions, and has a natural pH of ~ 3.0 . After soaking, the stamps were blown dry with nitrogen and placed in conformal contact with the positively

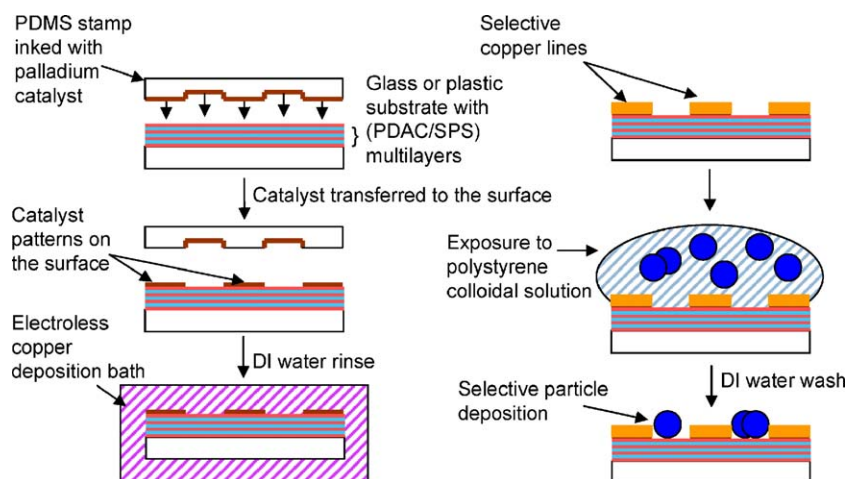


Fig. 1. Schematic of the overall fabrication process to create selective copper patterns on PEM coated substrates followed by colloidal deposition.

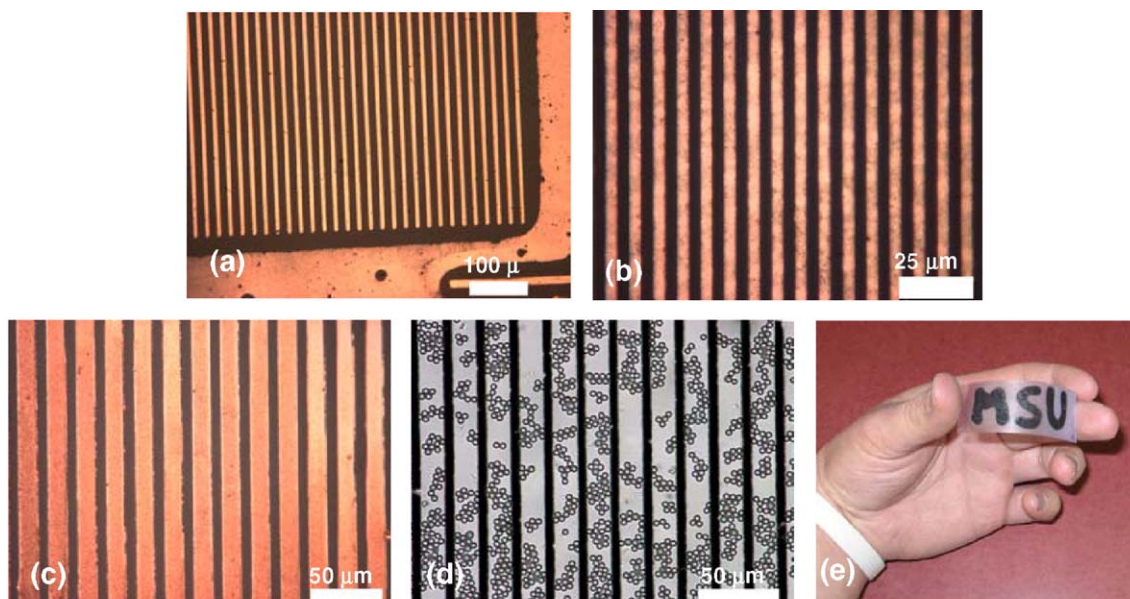


Fig. 2. Reflected light optical micrographs of selective copper lines on PEM coated substrates. Parts a) and b) have glass substrates while c) is on a polystyrene substrate. d) Transmitted light optical micrograph of polystyrene particles deposited on the active unpatterned regions of the PEM surface next to the black copper lines. e) A PEM coated flexible polyester transparency film substrate with electroless copper patterns which are ~ 30 nm thick.

charged surface of the PEMs. While in contact with the surface, the negatively charged palladium ions transferred to the positively charged surface via electrostatic interactions. After the stamp was removed, the patterned PEM surface was rinsed with DI water at a pH of ~ 3.0 to remove the excess catalyst. After rinsing, the substrates contained alternating regions of positively charged PDAC and negatively charged palladium catalyst complexes. These catalyst patterned substrates were then placed in an electroless copper bath. This bath which was previously optimized has

excellent selectivity and operates at a lower pH than the traditional formaldehyde based electroless baths [37]. The copper bath was heated to $50\text{ }^{\circ}\text{C}$ (± 2.0) and then DMAB was added to initiate the chemical reaction. The solution pH was reduced to 9.0 (± 0.1) using a small amount of 1.0 M HCl . The catalyzed substrates were placed into the electroless copper bath where DMAB reduced the positive copper ions to zerovalent metallic copper which selectively adsorbed onto the substrate in the regions of the surface where the palladium catalyst was present. Copper deposition did

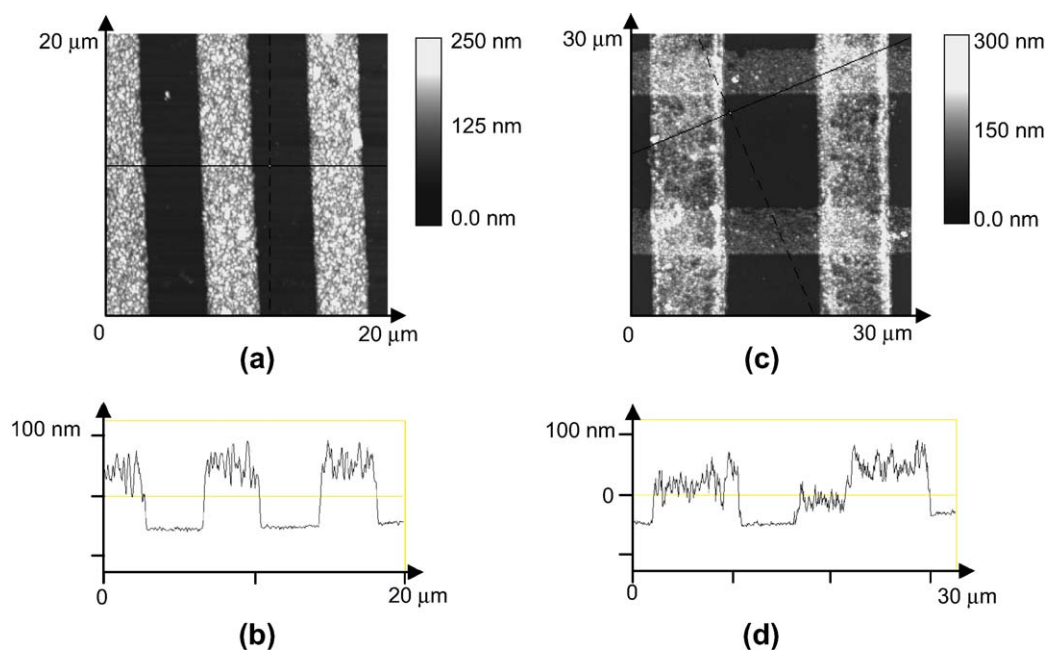


Fig. 3. AFM images of a) a $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ image of selective copper patterns and b) a $30\text{ }\mu\text{m} \times 30\text{ }\mu\text{m}$ image of multilevel structure created by stamping a substrate twice before electroless deposition.

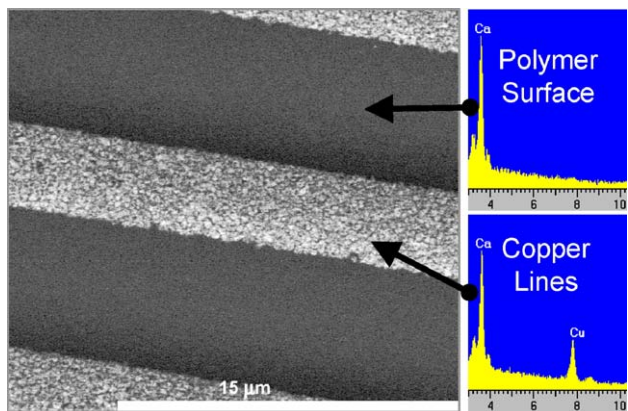


Fig. 4. SEM image of selectively plated copper lines on PEMs. The EDXS spectra shown are for the copper lines and the unpatterned polymer surface. The calcium peak was left to show the relative size of the copper peak.

not occur at the uncatalyzed regions of the surface, so the positively charged PDAC regions of the surface were copper free.

Fig. 2 shows optical micrograph images of the selective copper patterns. Reflected light optical microscope images of copper patterns on PEM coated glass and polystyrene substrates are shown in Fig. 2a–c. Plated copper was only found where the PDMS stamp was in contact with the positively charged polymer. It was possible to create highly selective results (i.e., nearly 100% selectivity) over areas as large as the entire stamp ($\sim 1 \text{ cm}^2$). Unlike our direct catalyst stamping on PEM coated substrates, the directed assembly of catalysts onto plus/minus (polycation/polyanion) micropatterned region by ‘polymer-on-polymer stamping’ [27,28] resulted in less selective copper patterns. We believe that this is because polycations and polyanions are integrated through the multilayers so that ‘plus’ and ‘minus’ patterned regions are not exclusively homogeneous at the molecular level on which the small charged catalysts cannot be completely directed to the oppositely charged regions. Only direct catalyst stamping onto PEMs can generate confined catalyst nano and micropatterns, which results in 100% selective metal patterns. In addition, the positively charged unpatterned PDAC surface was still active and could be modified further. To demonstrate this we deposited negatively charged polystyrene particles onto the unpatterned regions of the surface, Fig. 2d. Previously our group has shown that complete surface coverage of the particle monolayer is not expected from a simple drop coating [19]. Fig. 2e shows an electroless copper pattern on a polyester transparency film that was coated with a PEM adhesion layer. The palladium catalyst was patterned on the surface using a cotton-tipped swab. This image demonstrates that flexible polyester transparency films can be patterned using our technique.

AFM was performed to further analyze the sample topography. The AFM images in Fig. 3 again show that copper deposition scarcely occurs outside the patterned regions on the PEM surface. The sample Fig. 3a has an average copper thickness of 107.6 nm (± 4.3). The surface roughness of the deposited copper lines is 20 nm. Fig. 3c shows a sample that was stamped using two different stamps with a 90° separation in orientation and before

immersion into a copper bath. This illustrates that complex 3D metal structures can be fabricated on PEM surfaces.

Fig. 4 shows a SEM image of the selective copper patterns. EDXS analysis of the sample confirms that copper was being deposited in linear patterns on the PEM surface. More importantly, the second spectrum shows that there was no detectable copper present on the polymer surface between the copper lines. The calcium peak was kept so relative peak heights between the copper lines and polymer surface could be compared. All other detected elements were due to the PEMs and the glass substrate.

A QCM was used to study the kinetics of ELD on unpatterned homogeneously catalyzed or uncatalyzed surfaces. A carboxylic acid terminated thiol was used to create a SAM on the gold coated quartz crystals. This results in a negatively charged outer surface. $(\text{PDAC}/\text{SPS})_{10.5}$ bilayers were deposited on the thiol to create uncatalyzed QCM crystals. The crystals were catalyzed by immersion into an aqueous palladium catalyst solution followed by rinsing with DI water (pH ~ 3.0). The QCM crystal and the copper bath were simultaneously heated to 50°C . The copper bath was then activated and the pH was adjusted. The warm QCM crystal was placed into the activated copper bath. The change in copper thickness was calculated from the change in frequency of the QCM crystal using the QCM computer software. The QCM results are shown for a catalyzed (blue squares) and uncatalyzed (red triangles) PDAC surface in Fig. 5. The different plating rates shown in the plot verify the high selectivity of the electroless copper bath. Copper uniformly plates on the catalyzed surface and does not deposit on the uncatalyzed PDAC surface. The initial non-linear plating rate of the catalyzed sample is caused by the increasing area available for copper deposition. After seven minutes linear growth was observed with an average plating rate of 26.8 nm/min. This plating rate agrees well with the previously reported rate of 23.3 nm/min for the same copper bath under similar conditions [37].

We were able to create copper thicknesses of up to 300 nm using only electroless deposition. Delamination of copper films thicker than 300 nm occurred due to the build up of internal stress in the ELD copper thin films. This problem may be solved using a combination of electrodeposition and thermal annealing. Electrodeposition of a second copper layer onto the ELD copper

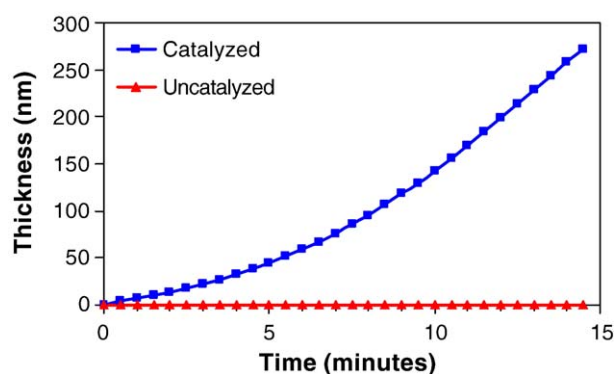


Fig. 5. QCM results of copper thickness versus time for homogeneously catalyzed and uncatalyzed surfaces.

seed layer followed by thermal annealing will increase the total copper thickness, reduce the internal stress and increase the strength of adhesion between the copper layers [38,39]. Currently, we are working to resolve this issue.

4. Conclusion

In conclusion, a novel versatile process incorporating PEMs, μ CP and ELD has been utilized to create copper patterns with excellent selectivity on top of PEM coated substrates. μ CP and ELD together reduce fabrication costs of metal patterns and structures compared to conventional photolithographic techniques. The ability of PEMs to coat any surface [13] allows bendable plastic to be used and can reduce the cost of materials in future electronic devices such as bendable displays, sensors, and RFID transponders. The combination of layer-by-layer assembly with μ CP gives nanoscale control of the feature dimensions. The copper free PEM surface is still functional and can be modified to fabricate 3D metal structures or even patterns composed of two or more metals.

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