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Polyelectrolyte Brushes as Efficient Ultrathin Platforms for Site-Selective Copper Electroless Deposition

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Ion-exchange in surface-initiated polyelectrolyte brushes provides a versatile route to the formation of catalytically active surfaces for electroless deposition of Cu. The advantage of this procedure is the covalent anchoring of the catalyst support layer, eliminating delamination of the metal film, even when deposited onto PDMS substrates. Furthermore, by tuning the concentration of PdCl_4^{2-} ions in the brushes, the rate of deposition and hence the thickness of the overall film can be controlled easily.

Introduction

Metallization is of major importance in the fabrication of chip interconnects, magnetic storage devices, printed circuit boards and a range of other applications in the microelectronics industry. Moreover, in the relatively new area of “flexible” or “polymer” electronics, metallization of polymer substrates is required, and the mechanical cohesion between the deposited film and the substrate (adhesion) is a significant challenge.^{1,2} Copper metallization can be accomplished by physical vapor deposition, chemical vapor deposition, and chemical or electrochemical plating.^{3–8} Electroless or chemical plating has emerged as a low cost tool enabling the production of high quality samples at room temperature, especially suitable for polymeric substrates, which would not withstand the high temperature required for vapor deposition strategies. Electroless deposition is an autocatalytic redox reaction in which metal cations in solution are reduced on a substrate forming a metal layer.⁹ The plating process is carried out in the presence of a catalyst, commonly surface-immobilized Pd, to initiate the reaction. The spatial resolution of the electroless process is governed by the quality of the site-selective immobilization of the catalyst.¹⁰ Different strategies to site-selective anchoring the electroless catalyst were developed. These include chemi- and physisorption of reactive species in solvent-imprinted nanocavities,¹¹ selective irradiation of SAMs,^{12,13} inkjet printing of patterned domains of catalysts^{14,15} and microcontact printing of Pd colloids and complexes.^{16–19} Furthermore, organic thin films bearing N-containing groups with strong affinity to PdCl_4^{2-}

species in self-assembled monolayers,²⁰ photografted polymers,⁶ dendrimers,¹⁹ or polyelectrolyte multilayers²¹ have been employed as anchoring layers in a variety of electroless deposition processes. When choosing organic thin films as anchoring layers there is tradeoff between the efficiency of catalyst immobilization and spatial resolution of the patterning process. Although SAM patterning is straightforward using soft lithographic techniques,^{22,23} the catalyst uptake is rather poor due to the limited number of surface binding moieties. On the other hand, macromolecular architectures such as dendrimers or polyelectrolyte multilayers are capable of significant catalyst uptake, but to achieve high spatial resolution by simple lithographic techniques is more difficult.^{24,25}

In this work, we report on the application of polyelectrolyte brushes as efficient adhesion layers for site-selective electroless deposition. We exploited the versatility of microcontact printing for the patterned chemisorption of initiator self-assembled monolayers. Subsequently, we grew polyelectrolyte brushes containing quaternary ammonium groups (QA^+) with strong affinity to PdCl_4^{2-} species via surface-initiated polymerization, leading to a large number of catalyst binding sites on the substrate.

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The brushes thereby not only serve as a very effective adhesion layer for the electroless deposited Cu film but, due to the controlled uptake of the PdCl_4^{2-} counterions, the amount of catalyst can be varied.

Experimental Section

Sample Patterning. Patterned samples were prepared by microcontact printing (μCP) using typical procedures reported in the literature.^{22,23,27} We used a thiol initiator (ω sulfanylundecylbromobutyrate) and a silane initiator (2-bromo-2-methylpropionic acid 3-trichlorosilanylpropyl ester) to grow the polyelectrolyte brushes from Au and Si/SiO₂ substrates, respectively.

Polymerization Solution. For the preparation of the polymerization solution, commercially available (75 wt % from Aldrich) 2-(methacryloyloxy)ethyl-trimethylammonium chloride (METAC) (46.3 g) was dissolved in MeOH (46 cm³) at 20 °C and degassed by passing a continuous stream of dry N₂ through the solution while being stirred (20 min). To this solution was added 2,2'-dipyridyl (2.411 g), Cu^ICl (0.611 g), and Cu^{II}Cl₂ (0.083 g). The mixture was then further stirred and degassed with a stream of dry N₂ (15 min). Initiator-modified substrates were sealed in Schlenk tubes, degassed (4 x high-vacuum pump/N₂ refill cycles), and left at 20 °C under N₂. The polymerization solution was then syringed into each Schlenk tube, adding enough solution to submerge each sample completely. The samples remained in the polymerization solution for 2–3 h. After polymerization the samples were removed, washed with MeOH and water and dried under a stream of N₂.

Electroless Plating Bath. For the preparation of the electroless plating bath, we used a 1:1 mixture of freshly prepared solutions A and B. Solution A: NaOH 12 g/L + CuSO₄·5H₂O 13 g/L + potassium sodium tartrate (KNaC₄H₄O₆·4H₂O) 29 g/L. Solution B: HCHO 9.5 mL/L.

Results and Discussion

For our studies, we used cationic brushes of 2-(methacryloyloxy)ethyl-trimethylammonium chloride (METAC) which were grown from different substrates using aqueous atom transfer radical polymerization (ATRP), following a procedure reported in the literature.^{26–28}

ATRP is a simple and effective method for fast polymerization under easily controllable reaction conditions.^{29,30} Surface-initiated ATRP can be applied to grow thin films of polymer brushes on different substrates. In our experiments, patterned growth of polyelectrolyte brushes was accomplished by microcontact printing initiator-terminated self-assembled monolayers using PDMS stamps (Figure 1). For surface-initiated polymerization from Au and SiO₂/glass surfaces, we used thiol (ω -mercaptoundecylbromobutyrate) and silane (2-bromo-2-methyl-propionic acid 3-trichlorosilanyl-propyl ester) initiators, respectively. Typical polymerization conditions yielded well-defined 16–20 nm thick patterned brushes in 2–3 h. The patterned METAC-modified substrates were then immersed in a 1 mM PdCl_4^{2-} solution (pH \sim 1) for 20 min. This procedure forced the replacement of Cl[−] counterions in the as-synthesized PMETAC brushes by PdCl_4^{2-} species.²⁷ The presence of the PdCl_4^{2-} in the brush layer was corroborated by UV–vis spectroscopy (Figure 2a). PdCl_4^{2-} species present a well-defined charge-transfer band

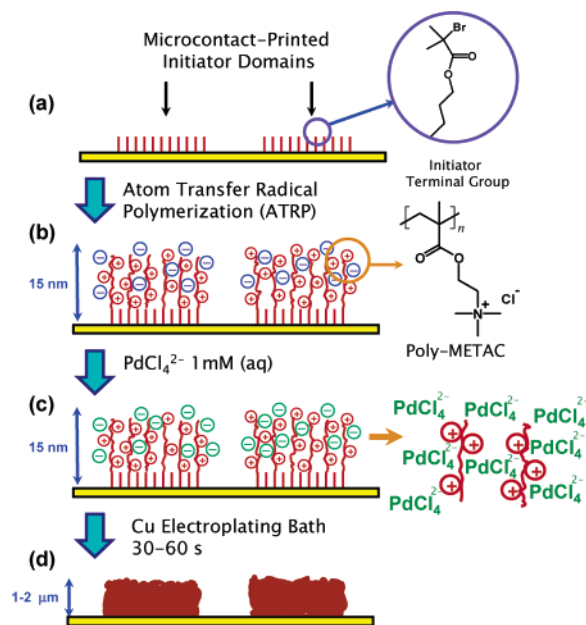


Figure 1. Scheme depicting the different steps involved on the site-selective electroless metallization using patterned polyelectrolyte brushes. Initially, the initiator molecules are microcontact printed on the substrate (a) followed by the aqueous atom transfer radical polymerization of the brush layer (b). Then, the cationic brushes are coordinated with the catalyst species (c) and immersed in the copper electroless bath (d).

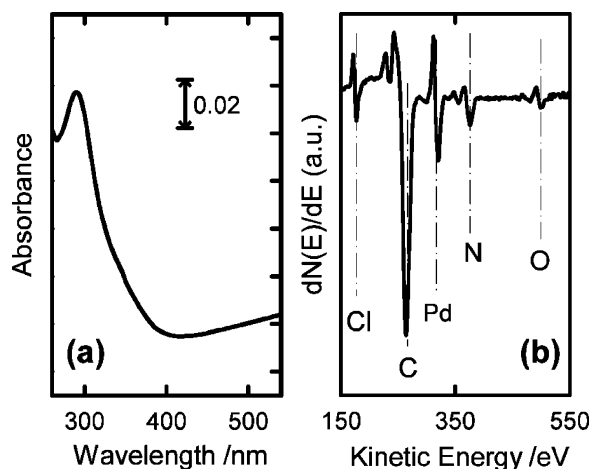


Figure 2. (a) UV–vis spectrum of a glass substrate modified with poly-METAC brushes after immersing during 30 min in 1 mM PdCl_4^{2-} . (b) AES spectrum of a PMETAC-modified SiO₂/Si surface coordinated with PdCl_4^{2-} anions. In the spectrum are detailed the signals corresponding to: Cl (LVV, 181 eV), C (KLL, 268 eV), Pd (MNN, 323 eV), N (KLL, 380 eV), and O (KLL, 506 eV).

in the ultraviolet spectrum at \sim 300 nm that can be easily detected UV–vis spectrum of PMETAC-modified glass or quartz substrates.

It must be noted that in most of the copper electroless deposition experiments catalyzed by palladium nuclei are obtained on the substrate surfaces via SnCl_2 sensitization due to the low reactivity of the substrate. The activation process requires the sequential use of acid solutions of SnCl_2 and then PdCl_2 (“two-step process”) or a colloidal mixture of SnCl_2 and PdCl_2 (a “one-step” process). However, these strategies have some major drawbacks. Palladium nuclei generated on the substrate present poor adhesion to the substrate because of the absence of a “chemical linkage” between palladium species and the substrate.^{7,8} As a consequence, desorption of the catalysts from the substrate may cause failure

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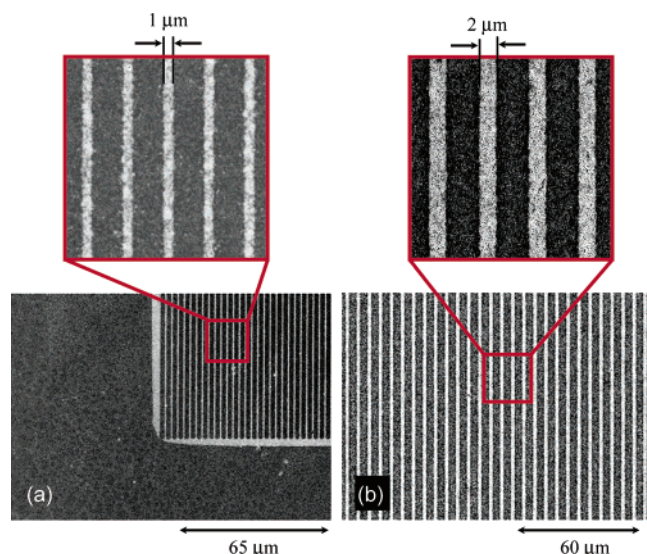


Figure 3. SEM images showing the site-selective electroless deposition of Cu on patterned poly-METAC brushes grown on SiO_2/Si substrates: (a) $1\ \mu\text{m}$ lines, (b) $2\ \mu\text{m}$ lines. Insets show a magnification of the well-defined Cu microstructures.

to achieve uniform metal deposits with good adhesion properties. Moreover, several precautions must be taken when using metallic palladium nanoparticles as catalysts since they are unstable and easily oxidized in the air.

In the case of microcontact-printed PMETAC brushes, we exploited ion-pairing as an extremely effective mechanism for site-selective anchoring of PdCl_4^{2-} species to an appropriate substrate. To corroborate the efficiency of binding, we performed elemental analysis of PdCl_4^{2-} -coordinated brushes with Auger electron spectroscopy (AES). Figure 2b depicts an AES spectrum of a METAC brush grown on SiO_2/Si immersed in PdCl_4^{2-} during 20 min and copiously rinsed with Milli-Q water prior to introducing the sample in the analysis chamber. To estimate the efficiency of binding, that is the fraction of QA^+ moieties that remains coordinated to Pd^{II} species, we quantified the atomic ratio Pd/N using the Auger signals corresponding to Pd (MNN transition, 323 eV) and N (KLL transition, 380 eV). Results derived from this estimation indicated that 90–95% of QA^+ moieties are coordinated to a PdCl_4^{2-} species, indicating the strong affinity of QA^+ to PdCl_4^{2-} ions.

After immobilizing the PdCl_4^{2-} catalyst in the (patterned) brushes, we immersed the substrates in a copper electroless plating bath. After a short time, 30–60 s, the formation of copper patterns on the immersed substrate could be observed with the naked eye. Scanning electron microscopy (SEM) and optical microscopy imaging confirmed the presence of well-defined copper micro-patterns deposited on the SiO_2/Si (Figure 3) and Au substrates (Figure 4), respectively.

One particular feature attributed to the polyelectrolyte brush is the ability to control the amount of PdCl_4^{2-} in the inner environment of the polymer film.³¹ To gain control over this parameter is very important since it will directly influence the efficiency of the plating process. Control over the amount of catalyst on the substrate is generally difficult or impossible when using polyelectrolyte multilayers or self-assembled monolayers.

In our case, we loaded patterned PMETAC brushes with different amounts of catalyst by simply immersing the brushes in two different solutions, $60\ \mu\text{M}$ and $5\ \text{mM}$ PdCl_4^{2-} , for 10 min. After immersing both substrates in the Cu plating bath for 20

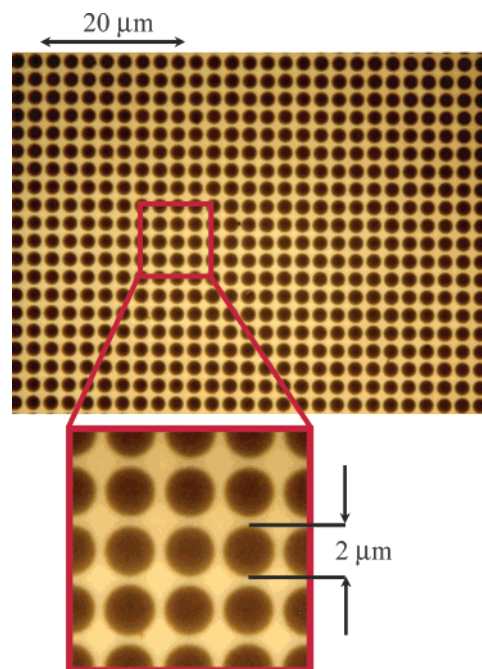


Figure 4. Optical microscope images showing the site-selective electroless deposition of Cu dots ($2\ \mu\text{m}$ in diameter) on patterned poly-METAC brushes grown on Au. The inset shows a magnification of the well-defined Cu dots grown on the Au substrate.

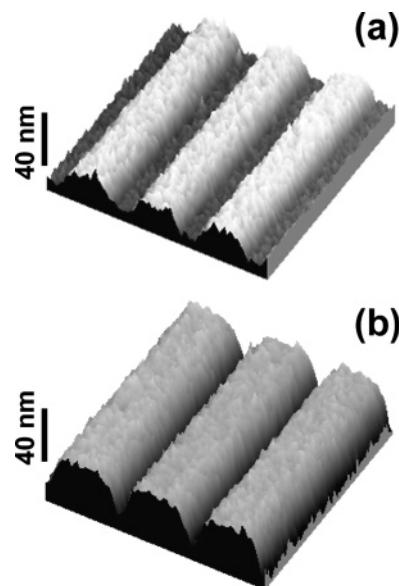


Figure 5. AFM images ($20 \times 20\ \mu\text{m}^2$) corresponding to patterned PMETAC brushes immersed during 10 min in (a) $60\ \mu\text{M}$ and (b) $5\ \text{mM}$ PdCl_4^{2-} and then placed in contact with the Cu electroplating bath for 20 s.

s, clear differences in the patterned grown films were observed, as evidenced by atomic force microscopy (Figure 5).

As expected, in the case of highly loaded PMETAC brushes, the copper films are thicker (39 nm) than in the case of scarcely loaded brushes (23 nm). This observation demonstrates the potential of brushes to control the amount of catalyst and in consequence the characteristics of the electroless plating process.

Subsequently, we checked the adhesion properties of the deposited films. Peel-off testing is a qualitative method that is commonly used as a tool to assess the strength of adhesion between deposited films and substrates.³² In our case, we firmly pressed Scotch tape into contact with the electrolessly deposited copper

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film and then peeled-off the adhesive tape at a nearly constant rate. The amount of metal transferred to the tape is a measure of the adhesive strength of the film. We used the peel-off test to evaluate the effectiveness of polyelectrolyte brushes as adhesion layers. We observed that 10–15 nm thick brushes show excellent adhesive properties as derived from the peel-off test after repeated experiments. This observation is based on the fact that after carrying out repeated times the peel-off test in the same sample no detectable amounts of the Cu film were transferred to the Scotch tape. It must be noted that in the absence of the PMETAC brush layer the copper films were always partially removed from the substrate after peeling off the tape. Delamination is one of the main problems of thin films deposited by electroless deposition. To further demonstrate the effectiveness of polymer brushes as anchoring layers, we deposited thin copper films on poly(dimethylsiloxane) (PDMS) surfaces modified with poly-METAC brushes. Peel-off tests revealed that the Cu film is firmly anchored to the PDMS substrate even after repeated bending of the elastomeric substrate following the peel-off test (see the Supporting Information for an optical image of the Cu-coated PDMS sample as well as a cross-section SEM image).

The excellent adhesion promotion of the polyelectrolyte brush interlayer could be associated to different factors: (a) the brush-like coating is a covalently bound layer thus enhancing the bonding to the substrate, (b) the quaternary ammonium moieties form ion

pairs with the catalyst, increasing the concentration of immobilized PdCl_4^{2-} species on the substrate, and (c) the brush layer involves a considerable number of anchoring groups per unit area.

Conclusions

In conclusion, polyelectrolyte brushes offer a valuable and unexplored tool for preconditioning substrates prior to electroless deposition. Surface-initiated polymerization provides a most versatile route to incorporate a large population of binding sites that can be applied on a large variety of substrates. The chemisorbed polyelectrolyte chains are obtained by using self-assembled initiator monolayers that can be microcontact printed on diverse surfaces. Moreover, microcontact printing provides the tool for the accurate patterning of these macromolecular architectures, thus leading to well-defined site-selective deposition of copper microstructures. This approach provides flexibility and control over the interfacial chemistry and the binding of catalyst species onto the functionalized surface.

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Supporting Information Available: Optical micrographs showing the bending of Cu films deposited on PDMS and scanning electron image of the Cu deposited on the PDMS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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