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A Novel Application of Alkanethiol Self-Assembled Monolayers in Nanofabrication: Direct Molding and Replication of Patterned Conducting Masters

P. L. Schilardi, O. Azzaroni, and R. C. Salvarezza*

*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA),
Universidad Nacional de La Plata - CIC - CONICET, Sucursal 4, Casilla de Correo 16,
(1900) La Plata, Argentina*

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The fabrication of nanostructures is one of the most relevant topics in modern technologies. Here, we present a new strategy that allows direct molding and replication of conducting patterns with sizes ranging from nanometers to millimeters. The method consists of metal electrodeposition on conducting substrates covered with an alkanethiol monolayer. This allows master molding and replication avoiding contact printing, masking, or photopatterning steps. The method is fast and inexpensive and requires only basic instrumentation available at any laboratory. The potential applications of this method are related to serial fabrication of nano/microstructured metallic architectures.

Introduction

Self-assembled monolayers (SAMs) of thiols on metals have attracted considerable scientific interest because they provide a method for creating well-defined surfaces with controllable chemical functionality.^{1,2} The possible applications of SAMs range from nanotechnology to fundamental surface science. SAMs can be used for prevention of corrosion,^{3–5} for modification of wetting and wear properties^{6–8} of solid surfaces, for development of nano-devices for electronics,⁹ and for pattern formation.^{10–12} In particular, by anchoring specific chemical groups to these molecular self-assemblies, well-ordered structures with controlled chemical features can be achieved for employment in molecular recognition,¹³ protein adsorption,¹⁴ and templates for crystallization of inorganic salts.¹⁵ Otherwise, the fabrication of nanostructures is one of the most relevant topics in modern technologies. Nanofabrication has been defined as a technique capable of generating structures with at least one lateral dimension between 1 and 100 nm.^{16,17} Nano/microfabrication is based mainly on photolithography,¹⁸ and its immediate implications are

related to the fabrication of microelectronic devices which have new architectures,¹⁹ biomimetic structures,²⁰ fiber optic communications,²¹ and microfluidic systems.²² The development of novel methods, in particular to build three-dimensional patterned microstructures, enables new options for microfabrication and creates the possibility of choosing the most convenient method by considering several factors such as complexity, cost, and elapsed time of fabrication.

Several strategies have been developed for fabricating micrometer- and nanometer-scale patterns.^{23–25} The method of fabrication often involves several steps of various degrees of complexity depending on the desired structure. In the case of patterned organic polymer surfaces using elastomeric masters,²⁶ intermediate steps include elastomer curing, peeling off, organic polymer curing, compressing, bending, and stretching. In the case of patterned metallic nano/microstructures, common intermediate stages are electroplating,²⁴ etching,²⁶ surface pretreatment, and electroless deposition.²⁷ In particular, micropatterned metal surfaces are considered very interesting in the electronic materials research field because of potential applications on printed wiring boards (PWB), magnetic recording materials, microwave conductors,

* To whom correspondence should be addressed: Dr. R. C. Salvarezza, INIFTA, Casilla de Correo 16, Sucursal 4, 1900, La Plata, Argentina. E-mail: robsalva@inifta.unlp.edu.ar.

- (1) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.
- (2) Flinkea, H. O. In *Electroanalytical Chemistry*; Bard, A. J., Rubinstein, I., Eds.; Marcel Dekker: New York, 1996; Vol. 19, pp 109–335.
- (3) Jennings, G. K.; Munro, J. C.; Yong, T.-H.; Laibinis, P. E. *Langmuir* **1998**, *14*, 6130.
- (4) Zamborini, F. P.; Crooks, R. M. *Langmuir* **1998**, *14*, 3779.
- (5) Boubour, E.; Lennox, R. B. *Langmuir* **2000**, *16*, 4222.
- (6) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7164.
- (7) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 1990.
- (8) Laibinis, P. E.; Nuzzo, R. G.; Whitesides, G. M. *J. Phys. Chem.* **1992**, *96*, 5097.
- (9) Haag, R.; Rampi, M. A.; Holmlin, R. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 7895.
- (10) Geissler, M.; Bernard, A.; Bietsch, A.; Schmid, H.; Michel, B.; Delamarche, E. *J. Am. Chem. Soc.* **2000**, *122*, 6303.
- (11) Moffat, T. P.; Yang, H. *J. Electrochem. Soc.* **1995**, *142*, L220.
- (12) Xia, Y.; Kim, E.; Mrksich, M.; Whitesides, G. M. *Chem. Mater.* **1996**, *8*, 601.
- (13) Chailapakul, O.; Crooks, R. M. *Langmuir* **1993**, *9*, 884.
- (14) Kidoaki, S.; Matsuda, T. *Langmuir* **1999**, *15*, 7639.
- (15) Küther, J.; Seshadri, R.; Nelles, G.; Assenmacher, W.; Butt, H.-J.; Mader, W.; Tremel, W. *Chem. Mater.* **1999**, *11*, 1317.

- (16) Xia, Y.; Rogers, J. A.; Paul, K.; Whitesides, G. M. *Chem. Rev.* **1999**, *99*, 1823.
- (17) Smith, H. I.; Craighead, H. G. *Phys. Today* **1990**, *24*.
- (18) Moreau, W. M. In *Semiconductor Lithography*; Plenum Press: New York, 1988.
- (19) Lent, C. S.; Tougaw, P. D.; Porod, W.; Bernstein, G. H. *Nanotechnology* **1993**, *4*, 49.
- (20) Golpel, W. *Biosens. Bioelectron.* **1995**, *10*, 35.
- (21) Lin, L. Y.; Goldstein, E. L.; Tkach, R. W. *IEEE J. Sel. Top. Quantum Electron.* **1999**, *5*, 4.
- (22) Unger, M. A.; Chou, H.-P.; Thorsen, T.; Scherer, A.; Quake, S. R. *Science* **2000**, *288*, 113.
- (23) Xia, Y.; Kim, E.; Zhao, X.-M.; Rogers, J. A.; Prentiss, M.; Whitesides, G. M. *Science* **1996**, *273*, 347.
- (24) Jackman, R. J.; Brittain, S. T. A.; Adams, A.; Prentiss, M. G.; Whitesides, G. M. *Science* **1998**, *280*, 2089.
- (25) Huck, W. T. S.; Tien, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1998**, *120*, 8267.
- (26) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.
- (27) Hidber, P. C.; Helbig, W. H.; Kim, E.; Whitesides, G. M. *Langmuir* **1996**, *12*, 1375.
- (28) Dulcey, C. S.; Georger, J. H., Jr.; Krauthamer, V.; Stenger, D. A.; Fare, T. L.; Calvert, J. M. *Science* **1991**, *252*, 551.
- (29) Dressick, W. J.; Calvert, J. M. *Jpn. J. Appl. Phys.* **1993**, *32*, 5829.

contact materials, display devices, and optical disks.²⁸ In some cases, nano/microfabrication has been made by patterning the substrate with self-assembled thiol monolayers by using contact printing or photopatterning.²⁹ The printed pattern can protect the underlying substrate, acting as a mask against etchants or for metal deposition.¹¹ Recently, Ag films covered by patterned SAMs formed by microcontact printing have been used to fabricate thin film transistors.³⁰

Electrodeposition is used to produce materials and architectures that cannot be built by traditional techniques. By means of this method, different materials such as nanometer-scale crystallites,³¹ nanocomposites,³² epitaxially deposited metal films,³³ compositional superlattices,³⁴ and ceramic materials³⁵ have been prepared. Electrodeposition is an intrinsically fast technique which is compatible with patterning and large-scale production.

Here, we report a new application of self-assembled alkanethiol monolayers that enables an easy way to mold and replicate patterned conducting surfaces in the nanometer range. The method consists of metal electrodeposition onto a conducting patterned master that is previously derivatized with an alkanethiol self-assembled monolayer. In our procedure, the inner face of the electrodeposited sample is the mold of the master. By a change of the electrodeposition time, the thickness of the mold can vary from micrometer to millimeter range to obtain a desired mechanical stability. After the preset thickness has been reached, the mold spontaneously detaches or it is easily removed from the master. Once the metallic mold is obtained, it is derivatized again with a SAM and a new metal electrodeposit is grown on it. After the metal film is detached, a replica of the master is obtained on the inner face of the electrodeposit. *In contrast to other methods for molding and replication of nanometer and submicrometer architectures that involve either contact printing, masking, or photopatterning, our method requires only a simple immersion of the masters on the alkanethiol "ink".* A scheme showing the steps to fabricate a mold and a replica of a given pattern by using our method is shown in Figure 1.

We organize the paper in the following sequence. First, we show that Cu films can be electrodeposited on Cu derivatized with a SAM of alkanethiol and that these films exhibit interesting properties; they replicate substrate features and can be easily removed. Then, we demonstrate by using scanning tunneling microscopy (STM) that the same procedure can be used to fabricate mechanically stable molds and replicas of Cu masters with features in the nanometer range. Finally, we discuss the physical chemistry involved in our method.

Experimental Section

Two different types of Cu substrates were used: (i) alumina polished and etched in 10% H₂SO₄ solution to remove oxide film and (ii) Cu grids with fresh (oxide free) surfaces prepared by

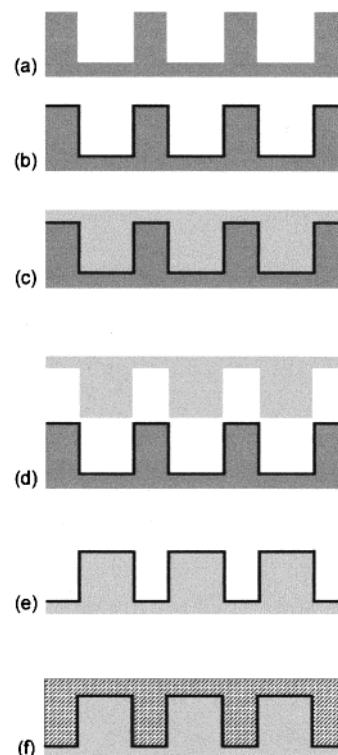


Figure 1. Scheme showing the different steps involved in molding and replication: (a) micropatterned conducting master (dark gray area); (b) micropatterned conducting master derivatized with an alkanethiol monolayer (black line, not in scale); (c) electrodeposit (light gray area) grown on the derivatized conducting master; (d) detachment of the electrodeposit, where the inner face is a mold of the master; (e) derivatized mold with an alkanethiol monolayer (black line, not in scale); (f) electrodeposit (hatched area) grown on the derivatized mold; (g) detachment of the electrodeposit, the inner face is a replica of the micropatterned conducting master.

electrodeposition of 10 monolayers from an acid plating bath containing thiourea as described below. After preparation, these Cu substrates were immediately derivatized by immersion for a time $t_a = 1$ h in a toluene solution containing 5 mM dodecanethiol. The exposure time of the Cu substrates to the atmosphere before immersion was less than a few seconds. It has been observed that under this experimental condition copper oxide formation is negligible.³⁶ This procedure results in the formation of a dodecanethiol monolayer on Cu.^{37,38} After the monolayer was formed, a Cu substrate was used as the working electrode of a conventional three-electrode glass electrochemical cell with a large Cu plate and a copper wire immersed in the electrolyte solution as counter and reference electrodes, respectively. Cu electrodeposition was made from a nitrogen saturated plating bath containing either aqueous 0.6 M CuSO₄·5H₂O + 0.5 M H₂SO₄ or aqueous 0.6 M CuSO₄·5H₂O + 0.5 M H₂SO₄ + 0.025 mM thiourea at 298 K at a current density of 20 mA cm⁻², equivalent to 30 monolayers s⁻¹.³⁹ Note that this current density is lower than the limiting current density calculated from the free-convective diffusion mass transport equation and the electrodeposition reaction is under charge-transfer control. Under these experimental conditions, deposition from the plating bath containing thiourea results in smooth Cu deposits consisting of nanometer-sized grains. Ex situ STM imaging was made using a Nanoscope III STM (Digital Instruments, Inc.). Images were taken in the constant current mode. Typical set point currents

(28) *Electrochemical Technology-Innovations and New Developments*; Masuko, M., Osaka, T., Ito, Y., Eds.; Gordon and Breach Publishers: Amsterdam, 1996.

(29) Tarlov, M. J.; Burgess, D. R. F.; Gillen, G. *J. Am. Chem. Soc.* **1993**, *115*, 5305.

(30) Rogers, J. A.; Tate, J.; Li, W.; Bao, Z.; Dodabalapur, A. *Isr. J. Chem.*, in press.

(31) Lu, L.; Sui, M. L.; Lu, K. *Science* **2000**, *287*, 1463.

(32) Switzer, J. A.; Hung, H.-J.; Bohannon, E. W.; Shumsky, M. G.; VanAken, D. C. *Adv. Mater.* **1997**, *9*, 334.

(33) Yang, F. Y.; Liu, K.; Hong, K.; Reich, D. H.; Searson, P. C.; Chien, C. L. *Science* **1999**, *284*, 1335.

(34) Switzer, J. A.; Shane, M. J.; Phillips, R. P. *Science* **1990**, *247*, 444.

(35) Switzer, J. A.; Shumsky, M. G.; Bohannon, E. W. *Science* **1999**, *284*, 293.

(36) Ron, H.; Cohen, H.; Matlis, S.; Rappaport, M.; Rubinstein, I. *J. Phys. Chem. B* **1998**, *102*, 9861.

(37) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022.

(38) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 1990.

(39) Schilardi, P. L.; Mendez, S.; Salvarezza, R. C.; Arvia, A. J. *Langmuir* **1998**, *14*, 4308.

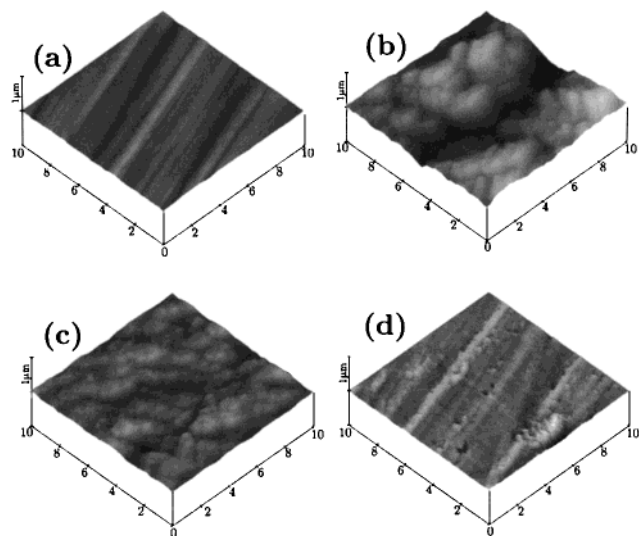


Figure 2. $10\ \mu\text{m} \times 10\ \mu\text{m}$ STM images of the polished Cu substrate (a); electrodeposited Cu from $0.6\ \text{M}\ \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 0.5\ \text{M}\ \text{H}_2\text{SO}_4$, electrodeposition time 9 min (b); inner face of electrodeposited Cu from $0.6\ \text{M}\ \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 0.5\ \text{M}\ \text{H}_2\text{SO}_4$, electrodeposition time 9 min (c); inner face of electrodeposited Cu from $0.6\ \text{M}\ \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 0.5\ \text{M}\ \text{H}_2\text{SO}_4 + 0.025\ \text{mM}$ thiourea, electrodeposition time 9 min (d).

and bias voltages were 1 nA and 0.1 V, respectively. Lithography on dodecanethiol-covered Cu was made using a set point current of 5 nA and a bias voltage of 0.05 V. Commercial Pt–Ir nanotips were used for STM imaging and lithography.

Results and Discussion

STM images of a polished Cu substrate derivatized with a dodecanethiol monolayer for $t_a = 1\ \text{h}$ and a Cu electrodeposit grown on it from $0.6\ \text{M}\ \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 0.5\ \text{M}\ \text{H}_2\text{SO}_4$ aqueous solution are shown in Figure 2a,b. As already reported,³⁹ the electrodeposit surface consists of Cu grains that form an irregular surface (Figure 2b). Following the time (t) dependence of the root-mean-square roughness (W), the growth mode of the deposit can be elucidated.⁴⁰ We have found that W increases with time as $W \propto t^\beta$ with $\beta = 0.7$. The growth exponent β is the same as that previously obtained for Cu electrodeposition on nonderivatized Cu substrates.³⁹ It means that the growth mode of the Cu deposit does not change under the presence of the SAM. However, the electrodeposited Cu samples spontaneously detach, or they are easily removed from the Cu substrate with tweezers without deformations. The easy detachment of the Cu deposits is not observed when electrodeposition is made on nonderivatized Cu substrates, indicating that it is related to the presence of the dodecanethiol SAM. Similar results were obtained from the same plating bath using a derivatized Au(111) as substrate. After detachment, the inner face of these electrodeposits, that is, the face in contact with the derivatized Cu substrate, also shows an irregular surface consisting of Cu grains of different sizes (Figure 2c). On the other hand, when Cu electrodeposition is made from the plating bath containing 0.025 mM thiourea, the growth mode of the Cu deposits is changed, leading to smoother Cu films. The grain size is much smaller, and the material is preferentially deposited at valleys rather than at protrusions.⁴¹ In this case, after detachment the inner face of the electrodeposit resembles the morphology of the

derivatized Cu substrate, reproducing its polishing lines (Figure 2d). These facts, substrate replication and easy detachment from the substrate, open the possibility for direct molding and replication.

The capability of the method to produce samples with a desired pattern in the nanometer/micrometer range is demonstrated by pattern formation using a copper grid as a master. The grid consists of 500 nm wide Cu rows separated by 900 nm wide and 90 nm deep channels, as shown in the STM image and cross section (Figure 3a,b). The master was then subjected to the procedure indicated in Figure 1. After deposition of a $7\ \mu\text{m}$ thick Cu film from $0.6\ \text{M}\ \text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 0.5\ \text{M}\ \text{H}_2\text{SO}_4 + 0.025\ \text{mM}$ thiourea, the copper sample was easily removed from the Cu master with tweezers. The STM image of the inner face (Figure 3c,d) of the $7\ \mu\text{m}$ thick electrodeposited Cu film now shows a pattern consisting of 900 nm wide Cu rows separated by 500 nm wide and 90 nm deep channels; that is, this face is a mold of the original Cu grid master.

To obtain replicas, this mold is again derivatized with the SAM, and then a Cu electrodeposit is grown following the same procedure described above. After removing the electrodeposited film from the mold, STM imaging of the inner face shows a replica of the original grid master (Figure 3e,f). We have made many (more than 20) Cu, Ni, and polymer replicas using the same Cu mold without modification of the mold architecture.⁴² This means that the wear of master caused by replica removal is not significant, possibly because of the high mechanical stability of the Cu mold.

Now, we focus on the mechanism involved in our procedure. Recently, there has been an increasing interest in studying metal electrodeposition on conducting surfaces covered by alkanethiol monolayers.⁴³ However, at present little is known about the growth mode and properties of metal films deposited on these modified surfaces. In fact, adsorbed molecules can modify the local deposition rate, can be buried into the bulk deposit,⁴⁴ or can float on the growing surface.^{45,46} The understanding of the surface structure and dynamics of adsorbates is a crucial point to control the growth of metal surfaces with a desired architecture. In a recent work, we have found that when Cu electrodeposition is made on a Cu electrode covered by a dodecanethiol SAM, nucleation of the depositing material takes place only at defective sites, allowing the growth of isolated crystals outward.⁴⁷ The dodecanethiol SAM remains buried.⁴⁴ Therefore, we propose that the initial step (Figure 4a,b) is the growth of metal nuclei outward, forming nanometer columns.^{47,48} The column width should be close to the defect size in the SAM, which is in the nanometer range, and its maximum height should be close to the molecular length, that is, $\approx 1.7\ \text{nm}$ for dodecanethiol monolayers.⁴⁹ After the column tips reach the outer limit of the SAM, they can coarsen, closely following the substrate morphology as schematically shown in Figure

(42) Azzaroni, O.; Schilardi, P. L.; Salvarezza, R. C. In preparation.

(43) Hagenström, H.; Schneeweiss, M. A.; Kolb, D. M. *Langmuir* **1999**, *15*, 7802.

(44) Eliadis, E. D.; Nuzzo, R. G.; Gewirth, A. W.; Alkire, R. C. *J. Electrochem. Soc.* **1997**, *144*, 96.

(45) Camarero, J.; Ferrón, J.; Cros, V.; Gómez, L.; Angel de Parga, A. L.; Gallego, J. M.; Prieto, J. E.; de Miguel, J. J.; Miranda, R. *Phys. Rev. Lett.* **1998**, *81*, 850.

(46) Sieradzki, K.; Brankovic, S. R.; Dimitrov, N. *Science* **1999**, *284*, 138.

(47) Schilardi, P. L.; Azzaroni, O.; Salvarezza, R. C. *Phys. Rev. B* **2000**, *62*, 13098.

(48) Sondag-Huethorst, J. A. M.; Fokink, L. G. J. *Langmuir* **1995**, *11*, 4823.

(49) Kondo, T.; Yanagida, M.; Shimazu, K.; Uosaki, K. *Langmuir* **1998**, *14*, 5656.

(40) Barabási, A.-L.; Stanley, H. E. In *Fractal Concepts in Surface Growth*; Cambridge University Press: New York, 1995.

(41) Vázquez, L.; Salvarezza, R. C.; Arvia, A. J. *Phys. Rev. Lett.* **1997**, *79*, 709.

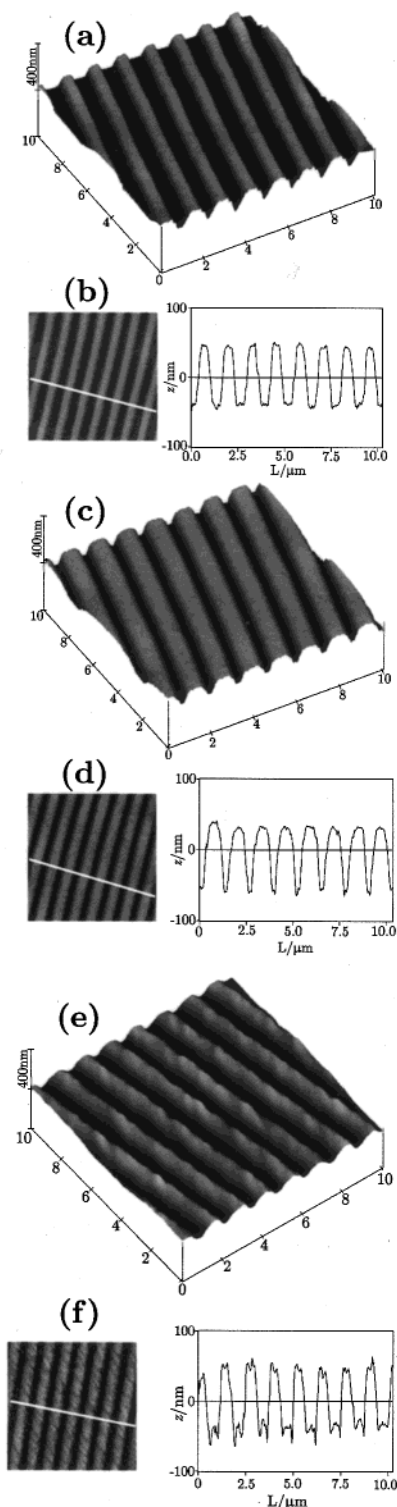


Figure 3. $10\ \mu\text{m} \times 10\ \mu\text{m}$ STM image of the micropatterned Cu master grid (a) and cross section (b); $10\ \mu\text{m} \times 10\ \mu\text{m}$ STM image of the Cu mold obtained after electrodeposition and detachment from the derivatized Cu master grid (c) and cross section (d); $10\ \mu\text{m} \times 10\ \mu\text{m}$ STM image of the micropatterned Cu replica after electrodeposition and detachment (e) and cross section (f).

4c–e. The presence of thiourea (TU) in the plating bath plays a key role in our method. In fact, TU molecules adsorb at the tip of the growing columns, enhancing lateral growth.^{39,41} This results in smooth films required for molding and replication. Besides, as shown in Figure 2 the average grain size (d) in the presence of TU (Figure

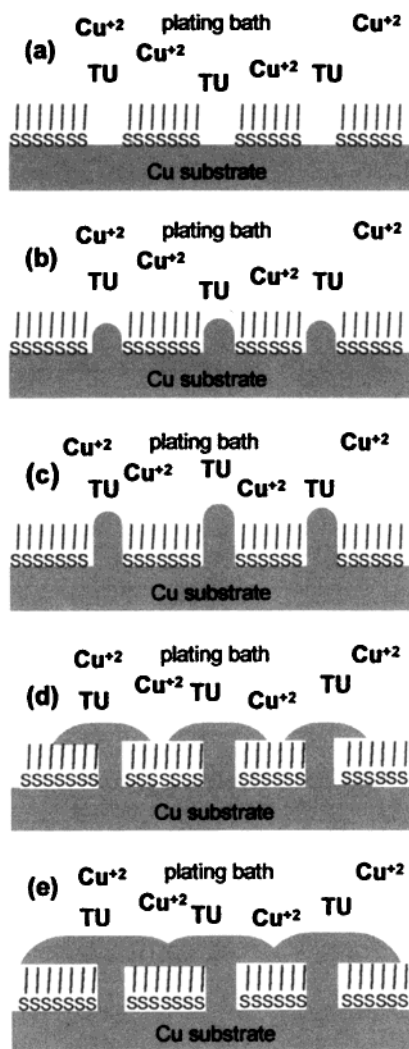


Figure 4. Scheme showing the steps involved in Cu electrodeposition on a derivatized Cu substrate: (a) The derivatized substrate in contact with the plating bath. Defects of the SAM are shown. (b) Cu crystals are formed at the defective sites of the SAM. The crystals grow outward. (c–e) The presence of thiourea (TU) molecules in the bath enhances lateral growth leading to smooth and flat metal films.

2d) is $d = 50\ \text{nm}$, much smaller than $d = 500\ \text{nm}$ produced in the plating bath without TU (Figure 2c). The value of d of the Cu deposit grown in the presence of TU allows the replication of nanometer-sized features. The decrease in grain size has been assigned to a decrease in the diffusion length of Cu adatoms because of the adsorption of the organic additive at the Cu surface.⁴¹ Detailed studies on the effect of TU in Cu deposit morphology have been reported.^{39,41,47} The experimental conditions indicated in this work can be considered as the optimum conditions for molding and replication of Cu nanostructures in the case of SAM-modified Cu electrode.

The deposited sample is connected to the substrate only by the nanometer-sized columns. They can be easily broken, allowing the detachment of the deposit; that is, the deposit adherence has been dramatically decreased. This poor adherence is an interesting interfacial property of metal electrodeposits on SAMs that is exploited in our method for molding and replication purposes. This phenomenon is not unexpected because SAMs act as a lubricant/antistick layer. Contact angle measurements show that the SAM remains on the derivatized electrode surface (the master or the mold) because of the strong

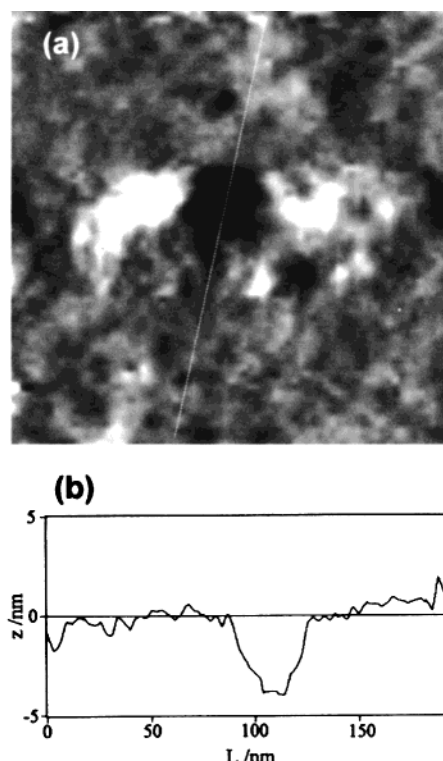


Figure 5. STM image and cross section of a Cu substrate derivatized for $t_a = 2$ days after detachment of an electrodeposited Cu film. The $25 \times 25 \text{ nm}^2$ black window at the central part of the image was produced by repetitive scanning of the STM tip on this area that removed the dodecanethiol multilayer.

binding energy that exists between the S atom of the alkanethiol head and the Cu surface. Also, we have verified it by derivatizing the Cu master for $t_a = 2$ days. In this case, a multilayer is formed on the metal surface. After Cu electrodeposition and film detachment, the master surface was imaged with STM. Repetitive STM scanning over a given area of the master results in window formation due to the removal of the alkanethiol multilayer by the tip (Figure 5). When the inner face of the electrodeposited metal film in contact with the master was subjected to the same procedure, no window formation was observed. These results also demonstrate that the alkanethiol layer

remains absorbed on the derivatized metal surface. In principle, it should be expected that multilayer formation should frustrate the plating process. However, the fraction of the surface covered by defects, that is, the fraction of the Cu surface exposed to the plating bath, decreases only from 1.7×10^{-2} to 4.8×10^{-3} as t_a increases from 1 to 16 h.⁵⁰ Then, the defect density decreases very slowly with the adsorption time. Therefore, even for a long adsorption time there are enough defects in the dodecanethiol multilayer to allow Cu electrodeposition. As mentioned above, electrodeposition from the plating bath is possible even on derivatized Au(111) substrates where the density of defects is expected to be much lower than that present on Cu. As expected, the decrease in the defect number favors the sample detachment but hinders the replication process because the growth centers are very separated. Note that the best condition for molding and replication involves $t_a = 1$ h; that is, the fraction of Cu substrate noncovered by dodecanethiol is $\approx 2\%$.

In conclusion, we have exploited novel and interesting interfacial properties of alkanethiol self-assembled monolayers, in reference to electrodeposit adherence, to develop a new, fast, and inexpensive electrochemical method that enables molding and replication of nanopatterned masters with immediate implementation to greater scales. Their potential applications are closely related to serial fabrication of nano/microstructured metallic architectures. The elapsed time of replication is about 2 h, and no hazardous reagents are involved in the preparation. This procedure is easily carried out using basic electrochemical instrumentation available at any laboratory. One of the outstanding advantages of this method is the possibility of replicating nano/micropatterned metallic structures in an extremely easy way with very few intermediate steps. Note, however, that our method is focused on molding and replication, so the complete nanofabrication process requires the fabrication of the master through some lithographic process.

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(50) Azzaroni, O.; Cipollone, M.; Vela, M. E.; Salvarezza, R. C. *Langmuir*, **2001**, *17*, 1483.