Electroforming of Copper Structures at Nanometer-Sized Gaps of Self-assembled Monolayers on Silver

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This paper describes a method to fabricate micro- and nanostructures of copper by electrodeposition onto nanometer-sized gaps in self-assembled monolayers (SAM) of alkanethiolates on metal surfaces. We have demonstrated that the approach can produce large numbers of metallic micro- or nanostructures over large (2 cm^2) areas with features as small as ≈70 nm. The electrodeposited copper structures can be transferred using Scotch tape onto both flat and curved substrates. Linear arrays of copper structures have been tested for use as optical polarizers. A polarization ratio $R = \approx 2.0$ was found for light with $\lambda = 633$ nm in transmission mode for linear arrays of copper wires (≈220 nm, with a 1-μm pitch) mounted on antireflective windows.

Introduction

This paper describes a method for electrodepositing submicrometer copper structures onto ≈5-nm-sized gaps in self-assembled monolayers (SAM) of alkanethiolates at the edges of topographically patterned metal surfaces. The gaps provide an initial template on which copper structures with critical dimensions as small as ≈70 nm can be produced simultaneously. These copper structures can be stripped from the structures on which they are generated and transferred onto flexible polymeric supports using Scotch tape. The process can be repeated multiple times with the same template.

Methods of fabrication for producing structures with critical dimensions <100 nm are an important part of current efforts to extend the progress of miniaturization in microelectronics, nanoscience, and nanotechnology.[1] The most extensively developed methods for making sub-100-nm structures include electron-beam (e-beam) lithography, proximity X-ray lithography, and extreme ultraviolet (EUV) lithography,[2,3] although conventional photolithography is also being extended to surprisingly small structures. The fabrication costs are typically very high for these approaches and the equipment is not universally accessible to the research laboratories. A range of unconventional methods—including “dip-pen” nanolithography,[4−6] nanoscribing,[7−11] nanoimprint lithography,[12,13] step-and-flash lithography,[14−16] near-field optical lithography,[17] and topographically direct etching (TODE)[18,19]—have been demonstrated for nanometer-sized structures.[2,20]

“Edge lithography” is the collective name for a class of techniques that use topographic edges in the fabrication of small features. A two-step process converts the original edges from a pattern generated by conventional photolithography to a structure on the surface that outlines the edges of the original pattern. Edge lithography includes near-field phase-shifting photolithography,[17] maskless lithography using embossed photoresist as its own optical element,[21] controlled undercutting,[22] and TODE.[18] TODE uses the defects of SAMs on metallic or silicon surfaces in the fabrication of struc-

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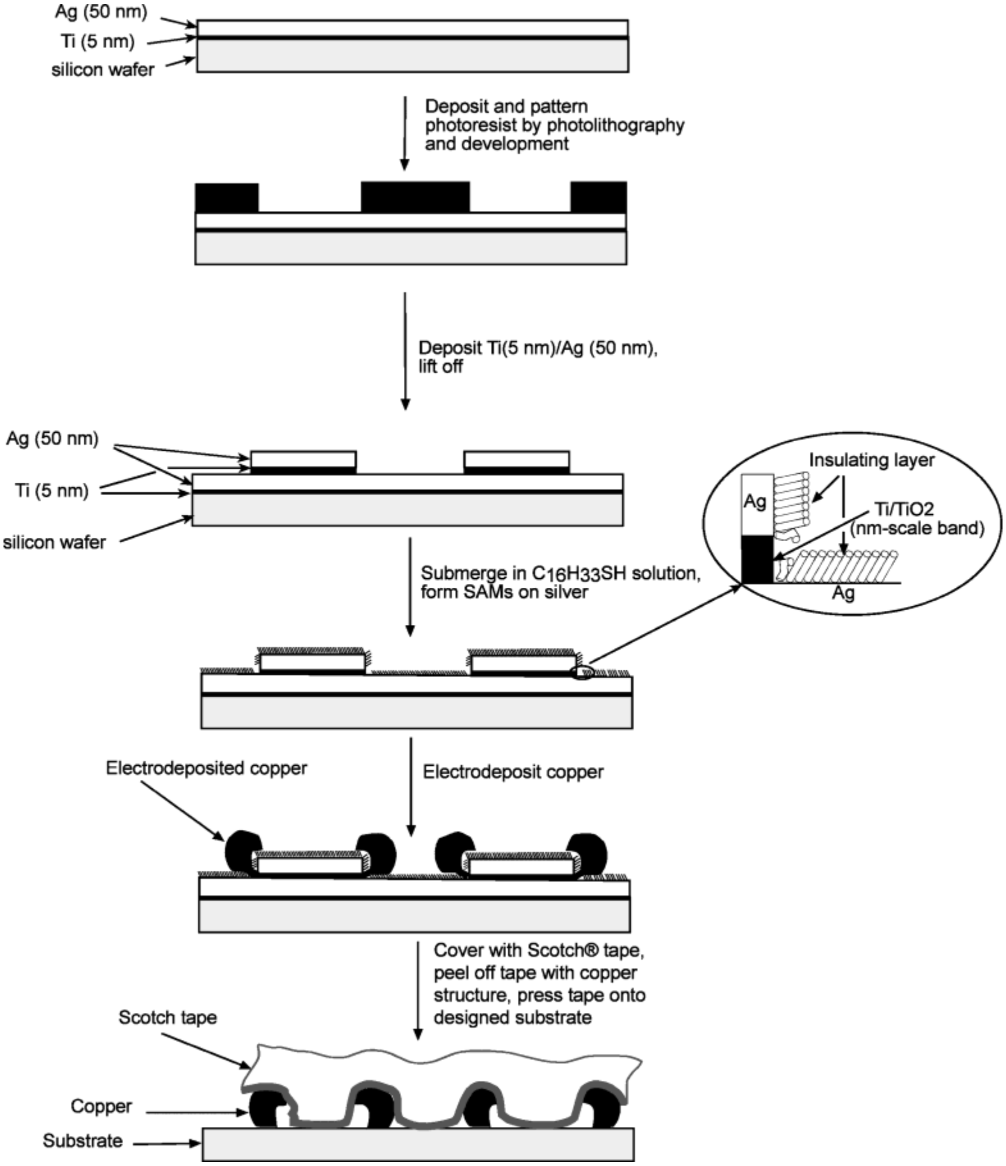

Figure 1. Schematic illustration of procedures for the electroforming of copper structures and the transfer onto solid supports.

tures composed of different materials—for example, metals and minerals.[19,23] Regions of disorder in the SAM at the edges of topographically patterned silver provide initiation sites for etching and crystal growth. Trenches in silver with lateral dimensions as small as ≈50 nm have been demonstrated using this approach.

The procedure described here is derived from TODE, but has an important difference. In TODE, the topography required is formed by depositing silver through windows (photolithographically defined gaps) in photoresist onto a silver substrate. In this work, we formed a topographically structured substrate with a thin titanium layer between a patterned silver layer and a planar silver substrate. The titanium layer has a thickness of a few nanometers. When this system is dipped into a solution, SAMs of alkanethiolates form on silver, but not on titanium (Figure 1). The exposed Ti/TiO_2 layer serves as a nanoelectrode upon which metal can be deposited. This approach is similar to recent work by Penner and co-workers[24,25] for electrodepositing metallic structures at the edges of the planes of graphite. The topographically structured substrates used here define the shape in addition to the size of the structures generated.

Copper is a metal that has been widely used in the electronics industry because of its high electrical conductivity and low cost. Electrodeposition of copper is one of the most important methods for fabricating printed circuit boards.[26] The introduction of copper interconnects into advanced integrated circuits has intensified the study of copper metallization.[27,28] In this paper, we demonstrate the fabrication of micro- and nanostructures of copper by electrodeposition at the edges of the patterned titanium nanoelectrodes.

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Experimental Section

Materials. Copper pyrophosphate plating solution (Technic Copper P solution) was purchased from Technic Inc., Cranston, RI (www.technic.com). This solution (130 mL) was passed through a filter with an average pore size of 0.2 μm and diluted with deionized water (250 mL) before use. Hexadecanethiol (92+%, technical grade) was purchased from Aldrich and used without further purification. Silicon wafers (test grade, Si ⟨100⟩, p- or n-type) were from Silicon Sense, Nashua, NH (www.siliconsense.com). Photoresist, Shipley 1805, and hexamethyldisilazane primer were from MicroChem Corp., Newton, MA (www.microchem.com).

Fabrication of Topographically Patterned SAM. Figure 1 summarizes the process used for the fabrication of copper microstructures on polymeric tapes. We made the silver substrates by first evaporating 5 nm of titanium followed by 50 nm of silver using electronic beam deposition. The primer and photoresist (Shipley 1805) were then spin-coated on the silver substrate at a spin rate of 4000 rpm. The photoresist-coated substrates were baked at 105 °C for 3.5 min and cooled to room temperature. We exposed the photoresist to ultraviolet light through a chrome mask and developed the patterns in a developing solution (5:1 water:Developer 351, Shipley). After making the photoresist patterns, we deposited titanium or chromium, typically ≈5-nm thick, onto the patterned photoresist and exposed silver surface followed by a second layer of silver (30−50-nm thick). The photoresist was then removed by sonicating the substrate in an acetone bath for 2−5 min. The topographically patterned metallic substrate was rinsed thoroughly using acetone and methanol and then placed in a solution of hexadecanethiol (≈1 mM) in methanol for >4 h. The substrate was removed from the ethanolic solution, rinsed thoroughly with ethanol, and dried under a stream of nitrogen.

Electrodeposition of Copper on Patterned Substrates. The substrate coated with SAM was cut into a small piece with a dimension of ≈$^1/_4 \times {}^3/_4$ in. and submerged in a plating bath for copper. We used the commercial plating solution of copper pyrophosphate diluted with deionized water by a factor of about 2. The temperature of this plating solution was raised to ≈55 °C under a moderate stirring rate (200−250 rpm). The time for electroplating varied from 20 s to a few minutes.

The exposed regions of the titanium or chromium adhesion layers on the SAM-patterned silver substrate served as the cathode for electrodeposition. We used an alligator clip to create an electrical contact between the SAM-coated electrode and the power source. The deposition was conducted in air under potentiostatic conditions with a typical voltage of ≈0.53 V. The substrates were washed with deionized water (≈100 mL) after the deposition.

Transfer of Copper Structures onto Solid Supports. The electroplated structures could be removed by Scotch tape and transferred onto solid supports. Alternatively, the copper structures could be embedded in thermally or photo-curable prepolymers, such as poly(dimethylsiloxane) (Sylgard 184, Dow Corning, Midland, MI; www.dowcorning.com) and polyurethane precursors (Norland Optical Adhesive, NOA). In this study, we used Scotch tape to transfer the copper structures onto a solid support. In this approach, we cut tape into an area slightly larger than that of electroplated structures. We then pressed this piece of tape firmly onto the electrodeposited structures of copper and removed the tape together with patterned structures of copper carefully from the SAM-coated substrate of silver. The patterned structures of copper on the tape could be transferred onto a variety of solid substrates such as glass rods, silicon wafers, and antireflective windows.

Results and Discussion

In this method, the SAM coating on the silver acts as an electronic insulating layer and prevents copper from depositing onto those regions. We have demonstrated earlier that the disorder of SAMs at sharp steps on metals is sufficient to generate ≈50-nm trenches in silver using wet chemical etching.[18,19] In this study, however, we did not observe selective copper deposition on the localized regions of disorder in a SAM on a silver substrate when there was no titanium layer between the silver film and the patterned silver overlayer. We did observe the localized nucleation and electrodeposition of copper when using a substrate in which a titanium/titania layer was between the silver substrate and patterned silver overlayer (Figure 1). This observation suggests that disorder in the alkanethiolate SAM on silver is not sufficient to initiate electrodeposition of copper on those regions selectively. We believe that the electrodeposition occurs at the bare edges of the thin film of Ti/TiO_2 and suggest that the nanometer-sized titanium electrode is a more suitable surface for initiating electrodeposition than a step in a topographically patterned homogeneous material. Our preliminary study showed no obvious difference in copper electrodeposited using titanium and chromium as the interposed layer.

Figure 2 shows field emission scanning electron microscope (FE-SEM) images of copper microstructures prepared by electroplating and stripping four consecutive times on the same patterned metal substrate after the treatment with thiol solution. After each deposition, the copper pattern was removed from the substrates using Scotch tape. The copper was first deposited on the edges of the steps as discontinuous single crystals or as polycrystals (Figure 2a). The structures produced in each subsequent cycle of electroforming and removal are continuous, as shown in Figure 2b−d. Submicrometer single crystals of copper were sometimes observed in regions away from the topographical edges. This observation suggests that defects in the SAM[29] could initiate electrodeposition as well.

Figure 3 shows the transition of the morphologies of the electrodeposited structures from isolated nanocrystals to continuous linear features of copper as a function of plating time. These data suggest that wire does not nucleate uniformly across the length of the exposed electrode. These discontinuities in the structure limit the minimum feature size of the continuous wires. The smallest continuous structures we observed had critical dimensions of ≈70 nm.

We infer (without firm experimental support) that the morphologies of the deposited copper depend on the uniformity of the titanium or TiO_2 surface exposed along the patterned edges.[30] Repeated electrochemical cycling of the electrode may remove adventitious material adsorbed to the Ti/TiO_2 electrode. The shapes of the crystallites could also depend on the compositions of the plating solutions, especially the organic additives.[26,31,32] We used the same substrates (masters) multiple times (up to ten) to replicate the electrodeposited structures of copper. Our observation indicates that the electroplating and removal of the copper structures did not cause severe damage to the patterned silver.

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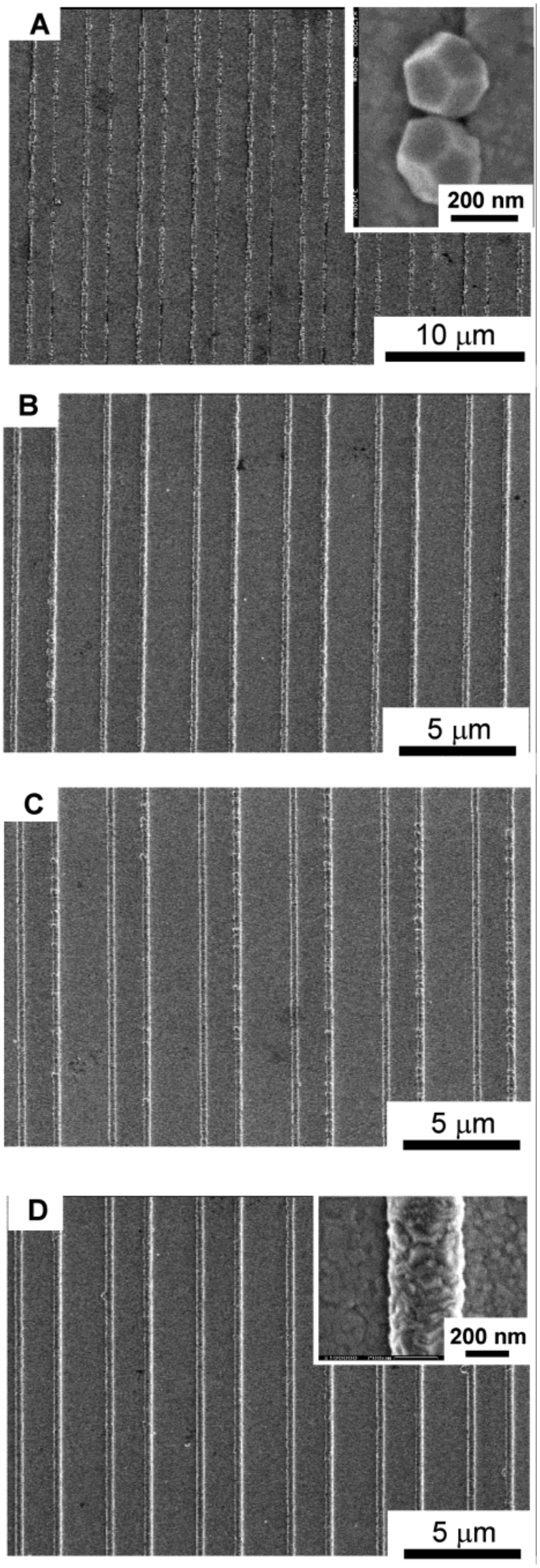

Figure 2. Field emission SEM images of electrodeposited linear arrays of copper at the edges of steps of 2 × 2 *μ*m linear arrays of SAM-coated metal features: The electroplating was conducted at 530 mV with a duration of about 2 min on the same substrate; (a) first deposition, (b) second deposition, (c) third deposition, and (d) fourth deposition.

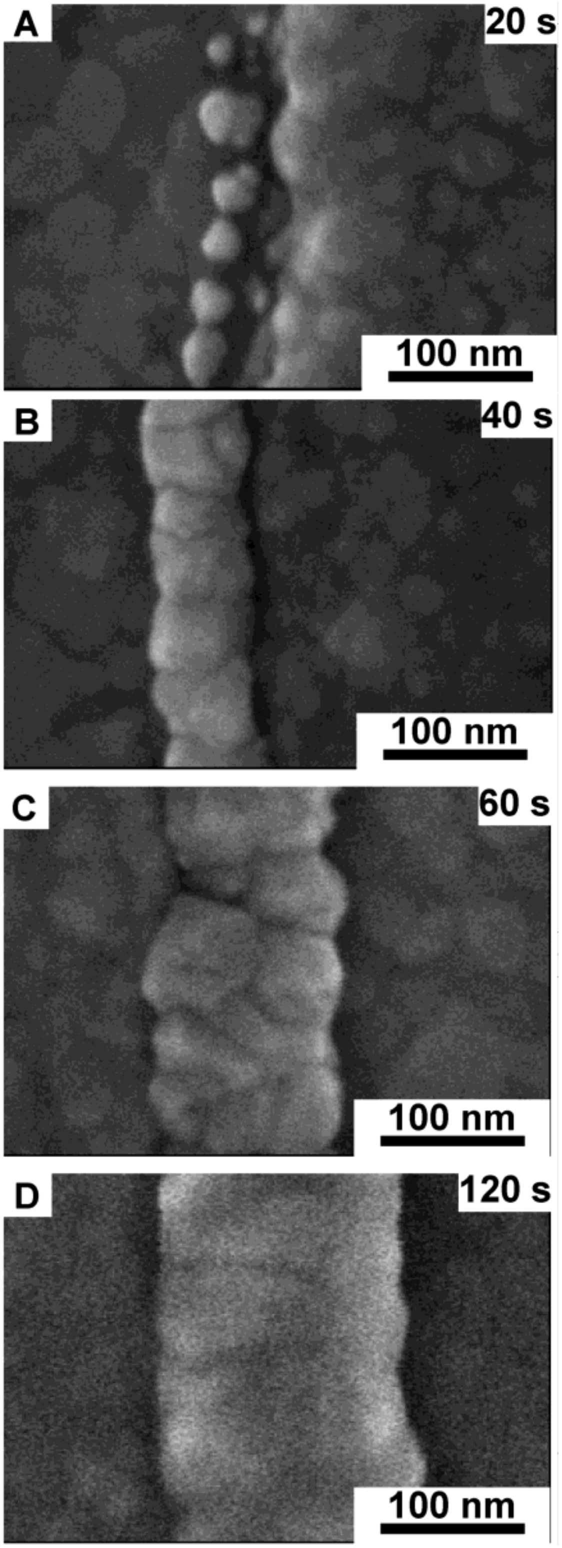

Figure 3. FE-SEM images of electrodeposited linear arrays of copper at the edges of steps of 2 × 2 *μ*m linear arrays of SAM-coated metal features after plating at a potential of ≈530 mV and a temperature of ≈55 °C for (a) 20 s, (b) 40 s, (c) 60 s, and (d) 120 s.

Versatility of the Fabrication Method. The critical dimensions achieved in the copper structures, ranging from sub-100 nm to micrometers, can be controlled by the rate and time of plating. Figure 4a shows arrays of copper lines with lateral dimensions of 70 nm. Only electroformed copper lines with lateral dimensions

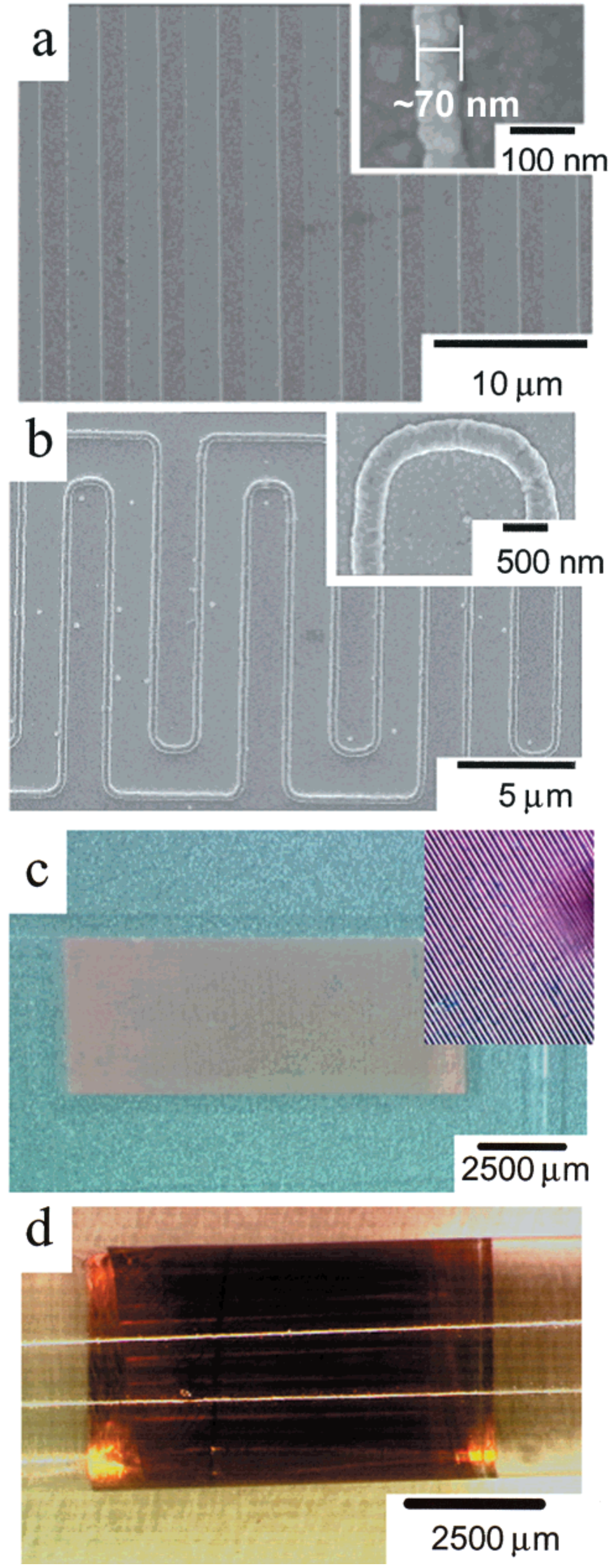

Figure 4. FE-SEM images of an electrodeposited copper line at edges of 2 × 2 µm silver lines decorated with SAM show the following: (a) coalesced copper lines with a lateral dimension of ≈70 nm (the duration of the deposition was ≈40 s), (b) copper serpentine designs; optical images of submicrometer-sized structures of copper at edges of 2 × 2 µm silver lines transferred on to (c) a flat glass slide and (d) a glass rod (diameter: 5 mm). Scotch tape remains covering the copper structures shown in both (c) and (d). The wires shown in the insert of (c) are 200−250 nm in width.

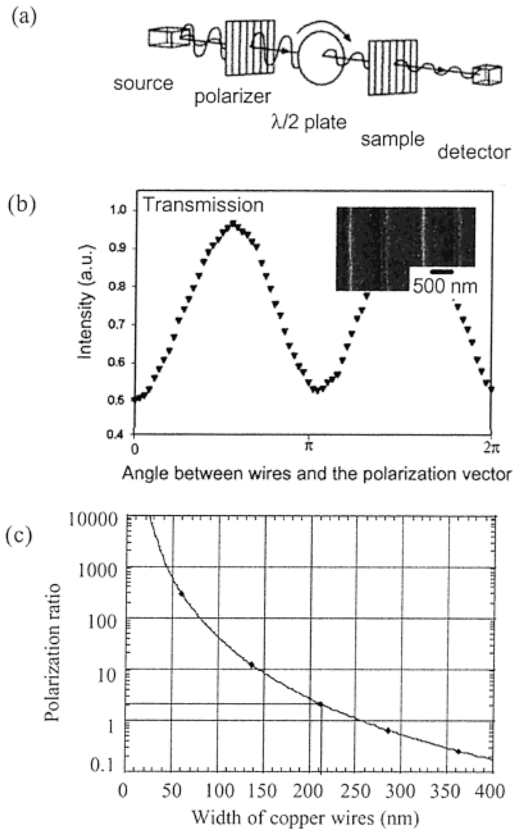

Figure 5. (a) An illustration of the setup for the measurements of polarization. (b) A plot of transmitted intensity of linearly polarized light as a function of the angle between the direction of copper wire and the vector of polarized light. The insert is a SEM image of the copper wires. The duration of electrodeposition for making such copper wires was ≈90 s at a constant potential of ≈0.53 V. (c) A plot for the predicted polarization ratio, Q_1/Q_2 vs width of a single metallic wire, *a*.

greater than ≈200 nm were mechanically stable enough to transfer to Scotch tape without breaking during the process of peeling the tape off of the original substrate.

This approach can fabricate curved metallic structures with radii of curvatures on the order of a few micrometers. Figure 4b shows SEM images of serpentine structures of copper on a SAM-decorated silver substrate. Submicrometer-sized structures could be observed across wide areas of the substrate (≈2 cm^2), and the curvature of the copper lines followed accurately the corresponding edges on the original template.

The transfer of copper using Scotch tape offers an easy way to fabricate micro- and nanostructures on either flat or curved surfaces. Figure 4c,d shows large areas of submicrometer-sized linear arrays of copper wires on flat float glass and on a curved glass rod (with Scotch tape on top of the structures). The copper was made by electrodeposition at the edges of steps of 2 × 2 µm parallel lines. The lateral dimension of the copper wires is ≈200−250 nm in the samples shown in Figure 4c,d. For some applications such as diffraction gratings and beam splitters on curved surfaces, this edge-lithographic technique may provide a useful method of fabrication.

Fabrication of Optical Polarizers Using Arrays of Electroformed Copper. Figure 5 schematically illustrates the experimental design for testing an array of parallel copper wires as an optical polarizer. The wires (1-µm pitch) were supported on optically transparent Scotch tape mounted on an antireflective glass window. We used a HeNe (633 nm) laser as our light source and a $\lambda/2$ plate to control the vectors of the incoming polarized light. We changed the angles between the vector of linearly polarized light and the polarization direction of the sample by rotating the $\lambda/2$ plate. The transmission intensity of the laser beam after passing through the half-wave plate and the sample was measured using a silicon positive-intrinsic-negative (PIN) diode. In transmission mode, a polarization ratio >2 was observed (Figure 5b).

A SEM image of the copper wires (prior to the transfer to the tape support) is shown in the insert of Figure 4b. The width of the copper wires was $\approx$220 nm. The polarization ratio measured is comparable with or slightly higher than the ratio measured with an array of gold wires that have widths of $\approx$100 nm.[33]

A simple theoretical model for validating the experimentally determined ratio of polarization calculates the efficiency factors for the extinction of a plane electromagnetic wave propagating perpendicular to a single reflecting metallic wire of infinite length and perfect conductivity.[34] The electric field (**E**) component of the wave perpendicular to the length of the wire interacts differently with the wire than the component parallel to the wire. The difference in transmission of these two components interacting with the wire yields a net polarization of the transmitted wave. The efficiency factors for extinction can be calculated using eqs 1 and 2:

$$Q_1 = \frac{2}{x} \cdot \frac{\pi^2}{\pi^2 + \{2\,\log(\gamma\chi/4)\}^2} \cdot \left[1 + \frac{1}{4}x^2 + \cdots\right] \qquad (1)$$

$$Q_2 = \frac{\pi^2 \cdot x^3}{16} \cdot \left[1 + \frac{1}{16}x^2 \cdot \left\{1 - \frac{8}{5}\log(\gamma\chi/4)\right\} + \cdots\right] \qquad (2)$$

Here, Q_1 is the factor for extinction of the **E** component of the electromagnetic field parallel to the length of the wire and Q_2 is the factor for extinction of **E** component perpendicular to the wire. The parameter x is equal to $k \cdot a$ where $k = 2\pi/\lambda$ ($\lambda = 633$ nm for a HeNe laser) and a is the width of the metallic wire. (Euler's constant, γ, equals 1.781.) The polarization ratio of the light transmitted through the wire is defined as the ratio Q_1/Q_2. These equations indicate that the narrower the conducting wire, the higher Q_1 and the smaller Q_2.

Figure 5c shows a plot of the expected polarization ratios, Q_1/Q_2 vs the width of a single conducting wire, a. The model predicts that a wire with a diameter between 210 and 220 nm polarizes incident light with a ratio Q_1/Q_2 of $\approx$2. This prediction matches the measured critical dimensions of the copper wires. This model based on Babinet's principle[34] provides an approximate value for the expected ratio of polarization to gauge the effectiveness of the polarizer. More accurate calculations of the polarization must account for several parameters ignored here including the density of the wires, the conductivity of the metal, the shape of the wires, and the refractive indices of the supporting surface.

Conclusions

We used a thin metal layer of titanium or chromium to create nanometer-sized electrically conducting bands in insulated SAM at the edges of topographically patterned silver substrates and electrodeposited submicrometer and nanostructures of copper at these narrow gaps. The technique is a new fabrication method for generating metallic micro- and nanostructures with the ability to control both the size and the shape. We believe that this approach is not limited to the fabrication of copper structures, but should be applicable to any metal or other material that can be electrodeposited at a voltage at which the SAM on silver remains stable. One limitation of this approach is that the structures generated are limited to replicas of the edges of the original patterns; this characteristic prevents the fabrication of arbitrary, open-ended structures. The method allows the replication of multiple metallic submicrometer structures from the same master by electrodeposition. The transfer of metallic structures onto curved and flat substrates may find applications in specialized areas, such as subwavelength optics.

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