Selective Electroless Copper Deposition within Block Copolymer Microdomains

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We demonstrate a method for the directed formation of layered metallic copper structure within the subsurface morphology of a bulk lamellar block copolymer. Using an electroless deposition process, copper was selectively deposited inside the interconnected microdomain network of the water-permeable block containing preloaded palladium ions. The relatively simple process yields a novel nanoscale composite consisting of alternating layers of metallic copper with those of the hydrocarbon block matrix. The extent of the copper deposition can be controlled by adjusting the deposition rate and deposition time.

Introduction

We present a successful method for producing a lamellar nanocomposite comprising alternating layers of dense metallic copper and layers of a hydrocarbon polymer. The selective formation of such structure involves electroless deposition of copper within the microphase separated bulk morphology of a lamellar diblock copolymer. A critical issue in the present work is the external reservoir of electroless plating reagents, which, with certain limitations described below, continuously supplies the growing copper structures. This is in contrast to our earlier works[1−3] which relied on the limited supply of reagents that were preloaded into the nanoreactors to synthesize nanoclusters.

An electroless plating process involves the chemical reduction of metal ions and the subsequent deposition of the metal onto a catalytic surface.[4−6] The metal deposition process is usually initiated on a surface which contains an activating agent (e.g., palladium); further deposition occurs via autocatalytic reduction of the metal ions at the surface of previously deposited metal. Because of the ability to create uniform coatings over small selected areas, electroless deposition has found a number of applications in template-directed formation of micro- and nanoscale metallic structures.[7−10]

Block copolymer morphologies have been employed as templates for the surface deposition of nanoscale metallic structures via electroless plating in recent years. In particular, Zehner et al.[11] selectively decorated the surface morphology of lamellar diblock copolymer films with palladium colloids. The Pd-decorated lamellae in turn served as template for electroless deposition, which resulted in an irregular surface pattern of 20 nm copper structures. From a bicontinuous morphology of a styrene−isoprene block copolymer, Hashimoto et al.[12] created void nanochannels inside the styrene matrix via the selective degradation of the preexisting isoprene microdomains to form a void network. The surfaces of the 30 nm void were then coated with nickel via electroless deposition.

In this work, we demonstrate the formation of metallic copper layers inside the three-dimensional subsurface morphology of a block copolymer. Our method relies on the diffusion of electroless copper plating reagents through the water-permeable lamellar network of a dicarboxylic acid-functionalized block embedded in a nonpolar hydrocarbon block matrix. The same lamellar microdomains also serve as templates for the selective copper deposition. The technique involves convenient aqueous chemistry and does not require additional physical modification of the original self-assembled block copolymer structure. The overall production scheme is a variation on the block copolymer nanoreator methodology we have employed in the past to synthesize various types of inorganic nanoclusters in block copolymer films.[1−3] Such layered copper-in-polymer composite presented here may be useful as an anisotropic electrical conductor. Flip-chip interconnection via anisotropic

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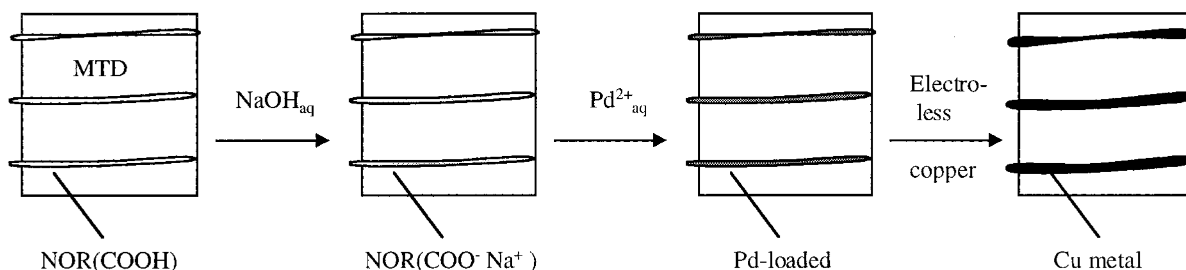
Scheme 1. Electroless Copper Deposition Process



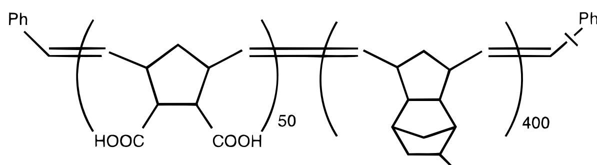
conductive adhesive films represents an example of applications that employ anisotropic conductivity.[13]

Experimental Section

Materials. MTD (methyltetracyclododecene) monomer, donated by BF Goodrich, was degassed and stored over sodium prior to use. NORCOOH (2-norbornene-5,6-dicarboxylic acid) monomer was prepared for polymerization as previously reported.[14] All anhydrous solvents used for monomer synthesis and polymerization were stored over sodium and filtered prior to use. All other solvents were used as received. The Shrock initiator 2,6-diisopropylphenylimido neophylidenemolybdenum(VI) bis(*tert*-butoxide) from Strem was used as received.

Sodium tetrachloropalladate(II) trihydrate (99%) and copper(II)sulfate pentahydrate (98+%) were purchased from Strem. Triethanolamine (97%), dimethylamineborane (DMAB) (98+%), and 1,5,8,12-tetraazadodecane (96.5+%) were purchased from Fisher Scientific. All reagents were used as received. All aqueous solutions were prepared with deionized water.

Polymer. Poly($MTD_{400}NORCOOH_{50}$) diblock copolymer:



was synthesized in anhydrous toluene using the Shrock initiator as previously reported.[2] The block copolymer was characterized by gel permeation chromatography using a series of Waters Ultrastyrogel columns (10^5, 10^4, and 10^3 Å) connected to a Waters Differential Refractometer R401. GPC carrier solvent was toluene running at 1 mL/min flow rate. The polystyrene equivalent M_n of the block copolymer was 82 kg/mol with a 1.15 polydispersity. A 60-μm-thick film was statically cast from a 5 wt % THF solution in a glass Petri dish over ~3 days. The resulting light-brown, transparent film was dried under vacuum before use.

Palladium Loading and Electroless Copper Deposition (see Scheme 1). Dispersion of palladium into the NORCOOH microdomains was achieved by immersing block copolymer films in a 0.04 M $NaOH_{aq}$ solution for 18 h, followed by rinsing in deionized water for 2 h. The films were then immersed in a 0.01 M $Na_2(PdCl_4)\cdot 3H_2O_{aq}$ solution for 1 h, followed by a 20-min rinse.

The Pd-containing films were immersed in an electroless copper plating bath of composition:[15] 0.032 M $CuSO_4$, 0.04 M tetraazadodecane (ligand), 0.3 M triethanolamine (buffering agent), and an adjustable amount of dimethylamine borane (DMAB) (reductant) to vary the copper deposition rate of the bath. For simplicity, we will designate baths containing 0.017 M DMAB as "slow-plating" baths, while "fast-plating" baths are those that contain 0.067 M DMAB.

Figure 1. Palladium-loaded poly($MTD_{400}NORCOOH_{50}$).

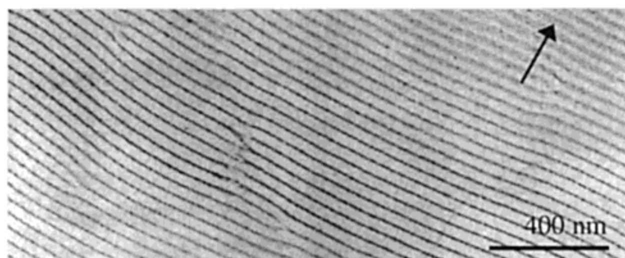


Figure 2. Morphology of palladium-loaded poly(MTD_{400}-$NORCOOH_{50}$) near film's free surface. (Arrow indicates direction toward free surface.)

Electron Microscopy. Ultrathin (50 nm) samples for morphological examination were prepared with a Sorvall Ultra Microtome MT5000. Microtomed sections were collected onto 300-mesh gold grids. Morphology investigation and electron diffraction were performed on a JEOL 200CX and on a JEOL 2000FX transmission electron microscopes operating at 200 kV. Scanning transmission electron microscopy was performed on a VG-HB603 operating at 250 kV.

Results and Discussion

Static casting yields the lamellar morphology in which the acid-functionalized (NORCOOH) block forms inter-

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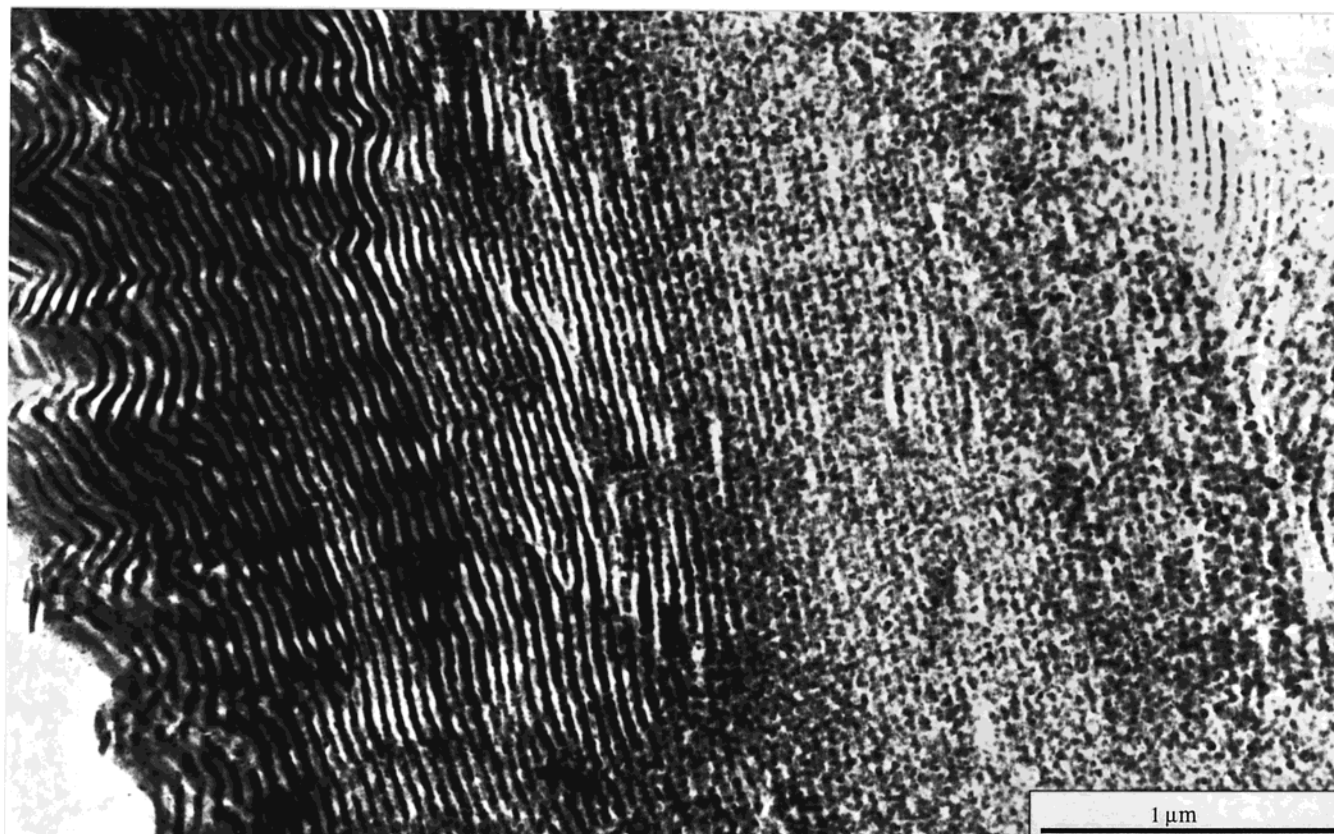

Figure 3. Pd-loaded film treated in "slow-plating" electroless copper bath for 16 h.

connected lamellar microdomains within the matrix of the hydrocarbon (MTD) block. Prior to electroless copper deposition, the 60-μm-thick diblock copolymer film was treated with $NaOH_{aq}$ solution to convert the acid groups into sodium carboxylate salt which, in turn, facilitates the selective loading of palladium ions upon immersion of the film in the aqueous solution of $Na_2(PdCl_4)$.

The block copolymer's morphology is shown in Figure 1, where the loaded palladium imparts dark contrast to the NORCOOH microdomains. The bulk of the film is made up of randomly oriented lamellar grains with an approximate lamellar long period of 40 nm. The NORCOOH microdomain thickness observed from the lamellar edge-on view is about 4 nm. The lamellar morphology is evident as the edge-on view of the lamellar thin dimensions rotates to show the wide dimensions of the sheetlike structures. Note that although the majority of lamellae are arranged in grains, we often find that within several microns from the film's free surface the lamellae orient themselves parallel to the plane of the free surface, as shown in Figure 2. (The arrow indicates the direction toward the free surface.)

The palladium-loaded films were then submerged in an electroless copper bath ("slow-plating" bath: 0.017 M DMAB) for 16 h, where the spatially sequestered palladium served as localized catalyst for the copper deposition process. Figure 3 is a TEM micrograph of such a sample, in which selective copper deposition along the lamellae of the NORCOOH microdomains appears dark and dense.

Scanning transmission electron microscopy (energy-disperse X-ray analysis) was performed on the copper-treated sample to verify the correlation between the dense structure observed in bright-field TEM and the copper deposition. Figure 4 a,b shows side-by-side images of a bright-field image and the corresponding copper map. The dark structure in the bright-field image correlates well with the structure of the copper map (where light contrast indicates copper); thus confirming the identity of such structure as a copper deposit.

We also performed selected-area electron diffraction of microtomed samples (on gold TEM grids). The resulting diffraction pattern (Figure 5) consists of multiple rings, consistent with a polycrystalline copper structure. The corresponding atomic plane spacing values were calculated from the diffraction ring radii using the Bragg equation (Table 1). The *d* spacing values derived from the six most intense diffraction rings match the face-centered cubic lattice plane spacings of copper metal.[16]

Figures 3 and 4 reveal a gradient in the apparent "density" and thickness of the copper deposit which exists from the free surface toward the center of the film. Figure 6 a,b are higher magnification images of a similarly treated sample taken at regions adjacent to and ~3.5 μm away from the sample's free surface, respectively. The deposit appears dense and continuous near the free surface, having an estimated lamellar thickness of 25 nm and a lamellar period of 55 nm. At 3.5 μm away from the same free surface, the copper deposit forms individual, roughly spherical clusters of size 15−20 nm along the NORCOOH microdomains with a 40-nm lamellar period.

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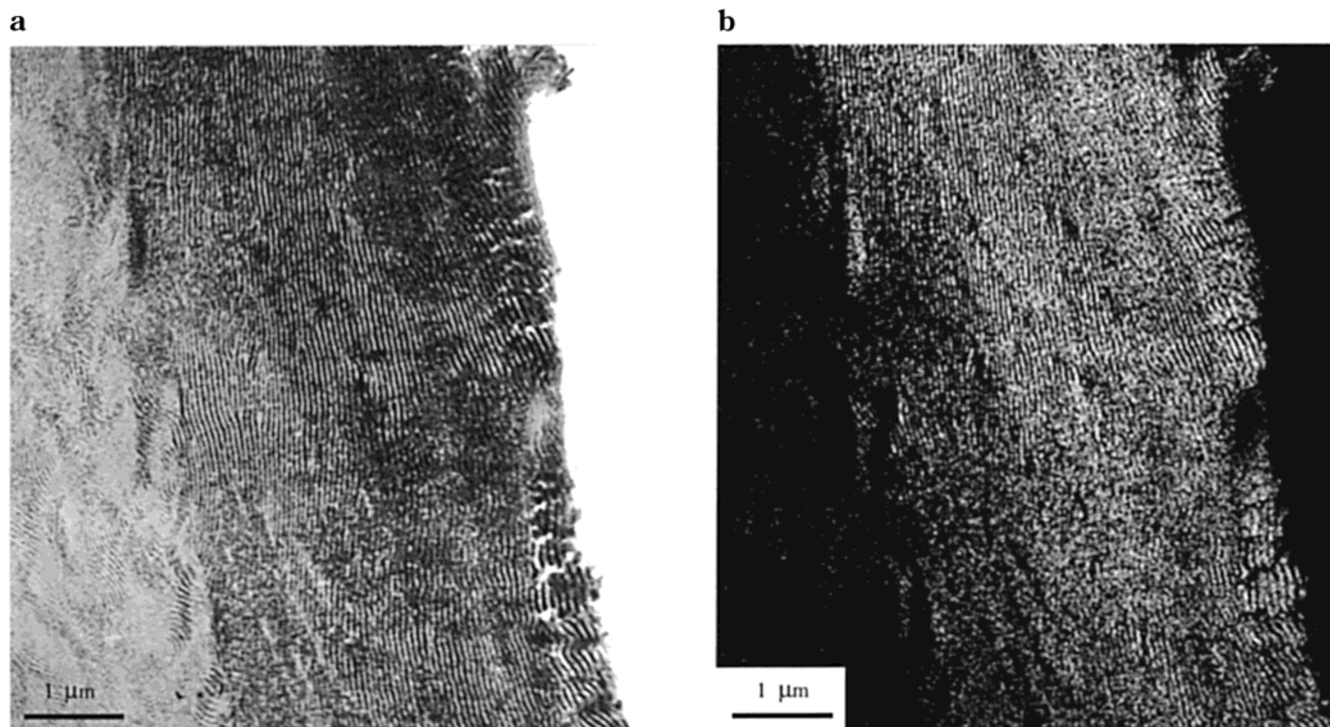

Figure 4. Scanning transmission electron micrographs of film treated in "slow-plating" electroless copper bath for 16 h. (a) Bright field image; (b) copper map.

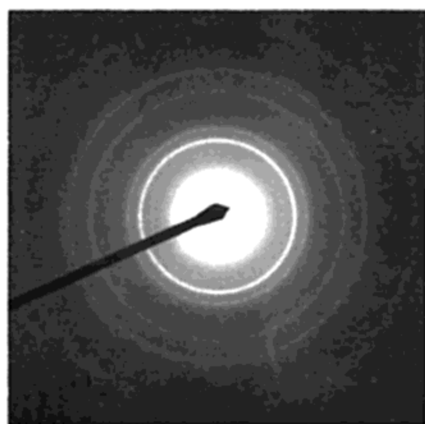

Figure 5. Selected-area electron diffraction pattern of the copper deposit.

Table 1. Atomic Plane Spacing Values Derived from the Diffraction Pattern

Copper[16]						
d (Å)	2.008	1.808	1.278	1.090	0.829	0.808
(*h*, *k*, *l*)	(1, 1, 1)	(2, 0, 0)	(2, 2, 0)	(3, 1, 1)	(3, 3, 1)	(4, 2, 0)
Measurement						
d (Å)	2.074	1.815	1.286	1.096	0.830	0.814
error (%)	−0.66	0.39	0.62	0.54	0.05	0.73

We emphasize the spatially confined production of the copper structure inside the preexisting lamellar microdomains of the NORCOOH block and the virtual absence of copper inside the alternating layers of the MTD hydrocarbon block. Although we observe thickening of the deposited copper beyond the thickness of the original NORCOOH microdomains near the film's surface—and the corresponding expansion of the lamellar period—we have seen no evidence of any "break-out" events where the growth of the copper structure would overwhelm the preexisting lamellar morphology of the block copolymer.

The observed selective deposition along the NORCOOH microdomains in the absence of "break-out" suggests that the transport of plating reagents occurs mainly through the NORCOOH microdomains. That is, the palladium-doped NORCOOH network serves a dual role, both as the reagent transport pathway and as the template for copper deposition. The observed gradient of copper deposit density perpendicular to the free surface evidently resulted from limitations on the supply of the plating reagents to the NORCOOH microdomains further away from the film's free surface compared to those microdomains located near the free surface. The diffusion of these reagents from the free surface toward the bulk of the film may also become further limited as the transport path near the free surface becomes increasingly clogged by the growing copper deposit.

Along this line of reasoning, we expected to be able to control the depth of copper deposition by adjusting the rate of copper deposition. An increased plating rate may result in a more rapid clogging of the NORCOOH network, which could lead to a reduced deposition depth. Figure 7 a,b are TEM micrographs of samples plated in "fast-plating" baths (0.067 M DMAB) for 1.8 and 16 h, respectively. The "fast-plating" bath has ~3 times the plating rate of the "slow-plating" bath (0.017 M DMAB) which was used in all of the experiments discussed thus far.[15] By comparison, for the same plating time of 16 h, the "fast-plating" sample (Figure 7b) exhibits a much smaller copper deposition depth than the "slow-plating" sample (Figure 3). (Notice in Figure 7 that the light TEM contrast of loaded palladium is clearly distinguishable from the heavy contrast near the free surface of the copper deposit.)

While this observation may be attributed to the rate of clogging of the NORCOOH nanochannels, extensive deposition of metallic copper on the fast-plating sample's free surfaces may have also contributed a macroscopic

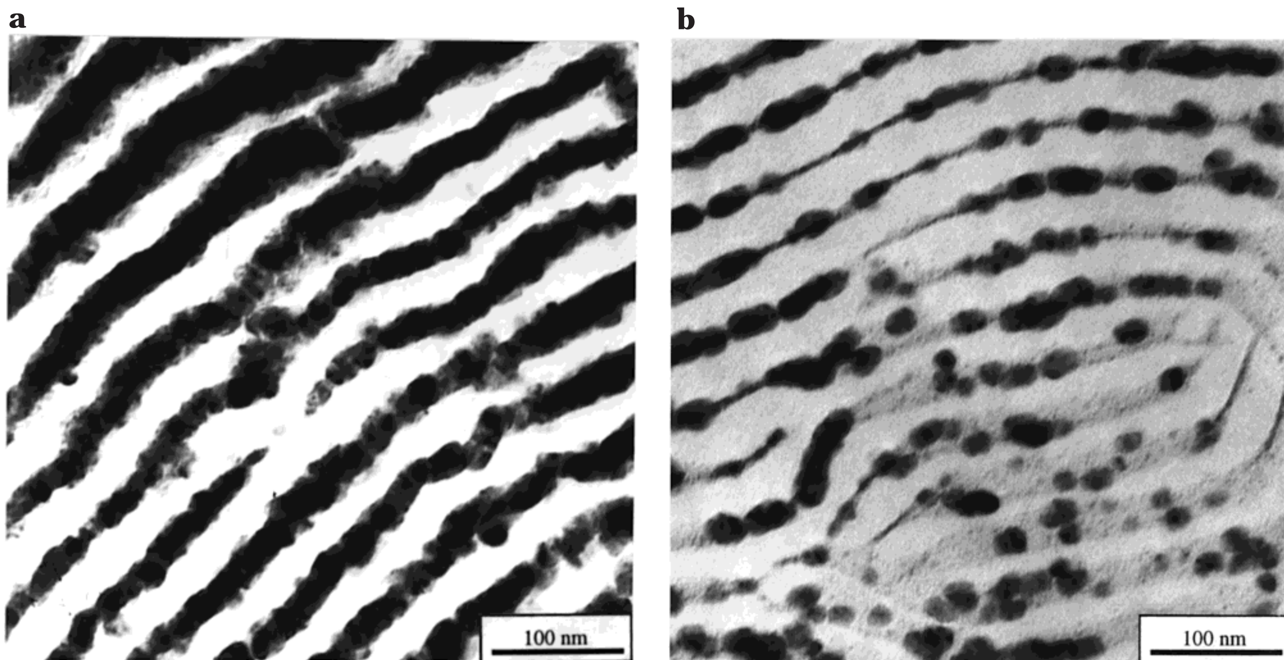

Figure 6. Film treated in "slow-plating" electroless copper bath for 16 h: (a) region adjacent to the film's free surface and (b) region ~3.5 μm away from the free surface.

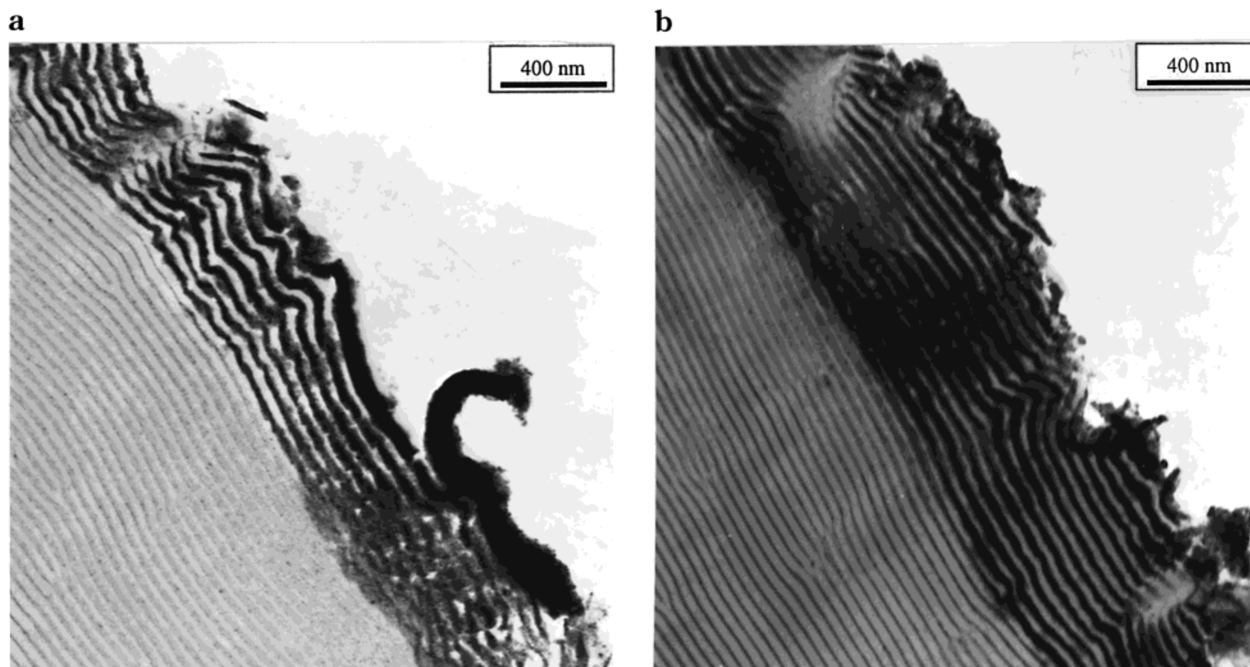

Figure 7. Films treated in "fast-plating" electroless copper bath (a) for 1.8 h for (b) 16 h.

retardation to the diffusion of plating reagents into the bulk of the film. We note that the free surfaces of the fast-plating sample are visibly covered with solid copper coatings, while the slow-plating sample's copper coatings are very sparse in comparison.

Aside from adjusting the deposition rate, we were also able to control the depth of copper deposit by varying the plating time, i.e., time allowed for the diffusion of plating reagents into the film. After 16 h of "slow-plating", the maximum depth of copper deposit is ~4 μm (Figure 3), compared to the approximate 8 μm depth of copper deposit after 41 h shown in Figure 8. We also observed an increase in copper deposit depth with an increase in plating time in "fast-plating" samples (Figure 7a, 1.8 h plating time, compared to Figure 7b, 16 h).

Our preliminary attempt to investigate qualitatively the connectivity of the copper deposit was to view the copper structure through the lamellae's thin dimensions. Figure 9 shows a region of a specimen in which the edge-on lamellae rotate to reveal the lamellar wide dimensions. Figure 9 represents a transmission view through the thin dimensions of single copper-plated lamellar layers since the thickness of microtomed sections was 50 nm, which is approximately equal to the lamellar period. At this length scale, the deposit appears to be a collection of spherical copper clusters in close contact with one another. That is, although not fully dense, the

Figure 8. Film treated in "slow-plating" electroless copper bath for 41 h. (Note: lamellae are arranged in randomly oriented grains.)

Figure 9. A view through the thin dimensions of individual lamellar copper structure.

structure of the individual copper layers appears to be percolated. We expect that such alternating layered structure of metallic copper and the insulating hydrocarbon polymer would display electrical anisotropy with respect to the lamellar orientation. We plan to investigate the electrical properties of these materials in the immediate future.

Although we confine our comments here to the observations of metallic copper deposition in a lamellar block copolymer, we recognize the possibility of employing other block copolymer morphologies, as well as electroless deposition of other metals. Such effort may lead to the potential production of arrays of metallic nanowires and interconnected structures with properties and orientations different from the lamellar copper structure (e.g., magnetic nickel and cobalt).

Conclusions

We have produced novel nanocomposites consisting of metallic copper layers embedded within a hydrocarbon polymer matrix via electroless deposition. Our process relies on the diffusion of the electroless copper plating reagents through the aqueously permeable microdomain network of a diblock copolymer. The same network also simultaneously serves as a template for the spatially selective copper deposition, which in turns presents some limitation to the transport of plating reagents through the bulk of the film. Nevertheless, our process yields nanoscale dense copper structure within the subsurface morphology of the polymer film. The extent of deposition can also be controlled by variation of the deposition rate and/or time.

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