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Binary oppositely charged polyelectrolyte brushes for highly selective electroless deposition of bimetallic patterns

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A B S T R A C T

Binary polymer brushes consisting of two oppositely charged polyelectrolytes are grafted on one substrate via two-step surface-initiated atomic transfer radical polymerization from contact printed initiator monolayer. The polymeric structures provide robust and effective platforms for highly selective loadings of catalytic-active ionic moieties with opposite charges [$PdCl_4^{2-}$ and $Pd(NH_3)_4^{2+}$] that can be used for electroless deposition (ELD) of metals in the subsequent steps. Binary metallic Cu/Ni patterns can thus be built up with high site-selectivity when the deposition was carried out in the order of Cu and Ni.

1. Introduction

Metal microstructures have attracted much attention for their fascinating properties that can be distinctly different from those of their bulk counterparts. They show applications in a wide range of technologies including microfluidic device [1], microelectronics [2], biochips, and biosensors [3]. Metal deposition can be achieved by several methods including physical vapor deposition, chemical vapor deposition, and electrochemical plating or electroless deposition (ELD). Among these, ELD is of particularly interest due to its high selectivity, feasibility and low cost [4–8]. Importantly, ELD is especially suitable for polymeric substrates which may deform or degrade at high temperatures in vapor deposition strategies.

Generally, an appropriate catalytic surface is required to initialize metal deposition, while charged polymers loaded with catalytic moieties can provide such surface. Using polyelectrolytes as seeding platforms, a combination of microcontact printing (μCP) and ELD has been demonstrated to selectively fabricate metallic nano/micro patterns [5–8]. In this paper, we report the synthesis of binary polymer brushes consisting of two oppositely charged polyelectrolytes prepared by μCP and surface-initiated polymerization, and the use of the binary brushes as seeding templates for subsequent site-selective electroless plating of Cu/Ni bimetallic structures. Unlike a number of methods developed by other groups [9–13], we directly used contact printed monolayer pattern of initiator to grow the first polyelectrolyte brush by atom transfer radical polymerization (ATRP). After cleaning the substrate, the initiator was re-assembled on the unmodified area to grow a second brush [14]. As proof-of-concept, we synthesized positively charged poly(methacryloyloxy)ethyl-trimethylammonium chloride (PMETAC) having quaternary ammonium group which has strong affinity to $PdCl_4^{2-}$ species, and negatively charged polymethacryloyl ethyl phosphate (PMEP) bearing phosphate groups which shows strong affinity for $Pd(NH_3)_4^{2+}$ species, Scheme 1. The ion-pairing-oriented binding does not only guarantee large amount of catalysts for efficient metal plating, but also diminishes nonspecific absorption by neighboring component, which is of paramount importance to the fabrication of highly selective bimetallic patterns. The as-made binary polyelectrolyte brushes were subsequently loaded with oppositely charged, catalytic-active metal ions respectively, and used for site-selective ELD of two different metals, i.e. Cu and Ni (Scheme 1) [15–20].

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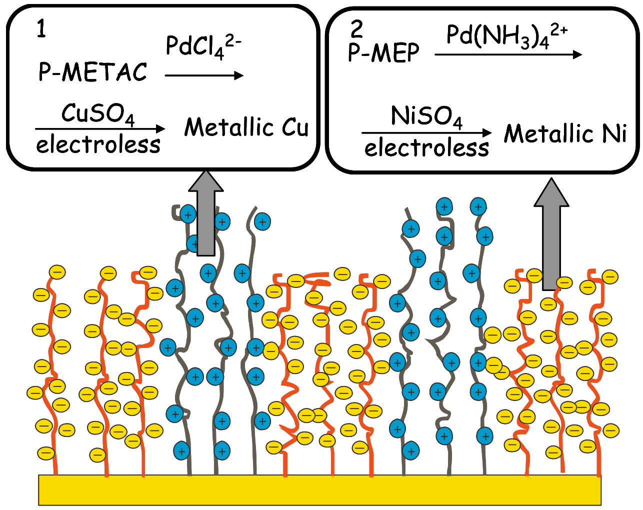

Scheme 1. Schematic of binary positively/negatively charged polyelectrolyte brushes for selective uptake of palladium seed for subsequent electroless deposition of Cu and Ni.

2. Experimental methods

2.1. Chemicals and methods

All chemicals were purchased from Aldrich, Fisher, or Lancaster. The inhibitors in the monomers, i.e., methacryloyl ethyl phosphate (MEP) and 2-(methacryloyloxy)ethyl-trimethylammonium chloride (METAC) were removed by elution through a neutral alumina plug before use. Gold film was prepared via thermo evaporation 200 nm gold on silicon wafers (Compart Technology Ltd., 100 mm diameter, boron-doped, (100) orientation, one side polished) with 2 nm Cr as the adhesive layer.

2.2. Characterization

AFM experiments were carried on a DI IV microscope (MI). AFM data was processed with WSxM software (Nanotec Electrónica, Spain). Optical and fluorescent image was taken with Nikon Eclipse ME600 optical microscope fitted with a Nikon DN100 Digital Net Camera. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were carried out using a LEO instrument using a GEMINI column. The samples were imaged without any conductive coating. Typically, measurements were carried out at a working distance of 4 mm (7 mm for EDX) at 5 keV with a vacuum below 5×10^{-5} mbar. The resolution of the EDX measurements fulfills the requirement to extinguish the signal difference between copper and nickel.

2.3. Surface-initiated polymerizations

ω-mercaptoundecyl bromoisobutyrate was synthesised following a published procedure [21]. Patterned samples on gold coated silicon wafers were prepared with typical procedures reported in the literature [14]. Polymerization was carried out as follows: MEP–Na 9 g was dissolved in 27 ml water and degassed by passing a continuous stream of dry N_2 through the solution whilst being stirred (15 min). To this solution was added bipy (0.62 mg), CuBr (0.288 g). The mixture was then further stirred and degassed with a stream of dry N_2 (15 min) and the temperature was raised to 60 °C [22]. Initiator patterned gold substrates were sealed in Schlenk tubes, degassed (four times high-vacuum pump/N_2 refill cycles). Polymerization solution was injected into Schlenk tubes to allow polymerization proceeding for 1 h. For the second brush growth, the polymerization solution contained 20 ml of 3 mol/L METAC aqueous solution (60 mmol monomer), CuBr (0.144 g, 1 mmol), bipyridine (0.33 g, 2 mmol). Polymerization was carried out for 5 h at room temperature. All the reaction solutions must be kept clear and clean, especially to ensure complete dissolution of all components in ATRP solution. Complete removal of the physisorbed initiator probably within the first brush network can avoid solution polymerization and generation of free 2nd polymer.

2.4. Electroless deposition of Cu and Ni

The electroless plating of Cu was performed in plating bath containing 1:1 mixture of freshly prepared solutions A and B [7]. Solution A consists of 12 g/L NaOH, 13 g/L $CuSO_4{\cdot}5H_2O$ and 29 g/L potassium sodium tartrate ($KNaC_4H_4O_6{\cdot}4H_2O$). Solution B is 9.5 mL/L HCHO in water. The electroless plating of Ni was performed in the following steps [5,6] in the plating bath consisted of 40 g/L nickel sulfate hexahydrate, 20 g/L sodium citrate, 10 g/L lactic acid, and 1 g/L dimethylamine borane (DMAB) in water. A nickel stock solution of all components except the DMAB reductant was prepared in advance. A DMAB aqueous solution was prepared separately. The stock solutions were prepared for a 4:1 volumetric proportion of nickel-to-reductant stocks in the final electroless bath. All the electroless depositions were carried out at room temperature. The samples were finally cleaned with copious rinsing of de-ion water, and blown dried with N_2 for characterizations.

3. Results and discussions

Binary PMEP/PMETAC structure was prepared by two-step surface-initiated living polymerization [14]. As shown in Fig. 1a, binary brushes were obtained in separate regions. AFM measurement indicates that the heights of PMEP and PEMTAC are about 30 nm and 20 nm, respectively. The distinct location of separate brushes was further demonstrated with dye staining and the fluorescence image is shown in Fig. 1b. The PMEP region exhibits strong fluores-

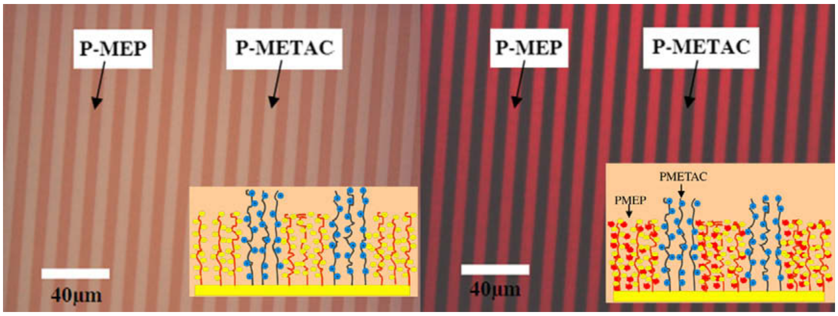

Fig. 1. Binary PMEP/PMETAC brushes from patterned initiators and two-step surface-initiated polymerization and dye staining (acridine).

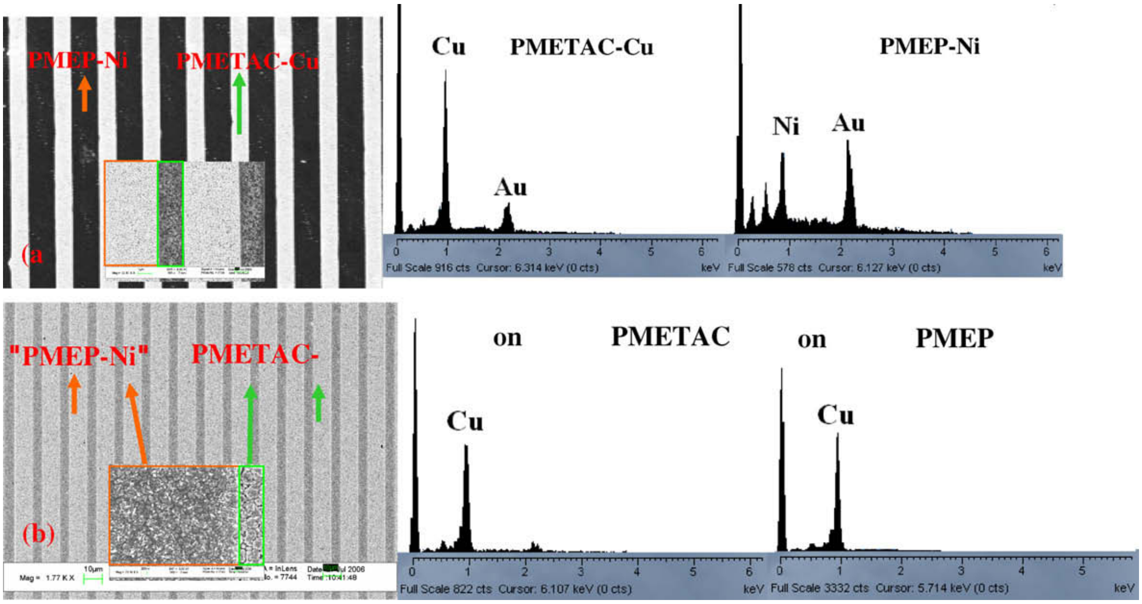

Fig. 2. (a) Binary Cu/Ni patterns electrolessly deposited on catalytic seed saturated binary PE brushes of PMEP/PMETAC in the order of Cu and Ni. The plating time was 2 min for both metals. Left image: SEM image. Middle image: EDX analysis of the bright area of the SEM image. Right image: EDX analysis of the dark area of the SEM image. (b) Binary Cu/Ni patterns deposited in the order of Ni and Cu. The plating time was 2 min for both metals. Left image: SEM image. Middle image: EDX analysis of the bright area of the SEM image. Right image: EDX analysis of the dark area of the SEM image.

cence emission while the PMETAC region is in deep black. This is because that the cationic dyes were preferably trapped in the anionic PMEP region, while no absorption was found in the cationic PMETAC region. The result also indicates that the secondly grown PMETAC does not exist on PMEP. This is of great importance to ensure differential charging state on the surface for successful electroless plating.

Palladium was used as the seed for electroless plating of both Cu and Ni. It must be absorbed onto specific surface areas recognizably. PMETAC was used to absorb, via ion-pairing interaction, the anionic $PdCl_4^{2-}$ complex, which is used in Cu plating. Subsequently, PMEP was used to absorb cationic tetraaminopalladium complex that initiates Ni deposition. Fig. 2a is the SEM image of the as prepared binary metallic Cu/Ni patterns deposited firstly with Cu and secondly Ni, showing that nickel and copper deposited onto respective area with very high resolution. A zoom-in SEM image indicates that electroless nickel has finer and more compact grains compared with copper. High selectivity can be firstly analyzed from successful deposition of Ni. In the first electroless process, any trace absorption of the seed palladium on PMEP area will undoubtedly result in Cu deposition on this area so that second Ni plating would not be possible. SEM characterization verifies that this did not occur at all. Ni pattern was successfully obtained. In order to prove Ni plating in the second step did not contaminate the already deposited copper, EDX analysis was performed on respective area, Fig. 2a. It is seen that on PMETAC area only Cu was detected while on PMEP area only Ni was detected. This indicates that Ni only deposited on PMEP region and had no contamination to the deposited Cu. However, if deposited in an inverse order (Ni first and Cu second), the existing Ni will initiate Cu deposition via replacement reaction. As a consequence, the whole surface will be covered with Cu layer. The SEM image of the binary patterned made with inverse order shows lower electron contrast and similar surface morphology on both PMEP and PMETAC areas, indicating the existence of Cu over Ni, Fig. 2b. The EDX analysis over two regions confirms the surfaces were both covered with Cu. The lateral expansion of the Cu line is also a result of Cu overgrowth on Ni.

The relative height of Ni and Cu can be easily manipulated via the plating time. Fig. 3 shows the AFM cross-section profiles of binary metallic patterns. Cu plating for 1 min resulted in a height difference of 160 nm between PMEP and PMETAC–Cu. We found minimal growth of Cu in lateral direction, indicating the high growth selectivity over specific area. Before absorption of cationic palladium ions, the PMEP/PMETAC-Cu was soaked in 1 M $NaNO_3$ for 0.5 h. This helps to recover PMEP brushes via cationic exchange from possible PMEP-Cu complex. Otherwise, the unavoidable complexation between phosphate group in PMEP and Cu will prevent absorption of $Pd(NH_3)_4^{2+}$ into PMEP. The anionic exchange is necessary to recover collapsed PMEP brushes. After uploading palladium seed, PMEP/PMETAC-Cu was soaked into Ni plating solution for different time. Two minutes plating reduced the height difference from original 160 nm to about 45 nm. The 116 nm differential thickness was directly ascribed to Ni growth. If Ni plating was carried on for even longer time, the height will exceed that of Cu as is shown in Fig. 3. After 3 min plating, the Ni region became much (130 nm) higher than that of Cu regions. This indicates the overall height of Ni reached to nearly 300 nm.

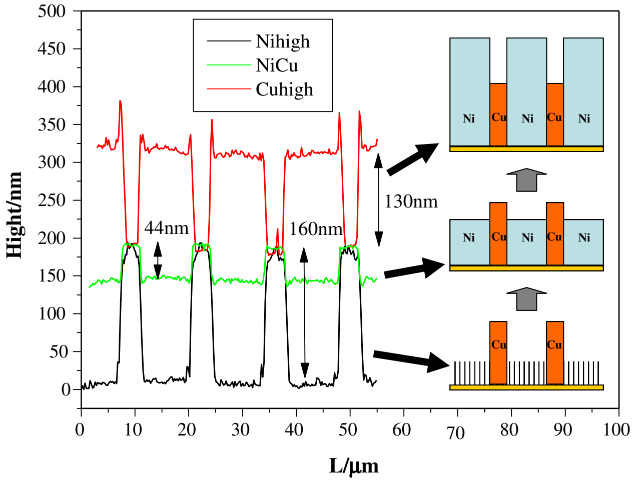

Fig. 3. Binary Cu/Ni patterns electrolessly deposited on catalytic seed saturated binary PE brushes of PMEP/PMETAC with tunable height.

In conclusion, we have demonstrated a facile approach to fabricate bimetallic pattern of nickel and copper with high selectivity. The strategy was initialized by growing oppositely charged polymer brushes on a substrate surface, which can bind oppositely charged metallic complex via ion-pairing interaction. The metallic complex upon reduction serves as the seed catalyst for electroless plating. The high selectivity benefits from highly selective adsorption of seed catalysts on oppositely charged polymers.

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