

Direct Patterning of Copper on Polyimide Using Ion Exchangeable Surface Templates Generated by Site-Selective Surface Modification

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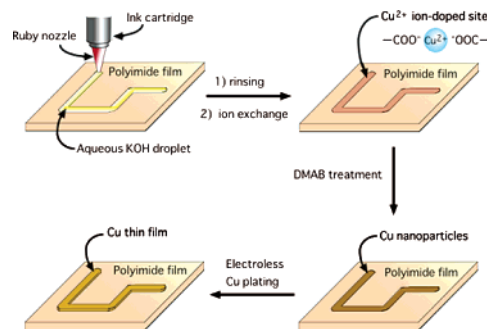
Metallized dielectrics such as polymers with metal overcoatings are extremely important in the fabrication of microelectronics devices. Recently, as an alternative to conventional lithography-based vacuum metal deposition, chemical metallization strategies have been investigated such as fabrication of metallic patterns on polymeric substrate using ion-doped precursors.¹ Such approaches utilize simple solution chemistry and could provide low-cost fabrication of metallized polymers with chemical diversity allowing control of the degree of surface metallization. We reported recently a photochemical approach using an ion-doped precursor for metallization of polyimide resin.² Polyimide is one of the most attractive interconnecting low-*k* materials for microelectronics engineering³ and has motivated many efforts to establish advanced interconnection,⁴ particularly with copper. Previous studies have demonstrated deposition of metallic thin films and patterns by applying photomask-mediated UV irradiation to poly(amic acid) metal salts that produces the metallic patterns. However, unreduced ions remaining between the deposited metal lines must be extracted after UV irradiation, and in the case of copper, the ions cannot be reduced without the use of a TiO₂ photocatalyst.^{2a}

To generate multichip systems for future electronics devices, it would be exceedingly useful and cost-effective to develop a novel, *direct* surface metallization strategy that directly deposits metallic circuits on flexible low-*k* substrates.⁵ Further, it would be desirable to control the interfacial structures associated with adhesion between the resulting metallic thin films and the underlying substrate. Herein, we demonstrate how it is possible to use previously developed chemical modification methods for polyimide and site-selective printing technology to fabricate copper thin-film patterns by chemical reduction only (Scheme 1). This method can be performed without any damage to the nonmetallized surface, and the copper patterns are highly adhesive and capable of initiating subsequent electroless deposition. The process can be described as a completely additive-based, all-wet chemical patterning method, providing an alternative process to our previous photochemical and to conventional metallization strategies.

The approach we present for site-selective copper metallization involves confining the polyimide surface that is chemically modified by aqueous potassium hydroxide solution. Previous studies⁶ and recent studies by our group² suggest that when the solution is dispensed to the polyimide surface, the solution diffuses into the bulk polyimide phase and cleaves the imide rings (hydrolysis) to form the poly(amic acid) metal salt. In this way, surface patterns of ion-exchangeable sites can be generated (Scheme 1).

We have studied this process on a pyromellitic dianhydride-oxydianiline (PMDA-ODA)-type polyimide film (125 μm thick,

Scheme 1



Kapton 500-H, Toray Du-Pont). To generate patterns by chemically modifying the surface, we used a customized, fine-precision dispenser equipped with temperature-controlled X–Y stage and ink cartridge (Musashi Engineering, SMP-III, ruby nozzle diameter: 40 μm). A solution of potassium hydroxide in a water/ethylene glycol mixture (3/1 by volume, final potassium hydroxide concentration: 5M) was printed on the polyimide surface as a circuit pattern using CAD software. The printing was performed at 30 °C for both substrate and cartridge and at a relative humidity of 33%. Addition of ethylene glycol effectively lowers the evaporation rate and improves the wettability of the solution to the hydrophobic polyimide surface. After printing and standing for 5 min followed by copious rinsing with distilled water, the resulting modified surface can be readily differentiated from the bare (unmodified) polyimide by optical microscopy. Figure 1A demonstrates typical patterns (darker color) consisting of straight and bent lines of 200 μm width on the bare polyimide surface (lighter color). Figure 1B shows an elemental (K) line profile of the printed surface and confirms localization of potassium to the printed area, which as mentioned is the poly(amic acid) potassium salt resulting from alkali-induced hydrolysis.⁶ Subsequent immersion of the film into aqueous copper sulfate solution (50 mM) for 5 min enables site-selective ion exchange. The successful reaction is verified by elemental (Cu) line profile, as shown in Figure 1C, which indicates that the width of the initially modified line has remained unchanged and that the potassium signals are no longer evident.

The line width depends on the nozzle scan speed and the dispense rate of the solution from the nozzle to the substrate; faster scan speeds and slower dispense rates give narrower features. In addition, the degree of surface modification is dependent on several other parameters including contact time of the solution with polyimide, concentration of the solution, and substrate temperature. In general, a longer contact time and a higher concentration and temperature led to greater modification and an increase in thickness of the modified layer.⁷ In the current unoptimized system, feature size (dots and lines) could be controlled from 50 μm to many centimeters

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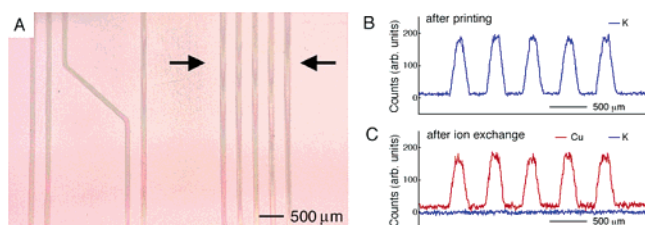


Figure 1. Site-selective surface modification of a polyimide film. (A) Optical microscope image of selectively modified polyimide film. The pattern was generated by printing at a scan rate of 5 mm s^{-1} and an ink dispensation rate of 5 mL min^{-1} at 30°C (relative humidity: 33%), and the printed film stood for 10 min at 30°C . (B) Potassium line profile (between arrows in A) taken after printing. (C) Copper and potassium line profiles (between arrows in A) after printing and subsequent ion exchange with copper sulfate solution.

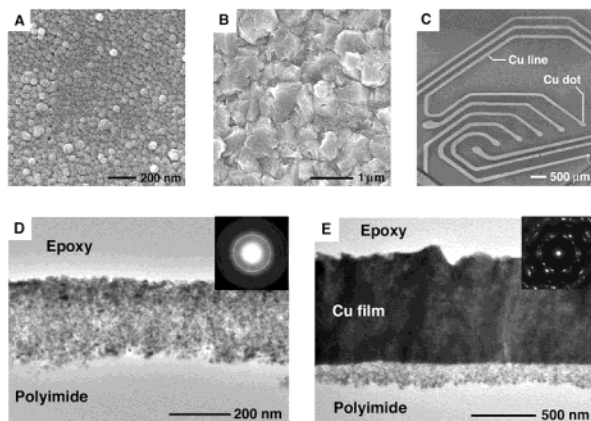


Figure 2. Direct formation of copper thin film and circuit pattern on a polyimide surface. (A) FESEM image of metallized area obtained after DMAB treatment. (B) FESEM image of the copper film after electroless deposition on the film shown in A. (C) FESEM image of copper circuit patterns consisting of lines of $200 \mu\text{m}$ width and dots of $300 \mu\text{m}$ diameter. (D) Cross-sectional TEM image of the film shown in (A). Inset is the electron diffraction pattern of a selected area of the nanocomposite layer. (E) Cross-sectional TEM image of the film shown in B. Electron diffraction pattern (inset) is taken from an electroless-deposited copper thin film.

and indeed should be dependent on the specificity (resolution) of the equipment, particularly the nozzle diameter.

One of the most attractive features of this process is that wet chemical reduction treatment of the selectively ion-doped film using aqueous dimethylamine borane (DMAB, 100 mM) “embosses” the copper circuit patterns on the polyimide surface (Figure 2C). This relatively weak reduction reagent initially reduces the doped copper ions near the modified surface, providing a concentration gradient of copper “ions” in the modified layer and thus leading to diffusion of copper ions toward the film surface, which are themselves reduced, resulting in the formation of copper nanoparticles (Figures 2A and 2D), a mechanism much the same as UV-mediated silver metallization.^{2b} The thin nanocomposite layer thus generated catalyzes subsequent electroless copper deposition, after which the microstructure of the interfacial composite layer between the underlying film and the deposited copper remains unaltered (Figures 2B and 2E). The copper thin films are conductive⁸ and highly adhesive; the films and patterns readily pass the Scotch-tape test. We suggest that the nanocomposite layer formed at the interfacial region acts as a glue between the deposited copper and polyimide

via a nanoscale mechanical interlocking effect, which ensures good adhesion of the circuit patterns and may also allow further miniaturization of circuit features in copper interconnections.

We have introduced site-selective surface modification for the generation of copper micropatterns on a high-performance polyimide surface. The concept of creating ion exchangeable sites on a polyimide surface represents a powerful and potentially wide-ranging approach to incorporating various kinds of metallic ions on surfaces used for resist-free, site-selective metallization.⁹ Since the process may be compatible with other existing patterning technologies, we believe that the feature size of circuit patterns could be further miniaturized by employing alternative high-resolution printing techniques such as inkjet and/or microcontact printing. Although we have demonstrated here single-source metallization of polyimide, the generality of ion exchange also points to potential development of multilevel, flexible printed circuit boards interconnecting with, for instance, resistors, capacitors, and other semiconductor elements.

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Supporting Information Available: Micrographs of a wide range of circuit patterns, changes in line width with contact time, and experimental details for electroless copper plating and TEM observation (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) Typical amount of doped copper ions was estimated to be ca. 950 nmol cm^{-2} by ICP measurements for films printed at 30°C followed by standing for 5 min. This value corresponds to a modified layer thickness of ca. $3 \mu\text{m}$. Note that in the present case, the printed solvents are gradually evaporated during standing (but not completely after 5 min), leading to an increase in potassium hydroxide concentration, which induces a gradual increase in hydrolysis rate. The contact time also affects the feature size; the solution can diffuse in the direction parallel to the polyimide surface. See Supporting Information for details.
- (8) Specific resistance (measured by a four-probe method) was $1.84 \mu\Omega \text{ cm}$ (bulk copper: $1.67 \mu\Omega \text{ cm}$), which is suitable for USLI applications.
- (9) We have extended our method to the fabrication of Ag, Pt, Ni, In, and Sn circuit patterns using their respective metal salts, and the general behavior is similar to that of copper.

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