

A Nanoscale Metal Alkoxide/Oxide Adhesion Layer Enables Spatially Controlled Metallization of Polymer Surfaces

T. Joseph Dennes and Jeffrey Schwartz*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

ABSTRACT Seeding polymer substrates for the attachment and growth of metallic contacts is an important problem in modern microcircuit fabrication. A new method to effect such polymer metallization is described in which the polymer is first treated with vapor of zirconium or titanium tetra-*tert*-butoxide and then thermally to give several monolayers of zirconium or titanium oxides that are attached to the polymer surfaces. The thickness of this layer can be controlled by the vapor exposure time. The thin oxide layers withstand removal by strenuous flexing of the polymers, and they absorb copper sulfate from an aqueous solution. Upon simple treatment with dialkylaminoborane or sodium borohydride, the polymer is metallized with copper. The tetra-*tert*-butoxides can be deposited through a mask, and patterned metallization of the polymers is easily accomplished.

KEYWORDS: polymer metallization • adhesion layer

Manipulation of the surface properties of organic polymers to enable the attachment of other organics (1), inorganic high-*k* dielectric materials (2, 3), or conducting metals or metal oxides (4) is crucial for the realization of flexible organic electronic devices (5). In particular, creating new methods to seed polymer surfaces for electroless deposition of copper (6–10) would be of immediate importance, especially if such processing were rapid, operated under mild conditions (9), and enabled a high degree of surface control. Such methods would be especially significant if they were nondestructive of the polymer device surface (8, 11) and did not require extensive chemical structural variation (6, 7), which might compromise the beneficial electronic or mechanical properties of the polymer substrate.

We now report a new, high-yielding strategy for the generation of surface adhesion layers on precast polymers that can be used to seed these polymers with metallic copper. We illustrate our new method using a polyester and a polyimide, both of which have been proposed for use in flexible electronics (4, 12). In our method, a simple zirconium or titanium alkoxide complex is vapor-deposited onto the polymer surfaces; the thickness of this layer can be controlled through exposure times. The surface-attached alkoxide is then thermally decomposed under controlled conditions to give a surface metal oxide/alkoxide adhesion layer (13). This layer adheres robustly to the polymer surface, even after physical manipulation, in contrast to the somewhat thick surface coatings (2, 9) that are obtained by solution-based methods, which adhere poorly to the polymer and can crack from it when the polymer is flexed. Because

our technique involves vapor deposition of the adhesion layer, it can be combined with simple photolithography. This enables spatial control of surface derivatization with resolution on the order of at least ca. 2 μm , a dimension that is smaller than that reported for metallization by microcontact printing (7, 11); atomic force microscopy (AFM) and energy-dispersive X-ray (EDX) analysis show that the adhesion layer forms only where the lithographic patterns allow.

Thermolysis of metal oxide surface-attached zirconium and titanium tetra-*tert*-butoxides (**1** and **2**, respectively) proceeds by the sequential decomposition of *tert*-butoxide groups with the loss of isobutylene (14); through controlled heating, mixed alkoxide/oxides are formed (13), and cross-linking of the oxide units imparts robustness to this layer. We reasoned that polymers with organic functionality that could coordinate zirconium or titanium might serve, too, as substrates for alkoxide complex surface deposition. Indeed, we find that when solid poly(ethylene terephthalate) (PET; **3**) or Kapton polyimide (**4**) is exposed to the vapors of **1** or **2** and then heated, the desired mixed alkoxide/oxides (**5**) are formed. The IR spectrum of **5** showed, in addition to Kapton features, a significant peak at 2976 cm^{-1} , which is indicative of *tert*-butoxy groups; the water wetting angle (Θ) for **5** was measured to be 90°. Exposure to ambient moisture causes hydrolysis of the remaining *tert*-butoxy groups to give **6** (no peak at 2976 cm^{-1} ; $\Theta = 35^\circ$), which adheres strongly to the polymer surfaces (Scheme 1). Significantly, **6** can be used to nucleate the growth of copper metal on and adhesion to the polymer surfaces.

EXPERIMENTAL SECTION

General Procedures. All reagents were obtained from Aldrich and used as received unless otherwise noted. Acetonitrile was dried over CaH_2 overnight and distilled prior to use. Surface-modified samples were analyzed using a Midac M2510C interferometer equipped with a surface optics SOC4000 SH specular

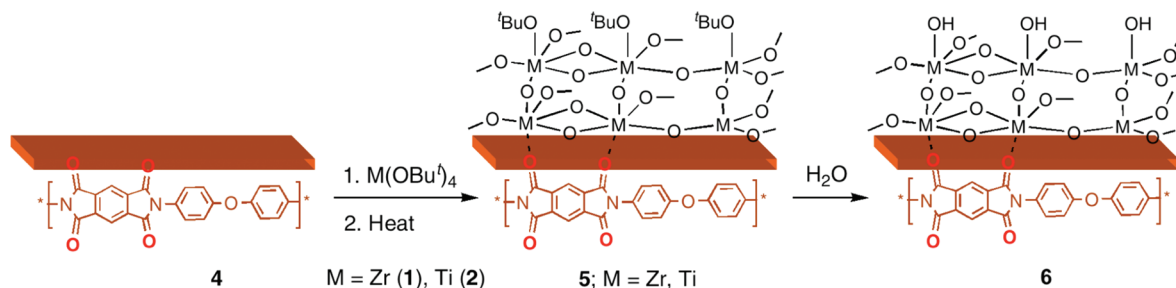
* E-mail: jschwartz@princeton.edu. Tel: 609 258 3926. Fax: 609 258 2383.

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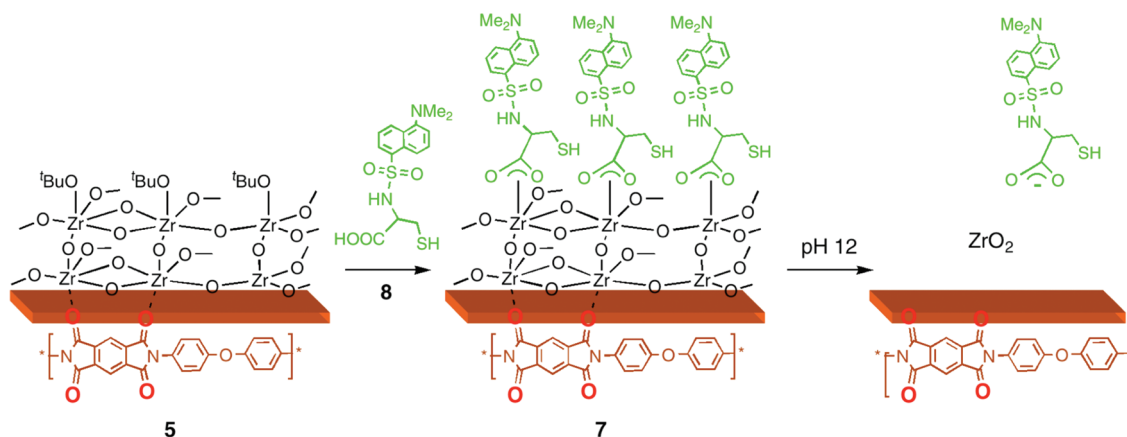
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Scheme 1. Deposition of Titanium or Zirconium Tetra-*tert*-butoxides onto Kapton, Followed by Heating, Gives Adhesion Layer 5, Which Is Hydrolyzed to 6



Scheme 2. Preparation and Hydrolysis of Fluorescently Labeled Polymer (DANSYL-Cys Fluoresces Green)



reflectance head attachment. Fluorimetry experiments used a Photon Technology International Fluorescence spectrometer. Quartz crystal microgravimetry (QCM) crystals were purchased from International Crystal Manufacturing.

Preparation of Polymer Films. Films of PET (3) and Kapton (4) (0.5 mm thick) were purchased from Goodfellow. The films were sonicated in ethanol for 15 min and blown dry in a stream of N_2 prior to use.

Formation of the Metal Oxide/Alkoxide Adhesion Layer (5). Coupons of the PET or Kapton films and a silicon-electrode-equipped QCM crystal were placed in a deposition chamber that had two stopcocks for exposure either to a vacuum or to the vapors of 1 or 2. The chamber was evacuated to 10^{-3} Torr for 30 min, and films of 3 and 4 were exposed to the vapors of 1 or 2 (with external evacuation) for 30 s, followed by 30 min of exposure without external evacuation. At this time, the stopcock for the metal alkoxide was closed, heating tape was applied, and the samples were heated to 75°C for 30 min and then allowed to cool to room temperature. The chamber was then evacuated for 30 min at 10^{-3} Torr to ensure the removal of excess 1 or 2 and to give surface-activated polymers, 5. The QCM crystal was rinsed with tetrahydrofuran and methanol. The measured change in the QCM crystal frequency indicated the amount of the alkoxide complex that had been deposited on it (13). These conditions yield an adhesion layer of 5 ± 1 nm; other deposition yields have been tabulated elsewhere (13).

Kapton Metallization. Kapton coated with a 5-nm-thick layer of 6 was soaked in a 200 mM aqueous solution of CuSO_4 for 12 h. Metallic copper was formed by a subsequent reduction by (dimethylamino)borane (1 M, aqueous, 6 h, 50°C) and was confirmed by EDX analysis.

Patterned Metallization of Kapton. Samples of 3 and 4 were spin-coated with a AZ 5214 (diazanaphthoquinonesulfonic ester) photoresist at 4000 rpm for 30 s and were cured at 95°C for 45 s. The samples were exposed to UV light (365 nm) through a mask and developed in a dimethylammonium hy-

droxide solution for 1 min. They were sequentially evacuated at 10^{-3} Torr for 1 h, treated with the vapors of 1, heated to convert the surface alkoxide layer to 5, hydrolyzed to 6, and metallized using CuSO_4 , followed by a reduction by (dimethylamino)borane (1 M, aqueous, 6 h, 50°C).

DANSYL-Modified Polymer Films. DANSYL-derivatized surfaces was prepared by immersing polymer slides coated with 5 in a 0.1 mM solution of *N*-[5-(dimethylamino)-1-naphthylsulfonyl]cysteine (DANSYL-Cys) in dry acetonitrile for 1 h.

Determination of the Interface Stability. Solvent-induced polymer swelling was studied using control polymer films that were prepared by soaking in a 0.1 mM DANSYL-Cys solution for 1 h. A calibration curve of fluorescence intensity versus concentration was measured for DANSYL-Cys solutions from 0.16 to $21 \mu\text{M}$ at both pH 7.5 and 12.5. Polymer films derivatized with DANSYL-Cys and control films were immersed in water at pH 7.5 for 3 days at room temperature, and the supernatants were analyzed by fluorescence spectroscopy. The polymer samples were then removed from solution, dried, and immersed in water at pH 12.5 for 3 h; under these conditions, the zirconium oxide layer is dissolved. The supernatants were again analyzed by fluorescence spectroscopy, and the initial spatial surface coverage by DANSYL-Cys was then calculated to be $90 \text{ pmol}/\text{cm}^2$.

AFM. AFM analysis of 6-coated PET and metallized Kapton was done using a Digital Instruments Multimode Nanoscope IIIa SPM equipped with silicon tips (Nanodevices Metrology Probes; resonant frequency, 276 kHz; spring constant, 40 N/m) in tapping mode. Polymer samples were prepared for imaging by mounting on a 1 cm^2 silicon wafer with double-sided tape.

EDX Analysis. EDX analysis of copper-metallized Kapton was done using a FEI XL30 field emission gun scanning electron microscope equipped with a PGT-IMIX PTS EDX system.

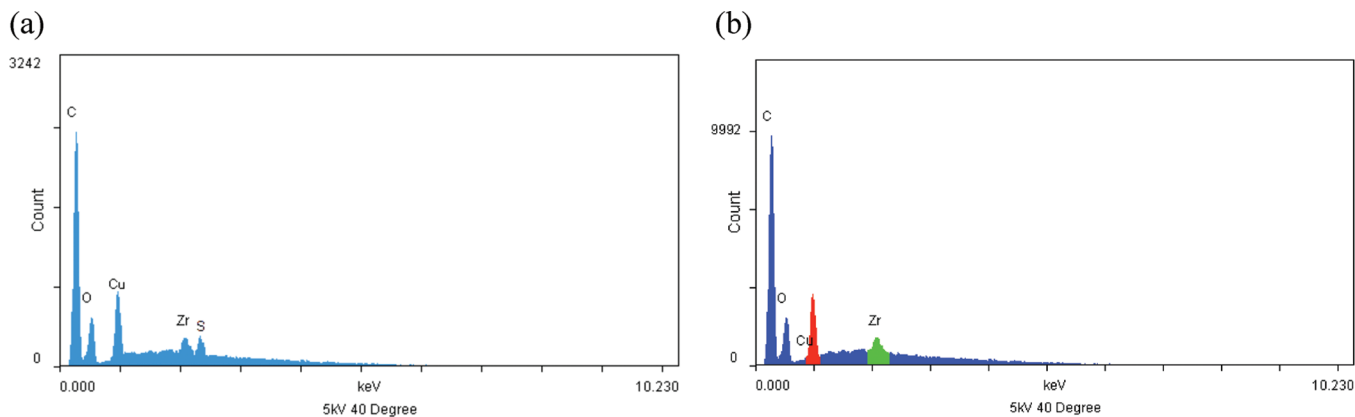


FIGURE 1. Elemental EDX scan of copper-treated Kapton (a) before and (b) after reduction (the colors are related to spatial distributions shown in Figure 2).

RESULTS AND DISCUSSION

Samples of PET (**3**) and Kapton (**4**) (0.5 mm thick) were cleaned in ethanol and blown dry in a stream of N_2 . Samples were then put into a chamber equipped with a QCM and exposed to the vapors of **1** or **2** (with external evacuation) for 30 s followed by 5 min of exposure without external evacuation. The chamber was then heated to 75 °C, cooled to room temperature, and briefly evacuated at 10^{-3} Torr to ensure the removal of excess **1** or **2** and to give **5**. The measured change in the QCM crystal frequency indicated the amount of alkoxide complex deposition (**13**).

Fluorescently labeled adducts (**7**) were then prepared on **5** (on both PET and Kapton) using DANSYL-Cys (**8**; Scheme 2) in order to demonstrate the stability of that oxide interface to hydrolytic cleavage from these polymers (**15**); the loss of fluorophore into solution under various conditions would be indicative of such a hydrolytic instability. The derivatized polymer substrates were immersed in water at pH 7.5 at room temperature, and supernatants were analyzed by fluorescence spectroscopy over 3 days. After removal of the residues of the initial synthesis, essentially no release of fluorescent material into solution occurred from either PET or Kapton during this time. The polymers were then removed from solution, dried, and immersed in distilled H_2O at pH 12.5 for 3 h; this cleaves the zirconium species from the surface to give ZrO_2 and releases the fluorophore into solution; analysis of the supernatants by fluorescence spectroscopy measured the amount of DANSYLated material in **7** to be ca. 90 pmol/cm².

Remarkably, **6** serves as a new type of matrix to enable straightforward polymer surface metallization using an aqueous solution of copper(II) as a precursor and simple borohydrides as reducing agents. Absorption of $CuSO_4$ onto **6**-coated Kapton was done by simple immersion in its aqueous solution. Reduction was accomplished using (dimethylamino)borane at 50 °C. EDX analysis before copper(II) reduction showed sulfur, consistent with nucleation of $CuSO_4$ at the polymer surface (Figure 1a). When evaporation of **2** onto Kapton was done through a photolithographic pattern, EDX analysis after $CuSO_4$ absorption and reduction showed patterns of both zirconium and copper on the

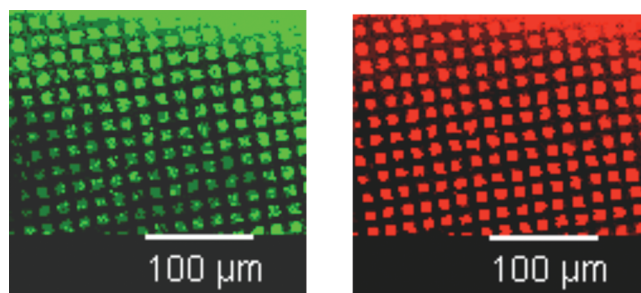


FIGURE 2. EDX map: zirconium (green) and copper (red) patterned on Kapton. Individual squares are 10 $\mu m \times 10 \mu m$.

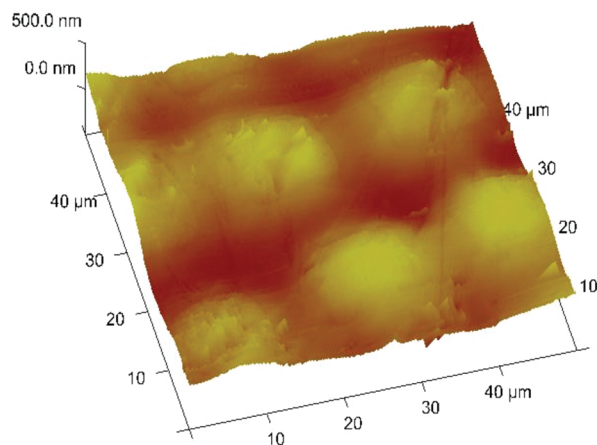


FIGURE 3. AFM of copper "seed" patterned on Kapton in 10 μm features by (dimethylamino)borane reduction of adsorbed $CuSO_4$.

Kapton surface that faithfully replicated the mask design (Figure 2); no sulfur was detected (Figure 1b).

The deposited and reduced copper pattern was subjected to sonication in water, rubbed with a Kimwipe, and then observed by AFM (Figure 3a). Intriguingly, the thickness of the generated copper "seed" was measured via AFM to be ca. 20 times thicker than the starting film of **5** (Figure 3a); apparently, **5** is capable of initiating and anchoring significant nucleation of $CuSO_4$ at the polymer surface. Samples of $CuSO_4$ -treated Kapton were also reduced rapidly using aqueous sodium borohydride to copper metal. Because adhesion layers **5** and **6** are thin (ca. 5 nm), they are resistant to cracking by physically flexing the polymer.

That **6** serves as a matrix for polymer metallization with copper is interesting because such “seeds” can serve as nucleation sites for further copper growth by electroless deposition (6–10). It is especially significant that **6** can be prepared in patterns on the polymer surface with micrometer-resolved spatial control. Further electroless metallization of the polymer would then provide a means to preparing copper-based electrical circuitry on a variety of flexible substrates under simple laboratory conditions.

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