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Adhesive Electroless Metallization of Fluoropolymeric Substrates

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Abstract

A process for producing patterned metal deposits on fluoropolymeric substrates is described. A metal ion-chelating organosilane is chemisorbed by self-assembly onto a fluoropolymer surface after radio-frequency glow discharge plasma surface hydroxylation. Positional modulation of the surface hydrophobicity is illustrated by wetting. the silane covalently binds an aqueous palladium catalyst, an subsequent electroless deposition yields homogeneous or patterned metal deposits that exhibit excellent adhesion to the fluoropolymer.

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Fluoropolymers such as poly(tetrafluoroethylene) (PTFE), or Teflon® are of considerable technological importance because the low surface energy and stable C-F bonds provide surfaces that are inert to most solvents and chemicals, and which prevent the adhesion of most chemical and biological materials. The low dielectric constant of fluoropolymers also makes them attractive as dielectric layers for microelectronic applications. However, for certain applications in which it is desirable to use fluoropolymers as a substrate, relatively few chemical pathways exist for stable attachment of materials to the fluorinated surfaces. In this paper, we apply the separately developed concepts of fluoropolymer surface hydroxylation, organosilane functionalization, and ligand-based EL deposition to yield a simple, effective method for producing adherent metal deposits on fluoropolymers, either homogeneously or in a pattern.

Approaches for promoting adhesive bonding of various materials, including metals, to fluoropolymer surfaces¹ typically use harsh chemical reagents (highly reducing alkalies, e.g., sodium naphthalide), or require complex sputtering or ion beam bombardment processes. A recently reported process² involves crosslinking of PTFE with x-rays followed by chemical etching, and then vapor deposition of Cu by decomposition of an organo-copper reagent. These methods are often difficult to use and can adversely affect the chemical and morphological characteristics of the surface.

We have recently shown that fluoropolymers can be functionalized by chemisorption of organosilane reagents to plasma-treated fluoropolymer surfaces.³⁻⁶ Radio frequency glow discharge (RFGD) treatment of the fluoropolymer surface using a novel gas-liquid mixture partially defluorinates the surface with simultaneous addition of hydroxyl functionalities. A unique aspect of this plasma treatment is that the surface is modified without inducing significant roughening.³ The hydroxylated surface exhibits similar reactivity to Si-OH groups on silicon oxide surfaces, and can be reacted with organosilane reagents to covalently immobilize various desired functionalities on the fluoropolymer surface.⁴⁻⁶ It has also been shown that plasma treatment can be restricted to particular regions of the surface using a mechanical mask; subsequent attachment of the organosilane

occurs only in the areas exposed to the plasma. Such patterned aminoalkylsilane/fluoropolymer surfaces have been successfully used as chemical templates for the selective attachment and growth of neurons.⁵

We have also shown that selective, adhesive metallization of a wide range of non-fluorinated substrates to sub-micron resolution can be accomplished by electroless (EL) deposition.⁷⁻¹³ Surfaces functionalized with self-assembled monolayer (SAM) films of ligand-bearing organosilanes covalently bind a Pd catalyst from aqueous solution, and are then metallized by immersion in an aqueous EL deposition bath.¹⁰⁻¹³ As shown below, fluoropolymer surface modification and ligand-based EL deposition can be combined to yield patterned, adhesive metallization on these substrates.

The increased concentration of surface hydroxyl groups in regions of a poly(hexafluoro-co-tetrafluoroethylene) (FEP) film exposed to RFGD plasma treatment is illustrated by placing drops of water and methanol on the patterned surface (Figure 1).¹³ The amount of outward curvature of the drop indicates the extent to which the liquid spreads on the surface; inward curvature indicates that the liquid does not appreciably wet the surface. Methanol, a much less polar liquid than water, exhibits considerably greater wetting of the 70 μm wide lines that correspond to the plasma oxidized regions. This result is consistent with the previously proposed model³⁻⁵ whereby RFGD treatment provides a controllable amount of defluorination of the FEP surface.

After plasma treatment, the FEP was functionalized in a solution of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (EDA). The attachment of the EDA SAM film to the FEP surface was confirmed by SIMS and XPS analysis.⁴⁻⁶ The silanized FEP films were placed into an aqueous PdCl_4^{2-} catalyst solution to bind Pd to the EDA surface. The substrate was then immersed in an EL Ni plating bath to deposit Ni metal on the catalyzed regions. Figure 2 shows 70 μm wide metal lines selectively deposited on FEP using this process.

For adhesion testing, an FEP substrate was homogeneously hydroxylated, functionalized with EDA, and metallized with EL Ni for 3 hrs. to produce a uniform, mirror-like

deposit of Ni ~2500 Å in thickness. Both Scotch® tape and ASTM standard tape peel tests resulted in complete adhesion of the metal to the FEP surface. Covalent bonding of the organosilane to the hydroxylated fluoropolymer surface and coordinative bonding of the Pd catalyst to the EDA surface ligand are likely the key contributors to the high adhesion of the EL deposit to the substrate. The use of mild plasma treatment and aqueous chemical treatments are desirable features that may be enabling for practical applications that require fluoropolymer surface modification and metallization.

Acknowledgements

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Figure Captions

- 1) Optical micrographs of sessile drops of water (left), and methanol (right) placed on a patterned plasma treated FEP surface. The patterned surface was prepared by placing a Ni mask having 70 µm lines separated by 150 µm wide open regions in mechanical contact with a free-standing 50 µm thick FEP film. Modification was performed in an RFGD plasma using 1W/liter RF power density at 0.1 torr of a H₂/CH₃OH mixture for 15 sec.
- 2) Optical micrograph of a selectively metallized FEP film. The film was hydroxylated in patterns as described in Figure 1. The surface was then functionalized by treatment in a 0.1% (v/v) solution of EDA in hexane for ~20 sec and then rinsed in hexanes. The EDA surface was catalyzed by immersion in a chloride-stabilized, buffered solution of PdCl₄²⁻ at pH 5 for 30 min. The catalyzed surface was then metallized by immersion in a modified NIPOSIT® 468 EL plating bath (Shipley Co.).

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Fig. 1



Fig. 2

