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13 July 1993; accepted 7 October 1993

Adhesive Electroless Metallization of Fluoropolymeric Substrates

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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 and subsequent electroless deposition yields homogeneous or patterned metal deposits that exhibit excellent adhesion to the fluoropolymer.

Fluoropolymers such as poly(tetrafluoroethylene) (PTFE) and 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 that prevent the adhesion of most chemical and biological materials (*1*). The low dielectric constants of fluoropolymers make them particularly attractive as dielectric layers for microelectronic applications (*2*, *3*). However, for certain applications in which it is desirable to use fluoropolymers as a substrate, relatively few chemical pathways exist for the stable attachment of materials to the fluorinated surfaces. In this report, we apply the separately developed concepts of fluoropolymer surface hydroxylation (*4*) and subsequent organosilane functionalization (*5–8*) with ligand-based electroless deposition (*9–13*); the combination of these techniques yields 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 surfaces typically use harsh chemical reagents (highly reducing alkalies, such as sodium naphthalide) or require complex sputtering or ion beam bombardment processes (*2*, *3*). A recently reported process (*14*) involves cross-linking of PTFE with x-rays followed by chemical etching and then vapor deposition of Cu by decomposition of an organocopper reagent. These methods are often difficult to use, may be environmentally problematic, 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 (*4–8*). Radio-frequency glow discharge (RFGD) treatment of the fluoropolymer surface using a novel gas-liquid mixture (*4*) partially defluorinates the surface with simultaneous addition of hydroxyl functionalities. An important aspect of this plasma treatment is that the surface is modified without inducing significant roughening. The hydroxylated surface exhibits a reactivity similar to that of Si–OH groups on silicon oxide surfaces and can be reacted with organosilane reagents to covalently immobilize various desired functionalities on the fluoropolymer surface (*5–8*). It has also been shown that use of a mechanical mask can restrict plasma treatment to particular regions of the surface; 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 (*7*, *8*).

We have also shown that selective, adhesive metallization of a wide range of nonfluorinated substrates to submicrometer resolution can be accomplished by electroless deposition (*11–13*, *15–17*). Surfaces functionalized with self-assembled monolayer (SAM) films of ligand-bearing organosilanes covalently bind a Pd catalyst (*10*, *18*) from aqueous solution and are then metallized by immersion in an aqueous electroless deposition bath. As shown below, fluoropolymer surface modification and ligand-based electroless deposition can be combined to yield patterned, adhesive metallization on these substrates.

It has been demonstrated that wetting is an extremely effective technique for imaging a surface that has patterns of functional groups with differing surface energies (*19*, *20*). Drops of liquid are placed on the patterned surface and observed by optical microscopy. 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. We used this approach to visualize the increased density of hydroxyl groups in selected surface regions of a plasma-treated fluoropolymer. Poly(hexa-

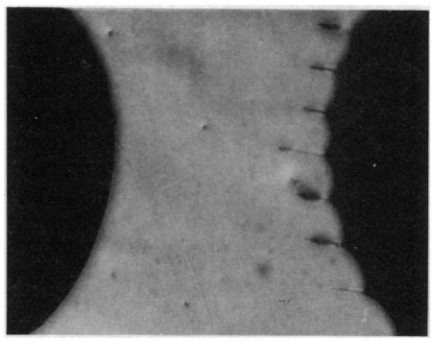

Fig. 1. Optical micrographs of sessile drops of water (left) and CH_3OH (right) placed on a patterned, plasma-treated FEP surface. We prepared the patterned surface by placing a Ni mask having 70-μm-wide lines separated by 150-μm-wide open regions in mechanical contact with a free-standing FEP film 50 μm thick. Modification was performed in an RFGD plasma with a radio-frequency power density of 1 W/ml at a pressure of 0.1 torr in a H_2-CH_3OH mixture for 15 s.

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fluoropropylene-*co*-tetrafluoroethylene) (FEP) film was exposed to a RFGD plasma that was composed of a flowing vapor mixture of H_2 and methanol (CH_3OH) (*4*). The polymer film was covered in the plasma by a metal mask with open regions each 70 μm wide spaced between covered regions each 150 μm wide. This produced hydroxy- lated regions each 70 μm wide, spaced by unmodified FEP. Figure 1 shows the differential wetting characteristics of this surface when probed with drops of CH_3OH (right) and water (left). Water, when applied to the plasma-treated FEP surface, shows little or no detectable difference in wetting between the protected and exposed regions. The observed lack of wetting of the water drop is consistent with the results of previous surface analytical studies (*7*), which showed that FEP is only partially defluorinated after treatment with the H_2-CH_3OH plasma; the resulting hydroxylated FEP surface is still considerably hydrophobic, which is characteristic of the bulk fluoropolymer. However, differential wetting is clearly observed with CH_3OH, a less polar liquid, on the exposed regions 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 secondary ion mass spectrometry and x-ray photoelectron spectroscopy analysis (*5–7*). 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 electroless Ni plating bath to deposit Ni metal on the catalyzed regions. Figure 2 shows metal lines each 70 μm wide selectively deposited on FEP by this process.

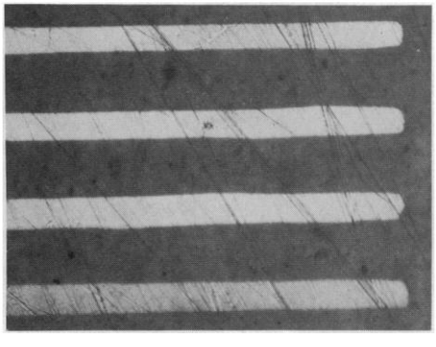

Fig. 2. Optical micrograph of a selectively metallized FEP film. The film was hydroxylated in patterns as described in Fig. 1. The surface was then functionalized by treatment in a 0.1% (v/v) solution of EDA in hexane for ~20 s and then rinsed in hexanes. The EDA surface was catalyzed by immersion in a chloride-stabilized, buffered solution of $PdCl_4^{2-}$ at pH 5 for 30 min. The catalyzed surface was then metallized by immersion in a NIPOSIT 468 electroless plating bath (Shipley Company).

For adhesion testing, an FEP substrate was homogeneously hydroxylated, functionalized with EDA, and metallized with electroless Ni for 3 hours to produce a uniform, mirror-like deposit of Ni ~2500 Å thick. Peel tests with both Scotch tape and American Society for Testing and Materials standard tape indicated the 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 electroless deposit to the substrate. The use of mild plasma treatment together with aqueous chemical treatments may find practical applications in fluoropolymer surface modification and metallization.

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21. This work was sponsored by the Office of Naval Research under the Molecular Engineering Advanced Research Initiative (at the Naval Research Laboratory) and under the Molecular Interactions at Marine Interfaces program (at the State University of New York–Buffalo) and also by the Shipley Company.

17 May 1993; accepted 2 September 1993

Translocation of Repetitive RNA Sequences with the Germ Plasm in *Xenopus* Oocytes

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Xlsirts are a family of interspersed repeat RNAs from *Xenopus laevis* that contain from 3 to 13 repeat units (each 79 to 81 nucleotides long) flanked by unique sequences. They are homologous to the mammalian *Xist* gene that is involved in X chromosome inactivation. Xlsirt RNA appears first in the mitochondrial cloud (Balbiani body) in stage 2 oocytes and is then translocated as island-like structures to the vegetal cortex at early stage 3 coincident with the localization of the germ plasm. Exogenous Xlsirt RNA injected into oocytes translocates to the location of the endogenous RNA at that particular stage. The Xlsirt RNA repeat sequences are required for translocation and can cause the translocation of heterologous unique RNAs to the vegetal cortex.

A universal characteristic of developing organisms is the acquisition and interpretation of spatial information. Studies in *Drosophila* have demonstrated a complex network of gene products involved in the spatial organization of the posterior pole of the oocyte; however, the understanding of vertebrate regulation of spatial patterning is less advanced (*1*). The vegetal cortical region of the *Xenopus* oocyte contains developmental information in the form of germ plasm, which is involved in germ cell determination, and specialized cytoplasm, which is activated upon cortical rotation and contributes to the future dorsal axis (*2*). Several transcripts, including Vg1, a member of the transforming growth factor–β family (*3*), and Xcat2, which has similarities to *Drosophila nanos* (*4*), are localized in overlapping spatial patterns at the vegetal cortex. Xcat2 is localized during stage 3 and Vg1 during stage 4, which suggests their possible dependence upon one another for proper localization.

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