Photopatterning and Selective Electroless Metallization of Surface-Attached Ligands

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Chemisorption of ligand-bearing organosilanes has proven to be a useful method for imparting specific physical and chemical properties to various surfaces.[1] For example, silica particles derivatized with appropriate ligands constitute efficient resins for preconcentration of trace metal ions prior to analysis.[2] Organometallic complexes bound by ligands at such surfaces can function as efficient heterogeneous catalysts.[3] Covalently anchored metal complexes have also been useful as probes in fundamental studies of electron transfer at chemically modified electrodes.[4]

The ability to attach ligands which bind proteins,[5] cells,[6,7] and other biomolecules to substrates forms the basis for a variety of technologies including affinity chromatography, biosensor development, and ELISA immunoassays.[1] With regard to these latter applications, it is especially desirable to precisely control the position of surface bound species in order to maximize activity, minimize background interferences, and provide for the detection of multiple analytes in the smallest possible sample volumes. Microlithographic techniques involving the photochemical modulation of ligating ability offer one potential route for achieving such objectives.[5-9]

Recently, we described a new photopatterning technique involving masked deep-UV irradiation of ultrathin films (UTFs) of nonligating organosilanes chemisorbed onto various surfaces.[6,10,11] Monolayer UTFs possessing simple chromophores such as a benzene ring were patterned via Si–C bond photocleavage. Selective electroless (EL) metallization of the masked UTF regions was demonstrated following irradiation and treatment with a colloidal Pd/Sn EL catalyst. Construction of working Si-based transistor test structures from the patterned metal surfaces was achieved using a previously described procedure.[10,12]

We report here an application of our patterning techniques to chemisorbed UTFs of ligand-bearing organosilanes such as 2-[2-(trimethoxysilyl)ethyl]pyridine (PYR). Figure 1 illustrates a general scheme for the patterning and EL metallization of PYR films. Clean fused silica slides and native oxide silicon wafers[6] are first treated with 1 wt % PYR in 1 mM acetic acid/toluene; the solution temperature is ramped to 60 °C during 1 h. Chemisorption occurs at the hydroxylated surface via siloxane (Si–O–substrate) bond formation. The treated substrates are rinsed and baked at 120 °C for 4 min to complete the chemisorption process. UV spectra (CARY 2400 spectrophotometer) of the treated fused silica slides show absorptions due to the pyridine chromophores at ~190 and ~265 nm. Film thicknesses on native oxide Si of 5 ± 1 Å as measured by ellipsometry (Gaertner L115C ellipsometer) are consistent with monolayer quantities of PYR on the surface. The constancy of ellipsometric film thickness and sessile water drop contact angle (50 ± 3°) data across extended regions of the treated substrates is indicative of good film uniformity.

The PYR UTF in Figure 1 is patterned by exposure to masked deep-UV radiation. For example, a 4 J/cm^2 radiation dose delivered at 193 nm using a Questek 2000 ArF excimer laser leads to removal of the pyridyl chromophore from the substrate surface as shown by UV spectra and ellipsometric measurements. Equivalent photochemical changes are observed using a variety of UV sources exhibiting a wide range of radiation intensities. Laser desorption Fourier transform mass spectrometry experiments indicate that photoproducts of $m/z = 107$ corresponding to 2-ethylpyridine (C_7H_9N) are generated during irradiation of the film at either 193 or 248 nm. No evidence for Si or organosilicon fragments is observed in the mass spectrum, and signal-to-noise ratios at each irradiation wavelength are consistent with the corresponding absorption intensities at the UV wavelengths in the PYR film UV spectrum. The photolyzed surfaces exhibit high wettability (contact angle <10°) associated with the presence of Si–OH surface groups. These results implicate Si–C bond photocleavage as a major pathway for the photodesorption of the pyridyl chromophore from the surface. Such a mechanism is consistent with that observed earlier[6,10] in our studies involving nonligating organosilane UTFs.

Masked deep UV irradiation of PYR ultrathin films in Figure 1 leads to production of a positive tone ligand image on the surface. Intact pyridyl ligands can interact with Pd(II) solution species to generate catalyzed surfaces amenable to EL metallization processes.[8] The catalyst (PD1) is prepared by dissolving 11.5 mg of $Na_2PdCl_4\cdot 3H_2O$ in 1 mL 1.0 M NaCl(aq), adding 10 mL of 0.1 M pH 5 morpholinoethanesulfonic acid(aq) buffer, and diluting to 100 mL with H_2O. After standing at 23 ± 1 °C for 20 h, a 10-mL aliquot of the solution is removed and replaced by 10 mL of 1.0 M NaCl(aq) to yield active PD1 catalyst. The solution exhibits a UV absorption maximum at ~280 nm tailing into the visible; this feature has been assigned to the presence of chloro/hydroxy-bridged Pd(II) oligo-

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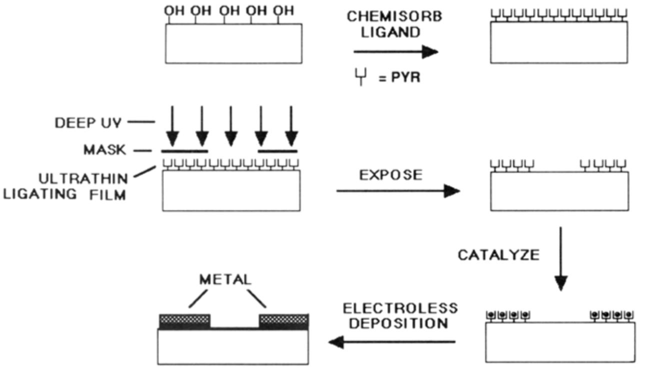

Figure 1. Patterning and selective EL metallization of the ligand-modified surfaces.

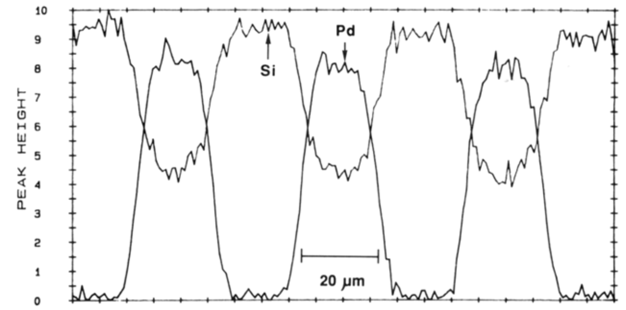

Figure 2. AES line scans of line-space pair patterned PYR films on native oxide Si after 30 min of treatment with PD1 solution. Scans for Pd and Si are shown. A model PHI660 Auger electron spectrometer operated at 3 kV and 1–10-nA beam current was used for the scans.

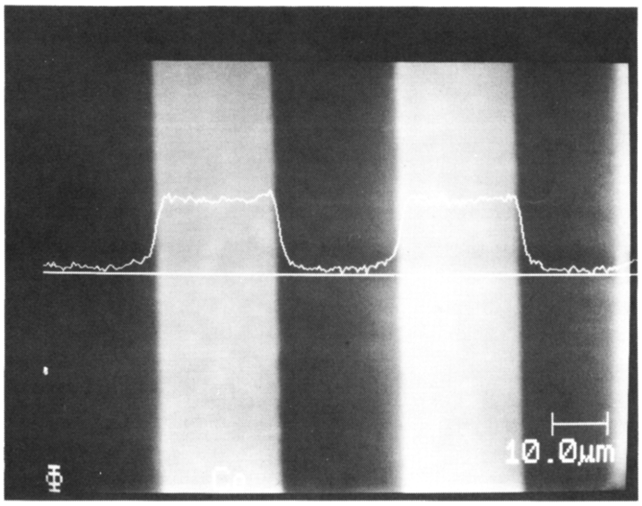

Figure 3. AES Co metal line scan and SEM micrograph of CoB metal patterns on native oxide Si. The metal was electrolessly deposited onto a patterned PYR film catalyzed with PD1 as outlined in Figure 1. AES parameters are as described for Figure 2.

mers.[13,14] The observation of this absorption on fused-silica PYR films catalyzed by PD1 indicates that catalysis involves uptake of Pd(II) oligomers by the film.

The reactivity of the bound oligomers toward solution reagents provides information concerning the nature of the binding of Pd(II) by PYR films. Negligible ion exchange or desorption (<5%) of Pd(II) as measured by UV absorption occurs following prolonged (20 h) treatment of the catalyzed film by 1.0 M NaCl(aq). The reaction of HCl with Pd(II) oligomers regenerates $PdCl_4^{2-}$ and related monomeric species.[15] The Pd(II) species remaining on catalyzed PYR surfaces following HCl contact is identified as the covalent $(PYR)_2PdCl_2$ complex by comparison with a known sample.[16] These observations support covalent bond formation as the dominant binding mode at the surface in agreement with studies involving related Pd(II)–ligand systems.[17–20]

Pd(II) deposition is selective; it does not occur in the absence of the PYR nitrogen group. For example, phenethyltrichlorosilane (PES) possesses no ligating N group but is otherwise isostructural with PYR. Films of PES do *not* interact with PD1 as determined by wetting, UV absorption, and metallization experiments. In contrast, conventional colloidal Pd/Sn EL catalysts adsorb to both PYR and PES films; PD1 therefore exhibits enhanced specificity with respect to Pd/Sn catalysts. The irradiated regions of the PYR film from Figure 4 likewise do not bind Pd(II). Binding selectivity is shown by Auger electron spectroscopy (AES) examination in Figure 2 of a line-space pair patterned PYR film following 30-min PD1 treatment. Line scans show the presence of Si, but not Pd, in the irradiated spaces consistent with the lack of ligating functions in these regions. In contrast, significant quantities of Pd(II) are observed on those lines which were unirradiated. The observation of a Si signal in these areas indicates that the Pd layer is either sufficiently thin or heterogeneous to permit escape of photoelectrons from the underlying Si substrate.

The surface bound Pd species selectively catalyze EL metallization. Treatment of catalyzed ligand patterns as depicted in Figure 1 with a 25% strength CoB EL bath[21] for 4 min at 25 ± 2 °C permits construction of positive tone metal patterns in Figure 3 on the original ligand patterns. The AES Co line scan in Figure 3 indicates the expected absence of metal in the irradiated spaces and a strong Co presence on the lines corresponding to the original ligand patterns. Surface profilometry (Dektak Model 120) indicates a Co metal thickness of ~300 Å for the sample. The AES results are consistent with Figure 1 and our understanding of PYR ultrathin film chemistry. Figure 1 therefore represents a viable alternative to earlier patterning/EL metallization techniques utilizing nonligating organosilane UTFs for the construction of metal patterns on surfaces.[6,10]

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[16] $(PYR)_2PdCl_2$ was prepared by addition of a stoichiometric quantity of PYR (0.108 mL) to a suspension of 96.3 mg $(PhCN)_2PdCl_2$ in 250 mL of anhydrous toluene. The red-orange suspension is converted to a clear, pale-yellow solution upon addition of the PYR. This solution is used to directly treat substrates as described for PYR in the text.

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[21] The EL cobalt bath is prepared by mixing 3 volumes of stock cobalt solution, 1 volume of stock reductant solution, and 12 volumes of deionized water immediately prior to use. Stock cobalt solution is prepared by dissolving 6.0 g of $CoCl_2 \cdot 6H_2O$, 10.0 g of NH_4Cl, and 9.8 g of tetrasodium ethylenediamine tetraacetate in 150 mL of deionized water. The solution pH is then adjusted to 8.1 using 2 M NaOH(aq). Stock cobalt solution is stored under Ar atmosphere until needed for EL metallization experiments; the useful lifetime of a solution stored in this manner is 3 days. Stock reductant consists of a solution of 8.0 g of dimethylamine borane complex in 100 mL of water.

In conclusion, we have demonstrated here an ability to pattern surface-tethered ligands and thereby spatially control the deposition of an EL catalyst at a surface. Such catalysts are active at the surface and serve to initiate selective EL deposition of metal features useful in microlithographic applications. The concepts of retained surface reactivity and ligand host–guest interactions are clearly general ones applicable to immunoassay, bioimplant, and sensor as well as microelectronics technologies. Successful applications in these areas will require a determination and understanding of the factors influencing ligand and catalyst interactions with the substrate surfaces. Generalizations of the scheme described in Figure 1 and the realization of applications in these technologies constitutes the continuing goal of our research.

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