Surface Patterning of Polychloromethylstyrene Films

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Abstract: We describe and characterize a simple process for the fabrication of patterned materials on polychloromethylstyrene thin film surfaces under ambient conditions. Patterned deep UV exposure ($\sim$60 mJ cm^{-2}, 193 nm) efficiently oxidizes the surface C–Cl bonds of the polymer film, producing an aldehyde species as the major photoproduct. Reductive amination in the presence of ammonium ion and cyanoborohydride reductant selectively converts the aldehyde into an alkylamine, which leads to an amine reactivity template on the film surface. The amines formed are sufficiently reactive to selectively and covalently bind fluorescent dye or electroless Ni metal to the template, which results in negative tone features with micron-scale resolutions (mask limited) in each case. Spectroscopic characterizations of the polymer surface following the photochemical transformation, reductive amination, and grafting steps are presented in support of the process. A key advantage of the method is the use of safe solvents, such as water or simple alcohols, to effect the reductive amination and grafting reactions. This approach mitigates waste disposal and associated environmental concerns, increasing the attractiveness of our method for use with high-throughput track-line processing equipment.

Keywords: conducting materials · immobilization · photooxidation · polymer thin films · surface chemistry

Introduction

The ability to spatially control polymer surface reactivity without affecting bulk properties for the selective deposition of materials, such as metals, ceramics, or other chemical and biological species, is critically important for microelectronics, optics, and sensor technologies.[1] Photoresist coatings currently provide the most common means for pattern definition on an underlying polymer surface.[2] However, organic solvents and development residues associated with their use can pose environmental problems, swell or otherwise distort the underlying patterned polymer, or inhibit its accessibility during subsequent reactions.[2, 3] Although direct irradiation of the polymer surface may induce useful chemical changes, many polymers lack the high photosensitivity required for cost effective patterning.[4] This situation has prompted us to examine polymers containing functional groups more amenable to direct photopatterning at low exposure doses. We describe here the efficient deep UV photochemistry of the chloromethylphenyl (CMP) group and illustrate selective grafting of amine, dye, and metal species to irradiated regions of the corresponding polychloromethylstyrene (PCMS) films.

Results and Discussion

PCMS and its copolymers have long been exploited as electron beam and deep UV photoresists due to the radiation sensitivity of their C–Cl bonds.[5] Work has focused mainly on optimizing crosslinking reactions of benzyl radicals formed within the film during exposure to tune photoresist solubility and plasma etch resistance, with little regard for the surface chemistry. However, as shown in Figure 1 A, deep UV irradiation at 193 nm under ambient conditions induces significant changes in the absorption spectrum and surface chemistry of a PCMS film. The spectrum prior to exposure shows a strong absorption band at $\sim$200 nm ($\varepsilon \sim 5 \times 10^7$ cm^2 mol^{-1}) and shoulder at $\sim$220–225 nm characteristic of the CMP chromophore (solid line; Figure 1 A). The intensities of these features monotonically decrease and are accompanied by the growth of a new band at $\sim$260 nm with

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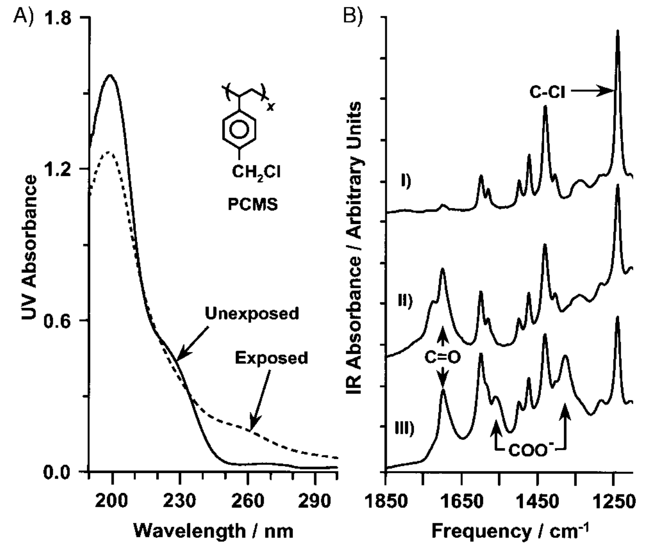

Figure 1. UV absorption (A) and IR (B) spectra for PCMS films. See text for details.

increasing exposure (dotted line; Figure 1 A). X-ray photoelectron spectroscopy (XPS) of the film shows that the XPS Cl(2p)/C(1s) ratio decreases from ~11% to ~3% after irradiation (80 mJ cm^{-2}), confirming loss of Cl from the surface. Analysis of the products photodesorbed from the PCMS surface by Fourier-transform mass spectrometry during exposure indicates that Cl is lost as volatile HCl gas. At the same time, the sessile water drop contact angle (θ_w) of the film drops exponentially with dose from ~87 ± 2° (3σ) to ~60 ± 5° (3σ) (1/*e* ~ 19 ± 2 mJ cm^{-2}) and the XPS O(1s)/C(1s) ratio increases from < 1% to ~20%, consistent with the formation of a more wettable, oxidized surface.

The nature of the surface photoproducts can be ascertained by examination of the PCMS film by IR spectroscopy (Figure 1 B). Prior to irradiation, spectrum I exhibits a strong signal at ~1250 cm^{-1} characteristic of the CH_2-Cl wag in the PCMS film, together with various C-C absorptions due to the aromatic ring in the 1400-1600 cm^{-1} region. However, after exposure at ~80 mJ cm^{-2} in spectrum II, the intensity of the ~1250 cm^{-1} band is reduced, as expected for C–Cl bond rupture. In addition, a broad bimodal absorption at ~1700-1725 cm^{-1} indicative of a carbonyl species is observed. The 1400-1600 cm^{-1} region remains essentially unchanged, consistent with localization of the photochemical changes at the benzyl carbon sites.[6] Treatment of the irradiated film with an aqueous NaOH solution (~0.1 mol L^{-1}) in spectrum III leads to the appearance of new bands at ~1569 cm^{-1} and 1397 cm^{-1} and eliminates the high-energy carbonyl component at ~1725 cm^{-1}. These new bands are characteristic of symmetric and antisymmetric carboxylate stretches, respectively, confirming the assignment of the band at ~1725 cm^{-1} as a carboxylic acid. The remaining carbonyl component at ~1700 cm^{-1} is consistent with the presence of an aldehyde co-product, an assignment confirmed by subsequent reactivity studies described below.

The degree of oxidation and the carboxylic acid/aldehyde ratio observed depend on the exposure dose and the presence of oxygen and water during irradiation. As the dose is raised, a monotonic increase in the carbonyl band intensity is observed. The fraction of the band attributable to carboxylic acid simultaneously increases at the expense of the aldehyde component, consistent with the known abilities of oxygen and atmospheric ozone (generated during 193 nm exposure) to oxidize aldehydes to carboxylic acids.[7] The fractional surface carboxylic acid contributions measured following exposures of 20, 50, and 80 mJ cm^{-2} are ~32 ± 2, 35 ± 3, and 40 ± 3%, respectively, suggesting that ozone oxidation provides a minor, though observable, contribution to the photoproduct distribution. Extrapolation of these data to zero dose provides a nascent product distribution of ~70 ± 4% aldehyde and ~30 ± 4% carboxylic acid, suggesting the possibility of multiple photochemical reaction pathways during irradiation. Analogous results are obtained during irradiation of model chloromethylphenylsiloxane monolayer films under N_2 atmosphere, where water is the likely oxygen source. In this case, however, the amount of carboxylic acid produced is reduced ~60% relative to levels observed during irradiation in air, providing a larger fraction of aldehyde at the irradiated surface. Consequently, irradiation of PCMS films at 193 nm under ambient or N_2 atmosphere produces aldehyde as the major surface photoproduct, at least for exposure doses ≤100 mJ cm^{-2}.

The formation of aldehyde and carboxylic acid provides a convenient means to covalently attach materials to the PCMS surface, whose C–Cl bonds are relatively inert under ambient, aqueous reaction conditions. For example, numerous aqueous methods based on peptide chemistry have been previously demonstrated for the attachment of amine- or alcohol-functionalized materials to surface-bound carboxylic acids.[8] Although fewer options are available, aldehydes are rapidly and reversibly reacted in aqueous or alcohol solution with amines to form imines, which can be selectively and irreversibly trapped by reduction to an amine using $NaBH_3CN$ (pH ~6).[9]

The possibility of creating a reactive amine group on the PCMS surface by reductive amination of the aldehyde photoproduct prompted us to further investigate this reaction as a means for grafting materials. We first determined an optimum exposure dose for aldehyde formation on the surface. PCMS films subjected to various 193 nm exposure doses were treated with CH_3OH or CH_3OH/H_2O solutions containing NH_4OAc (OAc = acetate) and $NaBH_3CN$ (see Experimental Section) at room temperature. The reduction in the film UV absorption intensity at ~260 nm due to the aldehyde/carboxylic acid photoproducts was monitored until no further changes were noted (i.e., ~12 h), indicating that complete conversion of the available aldehyde to the amine had occurred. An XPS N(1s) signal at ~400 eV confirmed the presence of amine on each of the reacted irradiated samples. The increase in XPS N(1s) signal intensity with exposure dose observed for the samples (Figure 2 A) was described by a single exponential with 1/*e* ~17 ± 3 mJ cm^{-2}, in good agreement with the oxidation behavior as measured earlier by θ_w (i.e., ~19 ± 2 mJ cm^{-2}). The N(1s) signal intensity reached a plateau for doses exceeding ~60 mJ cm^{-2}, consistent with maximum conversion of solution-accessible C–Cl bonds to oxidized products above this dose. Because aldehyde levels

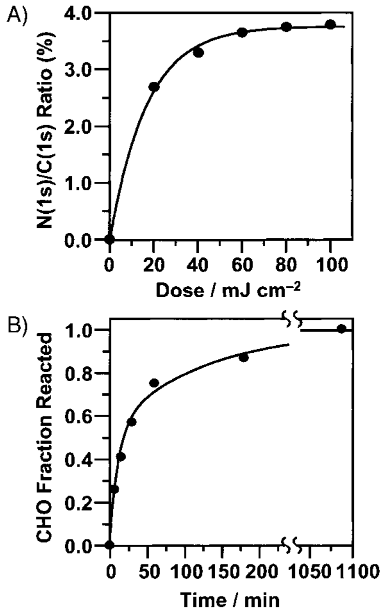

Figure 2. Dependence of the reductive amination of the surface aldehyde on exposure dose (A) and reaction time (B). The XPS N(1s)/C(1s) ratio, R, is fit to the exposure dose D by the function $R = 3.76[1 - \exp(-0.06D)]$ with $r^2 = 0.99$ in A. The fraction of aldehyde converted to amine F is determined from UV absorption spectra using the formula $F = (A_t - A_L)/(A_0 - A_L)$, where A_t is the absorbance at 260 nm of the exposed PCMS film after time t in the $NH_4OAc/NaBH_3CN$ solution, A_0 is the absorbance prior to amine grafting, and A_L is the limiting absorbance at the completion of the amine grafting reaction. The dependence of F on t is given by the double exponential of the form $F = 0.54[1 - \exp(-0.086t)] + 0.46[1 - \exp(-0.008t)]$ with $r^2 = 0.94$. Conditions for each experiment are discussed in the text.

were reduced at higher doses due to ozone oxidation, the 60 mJ cm^{-2} dose was chosen for the remaining experiments to maximize aldehyde levels for amine grafting.

Additional insight concerning the amine grafting process can be obtained by monitoring the time dependence of the reductive amination reaction for PCMS samples exposed at 60 mJ cm^{-2}. The fraction of the aldehyde reacted, as measured by the decrease in the intensity of the UV absorption at 260 nm, is plotted versus reaction time in Figure 2B. An initial rapid conversion of ~80% of the aldehyde to amine is followed by a much slower conversion of the remaining aldehyde at longer times. The processes are each first order, with $1/e$ ~12 ± 2 min and ~120 ± 25 min, respectively. While a detailed mechanistic study has not yet been completed, our preliminary observations are well described by a simple model involving conversion of the outermost, accessible aldehyde surface groups to amines during the initial, rapid step. The protonation of these amines, together with their ability to control the local structure of hydroxylic solvents through hydrogen-bonding,[10] suggests the formation of a steric or electrostatic barrier that impedes the approach of additional NH_4^+ species from the solution. Consequently, the reaction of aldehyde groups buried in underlying solvent-accessible nanocavities[11] should naturally proceed at a much slower rate, given the need to transport NH_4^+ reactant through the charge and steric barriers formed by the outer surface amine layer.[12]

The reactivity of the surface amine formed was tested in conjunction with amine grafting selectivity according to the scheme shown in Figure 3. UV exposure through a chrome on fused silica mask contacted with the PCMS film was first carried out to create a patterned reactivity template comprising spatially well defined photooxidation (irradiated areas) and intact CMP (masked areas) regions on the surface (step 1). The surface aldehyde pattern was then transformed to an amine template by treatment with $NH_4OAc/NaBH_3CN$ for ~3 h (step 2). In a first test, the amines formed were identified and their reactivity confirmed by treatment with an aqueous Cy3.5 dye solution, which selectively and covalently coupled dye through an amide linkage to the surface amine (step 3A). Subsequent examination of the surface by fluorescence microscopy in Figure 3 revealed a red luminescent, negative tone pattern due to the bound dye corresponding to the line-space pattern defined by the original mask. The reaction selectivity, determined by comparing integrated fluorescence intensities in the dye-coated (irradiated) and background (masked) portions of the surface, was at least 5:1. Features as small as ~2 μm were adequately printed, consistent with resolutions achieved elsewhere for patterned polymers using carboxylate-based dye grafting processes.[8]

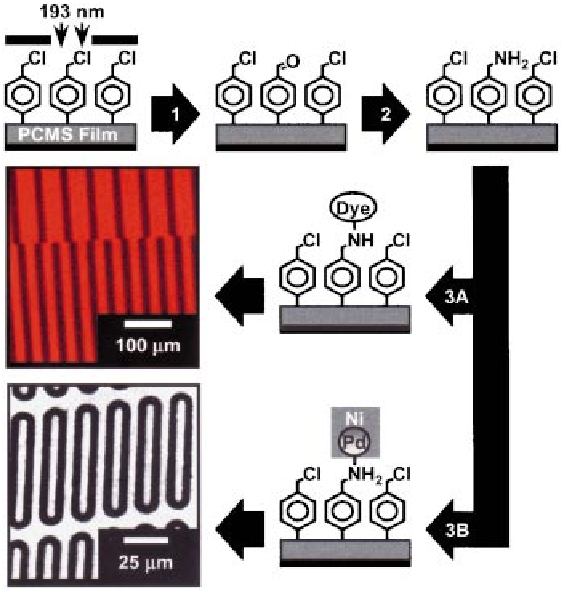

Figure 3. Patterned grafting scheme for PCMS films showing negative tone fluorescent Cy3.5 dye (red areas; step 3A) patterns and electroless Ni (light areas; step 3B) patterns. Details for each experiment are presented in the text.

As an additional test, the ability of the amine template to initiate and control deposition of electroless metal was examined. We have shown previously that alkylamines can effectively ligate colloidal Pd^{II} species, which catalyze electroless metal deposition upon reduction to Pd^0.[13] Amine surface templates, which were created using various exposure techniques,[3, 14] provide an efficient means for the selective deposition of patterned metal films using such catalysts. Thus, treatment of the amine template in Figure 3 with Pd^{II} catalyst,[13a] rather than Cy3.5, selectively binds a Pd^{II} colloid to the amine. Subsequent reduction in an electroless Ni bath selectively deposits Ni metal on the catalyzed surface regions corresponding to the original amine pattern (step 3B). A negative tone metal image comprising oval structures prepared according to this procedure is shown in Figure 3. Nickel features as small as ~5 μm are resolved in the patterned Ni film, consistent with the resolution limit of the mask used. In addition, no spurious metal on the masked PCMS film regions is observed by optical microscopy, as expected given the high catalyst binding selectivity (≥50:1) routinely observed for our metallization process.[13]

Conclusion

In conclusion, we have demonstrated the ability to spatially modify the surface reactivity of PCMS thin films by deep UV irradiation to allow selective attachment of materials in a negative tone process, complementing the positive tone method reported previously.[11] An imaging mechanism is described in which an aldehyde surface photoproduct formed during exposure at low UV doses is converted into a reactive amine capable of selectively binding other materials, such as dyes or metal, to the surface. Critical features of the process include environmental compatibility, track-line adaptability, and versatility.

In particular, the use of safe solvents, such as water or simple alcohols, to effect the surface grafting reactions minimizes environmental concerns associated with the use of organic solvents or acids in such applications.[15] While further optimization is clearly required, the ability to chemically bind materials under ambient conditions, coupled with the use of spin-coated, fast photospeed PCMS films, makes our approach attractive for use with high-throughput track-line processing equipment. In addition, the range of reactivities exhibited by the aldehyde, carboxylic acid, and amine species available at the PCMS surface using our method provides the potential for grafting other technologically relevant materials, such as biomolecules[1b–c, 16] or oxides,[17] to surfaces, a possibility that we are currently exploring in our laboratory.

Experimental Section

PCMS (sold under the name "polyvinylbenzyl chloride" with Chemical Abstract No. 121961-20-4; 60/40 mixture of 3- and 4-isomers; average $M_n \sim 55000$; average $M_w \sim 100000$ (by GPC/malls); Lot #HW-01025EW) from Aldrich Chemical Co. and Cy3.5 Monofunctional Reactive Dye from Biological Detection Systems, Inc. were used without further purification. All other materials were ACS Reagent Grade purity or better and were used as received. The colloidal Pd^{II} electroless catalyst, PD2, was prepared by the literature method.[13a] NIPOSIT 468B Electroless Ni bath from Shipley Co. was diluted to 10% strength with water and used at room temperature for Ni deposition. IR spectra of the films on Si wafers (Virginia Semiconductor, Inc.) were obtained in reflection mode using a Nicolet Magna 750 Series II spectrometer. Details regarding other instruments and procedures used for characterization of the polymer and metallized surfaces have been described previously.[13]

PCMS films were prepared on hexamethyldisilazane vapor primed ($\theta_w \sim 36 \pm 2°$) Si wafers or fused silica slides (2.5 cm × 2.5 cm × 0.1 cm; Dell Optics, Inc.) by spincoating (4000 rpm, 30 s) using a 1% wt. solution of PCMS in toluene filtered through a 0.22 μm Teflon filter. Films of thickness ~44 ± 2 nm, as determined by ellipsometry, were obtained after baking (90 °C, 30 min).[14e] Flood and patterned 193 nm film exposures were made using a Questek 2430 ArF excimer laser system operated at low pulse energies (≤ 2 mJ cm^{-2}pulse^{-1}) to avoid ablative film desorption as described elsewhere.[13d]

Reductive amination reactions were performed[9a] using a freshly prepared CH_3OH or 1:1 v/v CH_3OH/H_2O solution (pH ~6) containing NH_4OAc (~1.9 mol L^{-1}) and $NaBH_3CN$ (~0.1 mol L^{-1}). Exposed PCMS films were immersed in the solution (23 ± 2 °C) and allowed to stand for various times as indicated in the text. Treated samples were rinsed copiously with methanol and water, then dried in a stream of N_2 gas (liquid N_2 boiloff) filtered through a 0.2 μm cellulose filter.

For the dye grafting experiment, samples were placed in an aqueous Cy3.5 solution (~2 mg/50 mL, 90 min) in a darkened room at ambient temperature to avoid photolysis of the dye. Samples were rinsed vigorously with water and dried in the filtered N_2 gas stream after the dye treatment. The samples were immediately examined for evidence of fluorescence due to bound dye using a Molecular Dynamics Sarastro 2000 confocal microscope equipped with Nikon OPTIPHOT 2 microscope, Ar ion laser and a Nikon Model HB10101AF super high pressure Hg lamp. Images were obtained using an Ex 514 nm excitation filter and Em 540 nm emission filter set.

For metal deposition, samples obtained following reductive amination were treated using PD2 electroless catalyst (2 min), gently rinsed three times with water, and immersed in the room temperature electroless Ni bath (15-20 min). The nickel-plated samples obtained were rinsed with water and dried in the filtered N_2 gas stream. All Ni metallized samples were examined by optical microscopy to assess the quality and selectivity of the deposited Ni metal.

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[12] An alternate mechanism involving reconstruction of the polymer surface to bring underlying aldehyde groups to the surface-solution interface for reaction is unlikely under the room temperature conditions used in our experiments, given a T_g $\sim$82°C reported by the Aldrich Chemical Co. technical support group for our PCMS sample.

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