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Optical Modification and Metal Complexation of Ultrathin Spin-Coated Polymer Films

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Summary: We report the successful metal salt complexation of ultrathin terpolymer films spin-coated onto glass and silicon substrates and the subsequent reduction of the salt to metal clusters. The photolabile polymer consists of a diazosulfonate side chain polymer which may be decomposed under UV irradiation. Initial, complexed and reduced stages are characterized using optical transmission spectroscopy and X-ray photoelectron spectroscopy, while the film surface roughness, morphology and thickness are determined from atomic force microscopy and ellipsometry. On the one hand, our experiments show that non-irradiated diazosulfonate side groups complex with silver acetate provided from solution, and that silver ions chemically reduce when exposed to a sodium borohydride solution. On the other hand, the complete destruction of the photolabile diazosulfonate unit with UV irradiation was proven. Our experimental investigations are the first successful effort for selective metallization of deposited ultrathin diazosulfonate polymer films. Furthermore, we were able to show that the films can be optically structured by writing micrometer-sized patterns with a focused UV laser beam.

Introduction

Today, metallization and surface finishing are important fields of application in our macroscopic world as well as in nanotechnology.[1] Conventional methods for the deposition of metallic conducting films use the galvanotechnique, but this technique is limited to conducting surfaces or surfaces treated with a conducting precursor film, and not all metals are suited for deposition.[2] Moreover, spatial structuring of the metal surface is only possible via a subsequent process step and requires great expenditure.

Alternatively, the use of template polymers offers possibilities for defined positioning of metal clusters. Segregation phenomena in di- and tri-block-copolymers may lead to the formation of controlled surface structures due to phase separation in thin films, and in certain compositions such polymers incline to form micelles.[3-9] Such micelle formation, especially studied on block-copolymers with poly(2-vinylpyridine)-segments loaded with silver or gold salts, can assist the formation and deposition of uniform metal particles with a diameter of

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1-12 nm in quasi-hexagonal grid structures with 20 to 200 nm period on planar substrates. The template polymers have been removed by plasma etching processes after reduction of the embedded metal salts.[10-16] In that way, the defined synthesis and attachment of Co, Fe, Pd, Pt and Ru colloids on surfaces has been realized [11] and the principle has been applied already in the field of nanolithography, e.g. by Chaikin [17] and Spatz [18] who succeeded to structure SiN or GaAs substrates with holes or islands in the range of 20 nm. However, the use of template polymers usually results in metal structures or clusters in a given order and dimension as predetermined by the polymer phase morphology. The achievement of irregular but defined metal structures on surfaces therefore is still a challenge.

An alternative to template techniques is provided by procedures which can generate structured functional surfaces before metal salt complexation takes place. Generally, optical lithographic techniques using UV irradiation with or without masks can be applied for the spatially defined structuring of photosensitive surfaces or polymer films. Novel methods for surface structuring on a nanometer scale without masks are available by the use of laser writing technologies such as scanning near-field optical microscopy (SNOM).[19-26]

The property of the sulfonate group to complex oppositely charged organic compounds [27-29] or metal salts [30, 31] render polymer films containing the photolabile diazosulfonate [32-34] a promising candidate for selective complexation of metal salts after lithographic structuring.[35]

In this paper, we describe the use of a photoaddressable diazosulfonate terpolymer film, covalently attached on glass or silicon substrates, for the selective complexation of silver salts and the subsequent reduction of the salt to silver clusters. The metal salt complexation is achieved by counter ion exchange of the diazosulfonate group from Na^+ to Ag^+. It is shown that UV illumination destroys the diazosulfonate group and thereby removes the sites at which complexation takes place. A scanning optical microscope was used for creating a structure on the micrometer scale, which was confirmed by an in-situ transmission measurement.

Experimental Part

Polymer synthesis: The investigated photolabile terpolymer was synthesized from the three monomers methylmethacrylate (MMA), sodium-4-acryloyl-aminophenyldiazosulfonate (APAS), and 3-(trimethoxysilyl)-propylmethacrylate (TMSPMA).[36] The chemical structure is shown in Fig. 1. MMA is used as a spacer, the siloxane unit allows the covalent bonding to the glass or silicon substrates, and the phenyldiazosulfonate unit is the photolabile part. APAS was synthesized according to the literature,[33] while the other two constituents were purchased from Fluka. All solvents used were purified and dried. Reaction and purification were performed under nitrogen as an inert gas in a flame-dried apparatus. The terpolymer (molar ratio of the three monomers MMA 75 %, APAS 20 %, TMSPMA 5 %) was synthesized by radical polymerization of the three monomers in dimethylsulfoxide for 20 h at 70 °C. Azobisisobutyronitrile was used as an initiator. When the reaction had stopped, the solvent was removed in a vacuum and the terpolymer dissolved in methanol. Solution was added drop by drop to ice-cooled diethylether in order to purify the polymer. The resulting precipitate was filtered and dried in a vacuum.

Thin film preparation: Thin polymer films were prepared on cleaned glass substrates (Menzel Glasbearbeitungswerk GmbH & Co. KG, Braunschweig, Germany) or silicon wafers (orientation 100, p-doped, 50 nm SiO_2 layer). Substrates were first sonicated for 10 min in acetone followed by 10 min in "piranha" solution (75 % conc. H_2SO_4, 25 % conc. H_2O_2), rinsed several times in Millipore™ water and dried in nitrogen. Spin-coating was carried out from a 1 wt % methanol solution of the terpolymer by using a photoresist spinner (HEADWAY Research INC., Garland, Texas / USA). Films were then annealed 30 min to 80 °C in a water-saturated atmosphere, followed by a 2 h exposure at 120 °C to atmospheric pressure. The films investigated were spin-coated at 3000 rpm, which results in films of about 20 nm thickness with less than 1 nm roughness (rms). The film thickness was determined both using a variable-angle multiwavelength ellipsometer (A.J.A. WOLLAM CO. M44, INC., Lincoln, Nebraska / USA) and an atomic force microscope [37] (AFM, ThermoMicroscopes Explorer™, Sunnyvale, California / USA). For the first method, a 75 W xenon arc lamp was used for illuminating polymer-coated Si (100) wafers with 50 nm SiO_2 at 22 °C and 40 % humidity measuring at three different angles between 65° and 75°. AFM was used to determine the film thickness on glass substrates by scratching the terpolymer film and analyzing the height difference between substrate and film within the resulting scratch structure. These results on glass were comparable to ellipsometry measurements on silicon substrates.

UV exposure on the millimeter scale: UV laser illumination was performed with a HeCd laser (KIMMON IK5651R-G, cw, 24 mW @ $\lambda = 325$ nm and/or 69 mW @ $\lambda = 441.6$ nm). After passage of the light through various optical components (shutter, lens, filter, aperture) a power of 400 µW up to 4 mW on a sample area of 7 mm^2 was available, as measured by a calibrated power meter (Newport 1835-C equipped with a 818-UV/CM detector head).

Optical spectroscopy: Transmission spectra of the photolabile terpolymer thin films on glass were measured with a SHIMADZU UV 3100 UV-VIS-NIR spectrophotometer. All data displayed in the following show relative transmittance or absorbance changes in comparison to clean glass substrates. The investigated sample area measured approximately 3 mm in diameter.

UV exposure and optical spectroscopy on the micrometer scale: For UV laser illumination the HeCd laser was focused onto the sample with a microscope objective (ZEISS 900297, UV transparent). In order to write a structure, the sample was moved in the focal plane by a piezoelectric scanning stage according to the desired pattern.
For imaging the created pattern, broad-band light from a Xe lamp (XBO 101) was focused onto the sample. The transmitted light was collected by a multimode fiber coupled to the entrance slit of a grating monochromator (SPEX 1681B, 300 lines/mm) and the spectrum was monitored with a CCD detector (INSTASPEC4 ORIEL).

Complexation: The sodium counter ions of the above described films on glass were exchanged by silver ions by immersing the samples for 2 h in a 0.01 M solution of $Ag(CH_3COO)$ in water (silver acetate was purchased from Fluka). After the complexation, the samples were rinsed and sonicated several times in Millipore™ water, dried in a nitrogen stream and annealed for 30 min to 80 °C in a vacuum.

Reduction: The chemical reduction was obtained by immersing the silver-salt-complexed films for 10 min in a solution of sodium borohydride ($NaBH_4$, purchased from Fluka) in water. The samples were sonicated in Millipore™ water, dried in nitrogen and annealed for 30 min to 80 °C in vacuum.

XPS: X-ray photoelectron spectroscopy (XPS) data were acquired with a Leybold EA 10 energy analyzer (operated at a pass energy of 100 eV corresponding to a resolution of 2.5 eV) and a Mg-anode (Mg $K_\alpha = 1253.6$ eV) X-ray source under ultrahigh vacuum (UHV) conditions with an operating pressure $< 10^{-9}$ mbar.

Results and Discussion

Copolymers of a diazosulfonate monomer and e.g. methyl methacrylate have been studied previously as photoresins for the preparation of offset printing plates using UV light and a mask as well as IR lasers for lithographic structuring.[32-34] UV illumination modifies the structure of the diazosulfonate groups which decompose under nitrogen evolution. In water solution mainly phenol groups result, but the photochemistry of the diazosulfonate group is complex. Two mechanisms were found in the decomposition process: an ionic pathway in water (leading to diazonium salts and subsequent phenol groups)[38, 39] and a radical process in less polar solvents (leading to biphenyl groups)[40]. For thin films a radical process dominates which results in highly reactive intermediates and often in crosslinked products.[32] This change in the chemical structure of the diazosulfonate groups results in changes in solubility and surface polarity of the polymer films, both being suitable effects for novel applications of these polymers as photoresins.

For the purpose of selective metal complexation on ultrathin films of well structured diazosulfonate polymers, the polymer structure had to be modified since an improved adhesion to the glass or silicon substrate is required. Furthermore, the polymer film has to stick to the substrate surface also without irradiation and under water or aqueous salt solution treatment. Thus, we designed a terpolymer structure containing 75 mol % of a film-forming comonomer (MMA), 20 mol % of the photolabile diazosulfonate comonomer, and 5 mol % of an additional anchoring monomer (3-(trimethoxysilyl)-propylmethacrylate). Figure 1 depicts the terpolymer structure while Fig. 2 exemplifies the possible changes in the polymer after UV irradiation. Details on the polymer formation and the properties are reported elsewhere.[36]

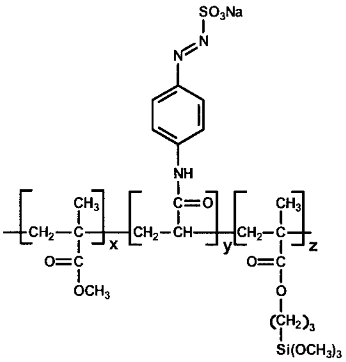

Figure 1. Chemical structure of the terpolymer. The molar ratio of the three monomers is MMA x = 75 %, APAS y = 20 %, and TMSPMA z = 5 %. (MMA: methylmethacrylate; APAS: sodium-4-acryloyl-aminophenyldiazosulfonate; TMSPMA: 3-(trimethoxysilyl)propylmethacrylate).

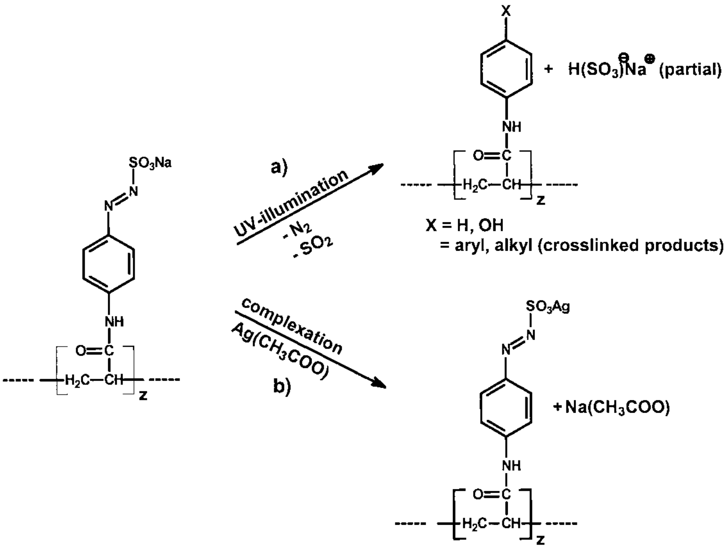

Figure 2. Structural change of the sodium-4-acryloyl-aminophenyldiazosulfonate (APAS) unit with UV illumination (a) and after complexation with silver acetate (b). In (a) the polar diazosulfonate groups decompose under nitrogen evolution while in (b) the sodium ion is replaced by a silver ion.

This polymer was used to prepare ultrathin films of 10-30 nm thickness via spin-coating onto glass or silicon wafers. Then the films were annealed to allow chemical bond formation to the substrate via the anchor groups. Unattached polymer was removed by intense washing with water. The polymer films on silicon were characterized by atomic force microscopy (AFM) and ellipsometry to verify film thickness and surface smoothness (in the range of 1 nm rms). Polymer films prepared on glass were mainly used for UV exposure and complexation studies. The diazosulfonate groups which provide the sites for complexation can be removed by UV irradiation, but the general polymer structure including the anchoring group remains intact. The transmission spectra of the untreated films depicted in Fig. 3 show a clear absorption peak at $\lambda = 336$ nm, which is attributed to the π-π^* transition of the diazosulfonate group.[32] UV laser illumination breaks the bond between the diazosulfonate and the phenyl group. The curves in Fig. 3 show the decreasing strength of the diazosulfonate absorption peak with increasing UV energy dose.

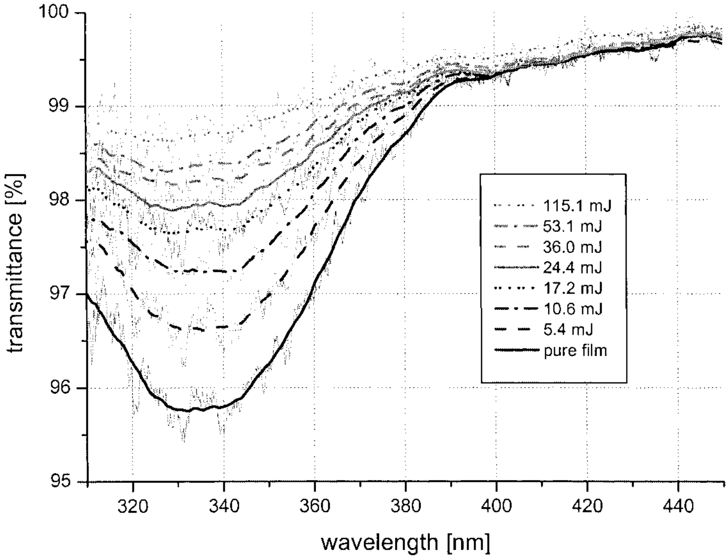

Figure 3. Transmission spectra of a terpolymer film on a glass substrate recorded during a step-by-step UV illumination on a millimeter scale.

In order to quantify successful decomposition of the diazosulfonate group we applied a thorough XPS study. To quantify XPS data the peak areas obtained from the raw data were transformed by using atomic sensitivity factors (ASF).[41] ASF take into account the atomic cross sections as well as the analyzer transmission characteristics. On the investigated polymer films prepared on glass substrates the charging effect exceeded the expected values of the chemical shift and therefore chemical shifts were not evaluated.

In accordance with Fig. 1, an untreated polymer film will show a significant contribution of Na^+ -saturated $-SO_3^-$-units. After UV exposure the Na^+ peak in XPS should thus change drastically provided all $-SO_3^-$ is washed out and no unspecific Na^+ adsorption is present. A comparative analysis of the sodium content in our XPS data of untreated polymer films and illuminated ones reveals a sodium content clearly corresponding to the chemical composition of the terpolymer before and after illumination.

Table 1 shows the theoretical values for the chemical composition of the prepared terpolymer films. The carbon content is used to calculate relative values in order to compensate for different film thicknesses. From the polymer synthesis we can exclude a specific pollution of the samples with carbon.

Table 1. Theoretical values for the chemical composition of the surface.

Condition of the polymer film	C / N	C / Na	C / Ag
pure	10.1	30.3	-
illuminated + washed	30.3	-	-
nonilluminatied + complexed	10.1	-	30.3
nonilluminatied + reduced	10.1	30.3	30.3

For the pure polymer there is no detectable silver content and the ratio C / N and C / Na are in good agreement with the theoretical values.

After illumination and the first washing and sonicating in Millipore™ water the sodium peak vanishes below the detection limit and, hence, the cracked sulfonate group was removed from the surface. This clearly proves chemical modification by UV laser exposure.

Having shown chemical modification of the thin terpolymer films by UV illumination, we exchanged in the nonilluminated films containing intact diazosulfonate groups the sodium counter ion by a silver counter ion using an aqueous silver salt solution. The structural change of the terpolymer upon metal salt complexation is described in Fig. 2. As shown schematically, the sodium ion in the diazosulfonate group is replaced by the silver ion of the silver acetate. Again the attached metal ion may be used for XPS monitoring.

XPS data of the complexed polymer films show a silver content of the sample surface. The UV absorption of the diazosulfonate group depends firstly on the substitution pattern on the aromatic unit but to some extent also on the complexed metal salt.[32] So far, no UV absorption data for diazosulfonate silver salts were reported. However, from early literature [31] the formation of stable low-molar-mass diazosulfonate silver salts is known which precipitated after addition of the silver salt solution to the dissolved sodium salt of a diazosulfonate derivative. Figure 4 shows the absorption peak before and after metal salt complexation of the polymer film. A peak shift from 336 nm (1) to about 345 nm (2) indicates successful metal salt complexation of the terpolymer films since similar shifts are observed when sodium diazosulfonate polymers in solution are treated with silver salts. Nevertheless we again emphasize, that the reported procedure was performed for films deposited onto substrates.

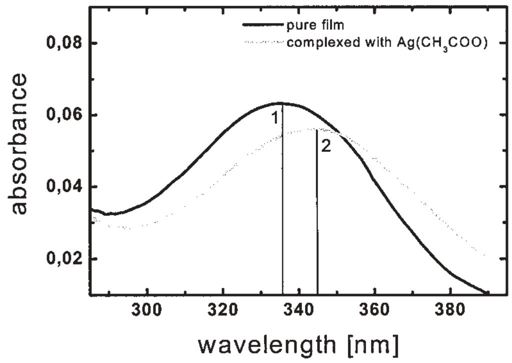

Figure 4. Absorption spectra of a pure film and a film complexed with Ag(CH_3COO).

The absorption peak caused by the diazosulfonate group shifts by about 10 nm to higher wavelengths after chemical substitution of the sodium ion with silver.

After chemical reduction, the silver ions on the diazosulfonate groups are partially substituted again with sodium ions from the $NaBH_4$ solution. Therefore, we expect a blue-shift of the diazosulfonate peak back towards its original position at 336 nm. In fact, we do observe such a shift, although its amount measures only 3 nm back from peak 2.

So far, it was shown that we can prepare smooth and thin films of a new photolabile terpolymer on glass substrates. The photolabile diazosulfonate group was either destroyed with UV laser illumination and removed from the surface, or it was complexed with silver salt. The silver salt finally could be reduced to silver. All these chemical changes of the polymer film were observed via changes in the optical transmission spectra and changes of the chemical surface composition via XPS analysis.

We were also able to differentiate between illuminated and nonilluminated samples having been treated with exactly the same procedure for metal salt complexation and chemical reduction, even though the silver content does not differ as much as expected between surfaces of illuminated and nonilluminated films. Figure 5 shows the XPS spectra for an illuminated and a nonilluminated sample after identical chemical treatement for complexation and reduction.

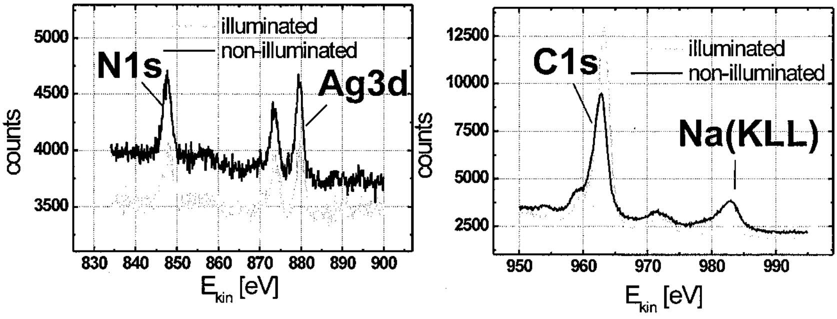

Figure 5. XPS spectra of an illuminated and a nonilluminated terpolymer film.

For the illuminated sample we expect no silver decoration and a theoretical ratio between carbon and nitrogen of C / N = 30 for the chemical composition of the surface (see Table 1). The measured ratio C / N = 34 is in good agreement with the expected value and proves that UV laser illumination and sonication successfully destroyed and removed almost all the diazosulfonate groups. Nevertheless, we observe residual silver on the surface (C / Ag = 206). Therefor we conclude that silver also tends to bond nonspecifically to other sites in the polymer than the -SO_3^--groups, such as phenolic groups which may result from the decomposition of the diazosulfonate group or, more likely, the ester and amide functions in the polymer backbone.

For the nonilluminated sample the ratio C/N is 14, which is close to the theoretical value of 10 and indicates that the phenyldiazosulfonate unit was not destroyed. Nevertheless, there is not as much silver on the surface as expected (theoretically C / Ag = 30). For the nonilluminated sample the measured C / Ag ratio of 106 is larger by a factor of 2 compared to the illuminated surface, indicating additional adsorption achieved by the presence of diazosulfonate groups. The factors on which the difference in silver content of the resulting surfaces depends most strongly are the duration of sonication in Millipore™ water after metal salt complexation, and the film thickness.

For only short or no sonication, XPS analysis shows an excess of silver on the sample surface independent of whether the samples were illuminated or not. After chemical reduction this excess silver salt forms silver clusters which gave rise to a typical absorption peak in the transmission data at $\lambda = 380 - 420$ nm, attributable to the plasmon resonance of small silver clusters.[35] These clusters were also imaged by AFM. So far, best results were obtained with 10 min sonication on nonilluminated surfaces which leads to a small deficit of the silver content after complexation. The film thickness also influences the silver content of the sample surface. Especially for very thin films (< 10 nm) the results on illuminated and nonilluminated films do not differ much. All films studied had film thickness below 50 nm. For such thin films we can guarantee that the photoreaction was complete throughout the film and no gradient should be formed in the chemical structure of the film upon irradiation.

Aiming at the creation of micrometer-sized metal structures, we continued the experiments on UV irradiation with the illuminated area reduced to the micrometer scale. We used the microscope setup to write a well defined structure with the HeCd laser operated at 325 nm. The writing speed was chosen such that complete decomposition of the diazosulfonate group should occur within the focus as concluded from the results obtained on the millimeter scale. To prove that the structuring was successful, the low-power Xe lamp was used to image the pattern in a second scan.

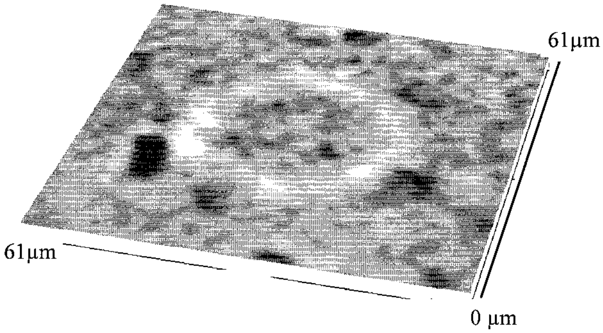

Figure 6. Transmission image of an optically structured polymer film, recorded in the spectral range between 430 – 450 nm.

Figure 6 displays the image obtained by recording the transmitted power in the wavelength range between 430 nm and 450 nm. Prior to imaging, four concentric circular rings with diameters of 30 µm down to 27 µm had been written into the film. The single rings cannot be resolved but a ring-shaped area of increased transmittance is clearly discernable. The ring was visible across the whole investigated spectral range from 320 nm up to 450 nm. Due to the objective being non-achromatic, the image with the highest lateral resolution was observed around 440 nm, even though the change in transmittance should be more pronounced at shorter wavelengths. Nevertheless the successful structuring on the µm scale provides the basis for creating metallic microstructures on ultrathin polymer films by the chemical treatment described above, provided that a higher degree of selectivity of the complexation/reduction process can be achieved.

Conclusions

The results described above show the first step towards a selective metallization of ultrathin diazosulfonate terpolymer films deposited onto substrates. Metal salt complexation and reduction of the nonilluminated films was proven via changes of the chemical surface composition and the optical transmittance. Although the resulting films do not yet show metallic surface layers, a significant change of the surface chemical composition was observed, especially between illuminated and nonilluminated films. Careful optimization of the complexation and reduction processes should lead to a more selective metallization.

In summary this work presents a promising way for selective metallization of polymer thin films. The terpolymer used was synthesized from three monomers: the first responsible for spacing, the second for covalent bonding to the substrate, and the third providing functionality due to incorporation of a photolabile diazosulfonate group for metal salt complexation. Stable, smooth, and photolabile films were prepared by spin-coating onto glass substrates. The most striking results of these experiments on thin films are (i) the metal salt complexation of the diazosulfonate group and subsequent chemical reduction to metal clusters, (ii) the destruction of the photolabile diazosulfonate group by UV laser irradiation, (iii) the difference of about a factor of 2 in metal content between the surfaces of UV illuminated and nonilluminated samples, and (iv) UV structuring < 6 µm line width.

Such films are promising candidates for optical structuring of polymers in order to create nanometer-sized metallic structures of any desired shape. As an important step toward this goal we demonstrated that local UV illumination allows us to structure the film on the micrometer scale.

Acknowledgments

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