Patterned Conductive Polyaniline on Si(100) Surface via Self-Assembly and Graft Polymerization

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ABSTRACT: A combination of surface graft polymerization of aniline and photopatterned self-assembly monolayer (SAM) was used to generate a well-defined pattern of conductive polyaniline on a Si(100) surface. A self-assembly of phenylsilane monolayer was first generated by reacting a hydroxylated silicon surface with phenyltrichlorosilane under a dry inert (N_2) atmosphere. The formed SAM layer has been photopatterned under an UV laser at 263 nm through a lithographic mask. The patterned SAM was reacted with triflic acid (HOTf) under a dry inert atmosphere to remove the benzene rings from the SAM layer. The OTf groups of the triflated SAM have been substituted with aniline under a dry inert atmosphere to generate an aniline-primed substrate which was further used for the graft polymerization of aniline to prepare a patterned conductive polyaniline (PANI) layer. The composition, microstructure, and morphology of PANI grafted silicon surfaces were examined by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM), four probe conductivity, and contact angle measurements. The surface conductivity of grafted PANI free of patterning was 23 S/cm and through the patterned wires was 21 S/cm (for the surface fraction grafted), which are larger than the usual value of the homopolymer PANI films (∼1 S/cm). Microscopy images revealed a compact grafted PANI and a high edge acuity of the pattern. The present method provides a new strategy for the generation of a pattern of conductive polymers via graft polymerization.

Introduction

In the past years, a great deal of research was concerned with the patterning of polymer films which can be used as components in molecular electronics,[1] optical devices,[2] etch resists,[3,4] and biosensors[5,6] and as scaffolds for tissue engineering and fundamental studies in cell biology.[7−9]

Among the polymers, the conjugated organic polymers are especially attractive since they offer several advantages over the metals and the conventional inorganic semiconductors, such as more facile processing and ease of adjusting the conductivity in a wide range by changing the dopant or the doping level. They can be considered as potential alternatives to the metals and semiconductors as connecting wires and conductive channels, which can be used as active materials in optoelectronics,[10] microelectronics,[11] microelectromechanical systems (MEMS),[12] sensors,[13] and related areas.[14]

The patterning of conjugated polymers on various substrates was achieved by using a variety of techniques, such as the deposition by scanning electrochemical microscopy,[15] screen printing,[16] micromolding in capillaries (MIMIC),[17] inkjet printing,[18] photochemical patterning by photolithography,[19] and microcontact printing through self-assembly monolayer (SAM).[20] The above methods employed the area-selected electropolymerization, the nonreactive patterning, or directly the photochemical patterning of conjugated polymers.[21] In another method, a combination of the microcontacting printing and the area-selective deposition method was used for the physical deposition of polyaniline (PANI) and polypyrrole (PPY) on a patterned SAM.[22]

It is generally believed that the "self-assembly" monolayer (SAM) provides the best control at the molecular level and constitutes a potential technique for the preparation of advanced materials.[23] In previous work,[24] we employed the aniline monomer neucleophilic substitution reaction of bromine atoms bound to a SAM silane monolayer on the surface of a glass substrate, followed by the grafting of polyaniline. The method involved the initial formation of a stable bromine silane monolayer through the reaction of a hydroxylated glass surface with 3-bromopropyltrichlorosilane. This was followed by the functionalization of the SAM monolayer through the aniline substitution of the bromine atoms and further by the surface oxidative graft polymerization of aniline on the covalently immobilized aniline sites. This method offered the advantage of flexibility in the selection of a suitable silane coupling agent, which could generate a homogeneous, stable monolayer without the use of synthetically challenging or unstable silanes. The surface conductivity of the PANI layer grafted to glass was higher than that of the homopolymer PANI films.

It has been shown that the alkyl/aryl trichlorosilanes are excellent molecules for the formation of monolayers through the condensation reaction with substrates that bear a surface layer of hydroxyl groups.[25] It was also reported[26,27] that the phenyltrichlorosilane is a reagent which does not undergo unfavorable side reactions. Phenylsilane monolayers can be formed on glass, silicon, metal oxides, and other ceramics, on which surface hydroxyls can be generated. These SAM monolayers are homogeneous and stable and do not have the drawbacks of other more exotic silane monolayers, such as irreproducibility, incomplete coverage of the substrate, and self-condensation of silanes in solution.[26] The phenylsilane monolayers can be photopatterned with high resolution,

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and for this reason they can be used in photolithographic processes. Furthermore, the dearylation of the phenylsilyne groups of the silyne network with the trifluoromethanesulfonic acid (triflic acid, HOTf) results in the generation of reactive silyl cation sites on the backbones, which can react with suitable monomers to form functionalized polysilynes.[27]

We have previously demonstrated that aniline can be bound to a SAM monolayer generating functional groups which allow the further grafting of polyaniline (PANI). The goal of the present paper is (a) to employ a SAM monolayer of phenylsilane generated by reacting phenyltrichlorosilane with the OH groups of a silicon surface, which are obtained by treating the surface with a "piranha" solution (a mixture of a concentrated sulfuric acid solution and a hydrogen peroxide solution), (b) to pattern this monolayer using an UV laser, (c) to dearylate the phenylsilane by its reaction with HOTf and formation of a weak bond between the latter acid and silane, (d) to substitute the −OTf group of the triflic acid with aniline, and finally (e) to graft polymerize aniline to the aniline-primed surface. In essence, a patterned PANI will be prepared through the combination of a chemical graft polymerization and patterned SAM technique. With the advent of nanolithography, such as the AFM lithography, this method can provide nanometer size features for patterns of conductive polymers.

Experimental Section

Materials. Single-crystal undoped Si(100) wafers, 76 mm in diameter, polished on one side were purchased from Gelest Inc., Morrisville, PA, and sliced into pieces of about 1.0 × 1.0 cm in size. The aniline, phenyltrichlorosilane, ammonium persulfate, and trifluoromethanesulfonic acid (triflic acid, HOTf) were provided by Aldrich/Sigma and used as received. The anhydrous toluene, aniline, and hexane were dried over 4 A molecular sieves prior to use. The solvents, acetone, ethanol, methanol, and *N*-methylpyrrolidinone (NMP), and other chemicals were of reagent grade and were also purchased from the Aldrich/Sigma Chemical Co. and used as received.

Substrate Pretreatment. The freshly sliced silicon substrates (1 × 1 cm) were first soaked in a soap solution and sonicated for 5 min to remove the organic residues from their surface and then rinsed with a large amount of distilled water. The substrates were then immersed in a "piranha" solution [a mixture of 70% volume concentrated sulfuric acid (98 wt %) and 30% volume of a hydrogen peroxide solution (30 wt %)] and boiled for about 50 min to generate OH groups. The silicon substrates were then washed with a large amount of nanopure water and dried under reduced pressure for subsequent surface treatment. The contact angle of water droplets on the silicon surface was low and almost constant over the entire surface, revealing that the surface was uniformly hydroxylated.

Silane Treatment To Prepare SAM. The pretreated hydrophilic silicon substrate was placed into a solution of phenyltrichlorosilane in dried toluene (25 μL in 25 mL), under a nitrogen atmosphere, for 12 h. Further, the substrate was washed twice with dried toluene in the same nitrogen atmosphere. Finally, the silicon substrate was removed from the nitrogen atmosphere and cleaned in an ultrasonic bath in toluene for 1 min, rinsed successively with acetone and ethanol, and finally dried.

Photolithography To Pattern a SAM Monolayer. The photolithography was conducted using a Spectra-Physics model 3960-LIS Ti:sapphire laser. Pulses of about 90 fs in length at a wavelength of 790 nm were generated and directed into a frequency tripler (U-Oplaz Technologies model TP-1B) to obtain pulses of UV light at a wavelength of 263 nm. The as-obtained 263 nm UV laser was directed to a modified silicon surface through a photomask. The total irradiation energy on the sample was about 60 J/cm^2.

Triflation Procedure and Aniline Monomer Functionalization through a Substitution Reaction. SAM-Si substrates were immersed in 99% triflic acid under a nitrogen atmosphere and allowed to stay for 3 days. Each substrate was then individually rinsed twice successively in dried toluene and hexane and placed in dried aniline located in a Pyrex tube at room temperature, under a nitrogen atmosphere, for 24 h. After the covalent substitution of aniline to the triflated surface, the silicon substrate was washed thoroughly with large amounts of dried toluene and NMP to remove the unreacted aniline. The residual NMP present on the aniline-SAM-Si substrate was removed by washing with a large amount of methanol.

Surface Oxidative Polymerization of Aniline. The oxidative graft polymerization of aniline to an aniline-SAM-silicon substrate was carried out in an 1 M HCl solution containing 0.3 M aniline and 0.3 M $(NH_4)_2S_2O_8$ (as the oxidative homopolymerization of aniline to the conductive emeraldine (EM) salt[28]). The reaction was allowed to proceed at 0 °C for 12 h. The surface-modified silicon was subsequently immersed in a large volume of NMP for at least 24 h in order to remove the physically adsorbed EM salt. The polyaniline (PANI) grafted silicon surface was further washed with alcohol to remove the residual NMP. The EM salt grafted on the silicon surface was converted to the neutral EM base by the immersion of the silicon substrate for 24 h in a large amount of doubly distilled water before being dried under reduced pressure.

Characterization of the Surface-Modified Silicon Wafer Surface. The graft-modified silicon surfaces were characterized on their polished side by contact angle, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM), and four-probe conductivity measurements. The contact angle measurements were carried out using a NRL CA goniometer model 100-00-(115) from Ramehart Inc. The telescope with a magnification power of 23× was equipped with a protractor of 1° gradation. The angles reported are accurate within ±3°. For each substrate, at least three measurements on different locations were averaged. The XPS measurements were carried out on a Surface Science model SSX-100 Small Spot ESCA, possessing an Al Kα monochromatized X-ray source (1.48 keV photons). The pressure in the analysis chamber was maintained at 10^{-9} Torr or lower during the measurements. To compensate for the surface charging, all binding energies were referenced to the C 1s hydrocarbon peak at 285 eV. In the peak analysis, the line widths (the width at half-maximum) of the Gaussian peaks were kept constant for the components of a particular spectrum. The surface elemental compositions were determined from the peak area ratios and were accurate to within 1%. The morphologies of the pristine and surface-modified silicon wafers were examined by a Quesant Resolver atomic force microscope (AFM), using the tapping mode at a scanning rate of 1.0−4.0 Hz. The thickness profile of the film on the Si surface and the root-mean-square surface roughness (rms) of the film were directly evaluated from the AFM images. The ellipsometric thickness was determined with a Gaertner Ellipsometric from Gaertner Scientific Co., Chicago, IL. The patterned images of PANI on the silicon wafers were obtained by SEM using a Hitachi S-4000 FESEM instrument operated at 20 kV with the specimen mounted on a double-sided adhesive carbon tape. The conductivity of the graft-modified silicon surface was determined by the four-probe method, using a Hewlett-Packard model 3478A digital multimeter. For each of the conductivities reported, at least three measurements were averaged.

Results and Discussion

Two kinds of experiments have been performed. Most of the characteristics of the system have been determined by carrying out experiments free of patterns. In addition, experiments have been performed that in-

Scheme 1. Strategy for Surface Graft Polymerization of Polyaniline (PANI) on a Silicon Substrate

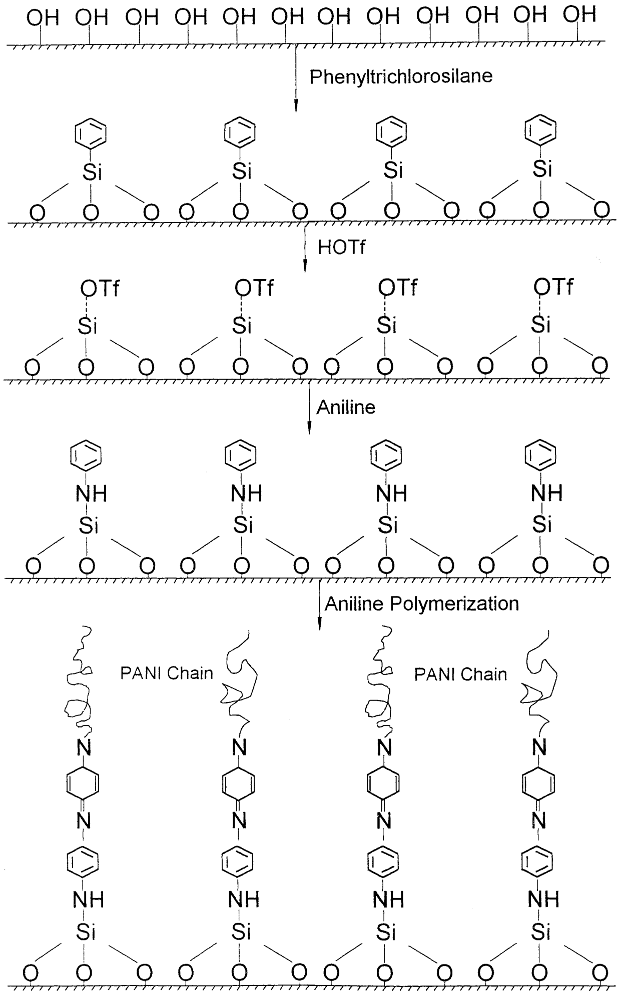


Table 1. Water Contact Angles after Surface Treatment

	contact angle (deg)
pristine silicon wafer	51
silicon surface after treatment with the piranha solution	20
surface after reaction with phenyltrichlorosilane	76
surface after treatment with triflic acid	36
surface after substitution reaction by aniline	73

volved patterning. The surface modification of the hydroxyl-terminated silicon substrate by phenyl silanization with phenyltrichlorosilane, the dearylation of the benzene ring monolayer with the triflic acid to generate a reactive Si-OTf surface, the functionalization of the surface through the aniline nucleophilic substitution reaction of −OTf, and finally the oxidative graft polymerization of aniline are sketched in Scheme 1. Each of the above steps is described in detail below.

Formation of Phenylsilane on the Silicon Surface. Before generating an uniform functionalized surface by the method outlined in Scheme 1, a hydroxylated silicon surface was formed by immersing the substrate in a boiling piranha solution for at least 30 min, but less than 1 h.[27b,29,30] The contact angle of the surface so treated changed from 51° for the pristine substrate to 20° (Table 1) and was the same all over the surface; this revealed that the substrate was uniformly covered with hydrophilic hydroxyl groups. Further, the hydroxylated silicon surface was exposed, in a dry N_2 atmosphere, to a solution of phenyltrichlorosilane in dried toluene at room temperature for about 12 h, during which the trichlorosilane groups of the phenyltrichlorosilane reacted with the hydroxyl groups of the Si surface. Thus, the silicon surface became chemically bound to an uniformly dense phenylsilane film. The increase of the water contact angle of the surface from 20° after hydroxylation to 76° after silanization indicated that the hydrophobic $\equiv$SiPh layer has replaced the hydrophilic hydroxyl layer. The contact angle of the $\equiv$SiPh layer on silicon varied by less than 3° between different locations, which together with a small value of the root-mean-square surface roughness (rms = 3.1 Å) of the film, demonstrated the uniformity of the phenylsilane monolayer.

Surface Functionalization with Aniline. The $\equiv$SiPh layer was dearylized by reacting the phenylsilane sites with HOTf to produce reactive sites for the substitution reaction with aniline. Parts a and b of Figure 1 present respectively the wide-scan XPS spectra of the silicon substrate with monolayers of $\equiv$SiPh before and after triflation followed by solvent washing. The appearance of the fluorine peak in Figure 1b indicates that the −OTf groups of the triflic acid were covalently bound to the silicon surface. Further, the triflated silicon substrate bearing a $\equiv$SiOTf layer was placed under a dry N_2 atmosphere in a well-dried aniline, at room temperature, for 24 h. Then the substrate was rinsed with dried toluene, washed again with NMP, and sonicated in spectroscopic grade methanol. Figure 1c presents the wide-scan XPS spectrum after the surface functionalization with aniline. Comparing parts b and c of Figure 1, one can see that the F 1s signal of the −OTf group (688.5 eV) from Figure 1b was replaced by a new N 1s signal in Figure 1c. The binding energy (BE) of N 1s, 399.3 eV, indicated that a NH group was covalently connected to a benzenyl ring.[31] These results show that a chemical substitution reaction occurred between aniline and −OTf on the silane monolayer and that aniline was anchored to the silicon surface through a chemical bond. The examination of the substrate by the sessile water drop contact angle method indicated that the contact angle increased from 36° after triflation to 73° after the aniline substitution (Table 1). The above changes demonstrated that the more hydrophobic Si-NH-benzyl ring layer has replaced the hydrophilic $\equiv$SiOTf layer, and this is consistent with the aniline substitution.

Graft Polymerization of Aniline on the Aniline−Silicon Surface. The graft oxidative polymerization of aniline was carried out via the conventional method. Parts a and b of Figure 2 present the wide-scan XPS and the N 1s core-level spectra of the aniline−SAM-silicon surface after the oxidative graft polymerization in an 1 M HCl solution containing 0.3 M aniline and 0.3 M ammonium persulfate. After polymerization, the surface-grafted polyaniline (PANI) salt was first washed thoroughly with NMP and then deprotonated by dipping the specimen in a large amount of double distilled water for a long time, to convert the PANI salt to its neutral emeraldine (EM) base form. The increase in the intensity of N 1s and C 1s signal in the XPS wide-scan spectrum (Figure 2a) indicated that the oxidative graft polymerization of aniline, which brought more carbon and nitrogen on the silicon surface, has taken place. Figure 2a also shows that no Si was detected; this

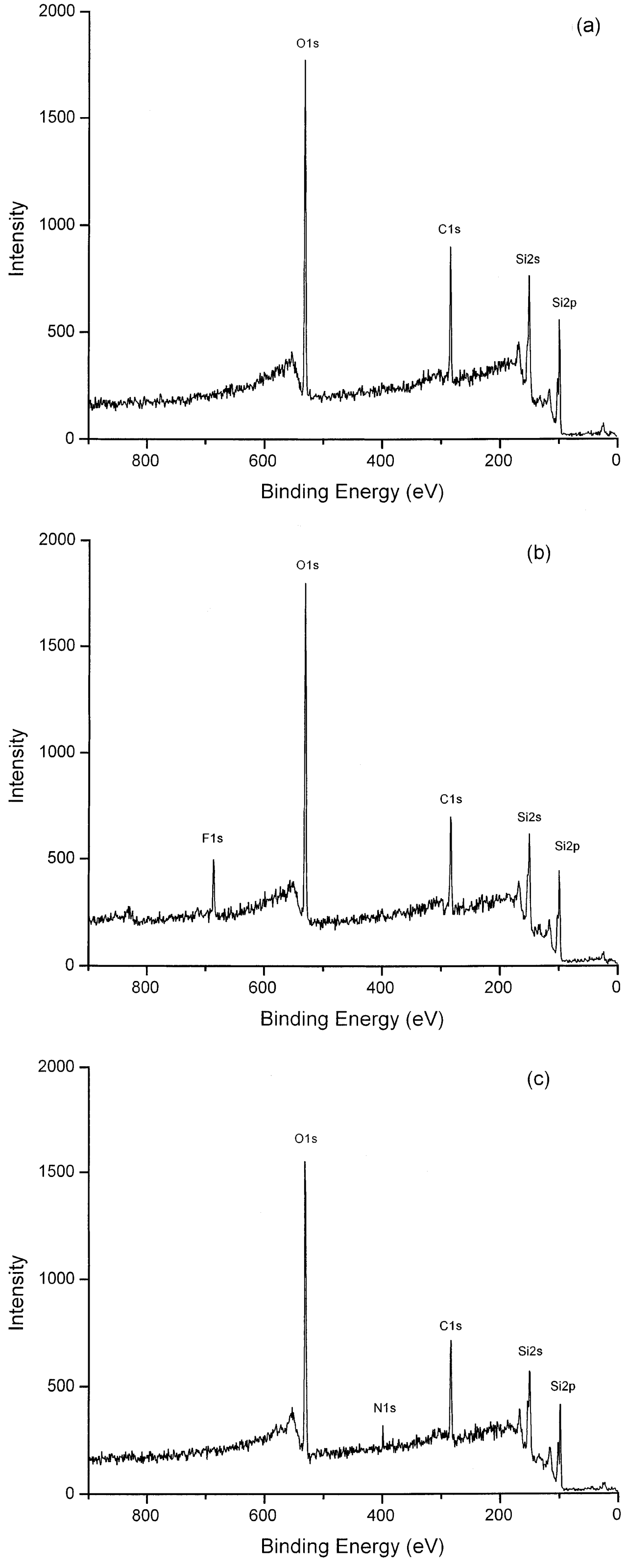


Figure 1. XPS wide-scan spectra of silicon substrates with monolayers of (a) ≡SiPh; (b) after the treatment with triflic acid and (c) substitution reaction of −OTf with aniline.

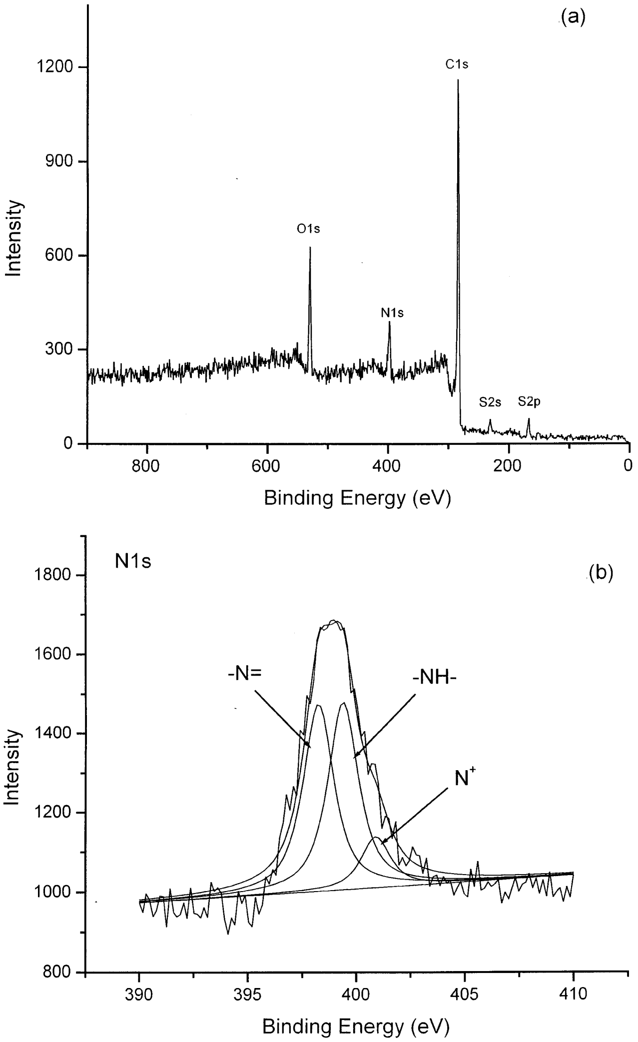


Figure 2. (a) XPS wide-scan spectra and (b) N 1s core-level spectra of PANI grafted on a silicon substrate.

means that the surface was completely covered by PANI. The small sulfur signal is most likely due to the impurities accumulated during grafting, which involved ammonium persulfate. The curve-fitted N 1s core-level spectrum of the EM state of PANI-aniline-SAM-silicon surface (Figure 2b) revealed the predominant presence of two types of structures corresponding to the binding energy (BE) peaks of 398.2 and 399.4 eV, which can be assigned to the quinonoid imine (=N−) and benzenoid amine (−NH−) structures,[31] respectively. The almost equal proportions of the imine and amine nitrogen in the N 1s core-level spectrum of the deprotonated surface are consistent with the EM base form ([=N−]/[−NH−] ratio ~ 1) of PANI. The residual high binding energy tail (>400 eV) in the N 1s spectra is probably due to some surface oxidation products or a weakly charged-transfer complexed oxygen.[32] The above N 1s spectra are similar to those of the polyaniline homopolymer films, and this indicates a successful grafting of PANI to the surface of silicon.

AFM Images. The AFM images obtained are presented in Figures 3a−c, which reveal differences in morphologies. The pristine silicon wafer substrate is imaged by AFM in Figure 3a. It has a smooth surface, and its root-mean-square roughness (rms) was 1.6 Å. The assembly of a phenylsilane monolayer, the triflation by HOTf, and the substitution reaction by aniline (Figure 3b) increased the roughness, producing many fine aggregates distributed evenly on the silicon surface. While the rms roughness changed from 1.6 to 4.3 Å, the surface remained smooth. In Figure 3c, the area is well covered with PANI, and the roughness can be more

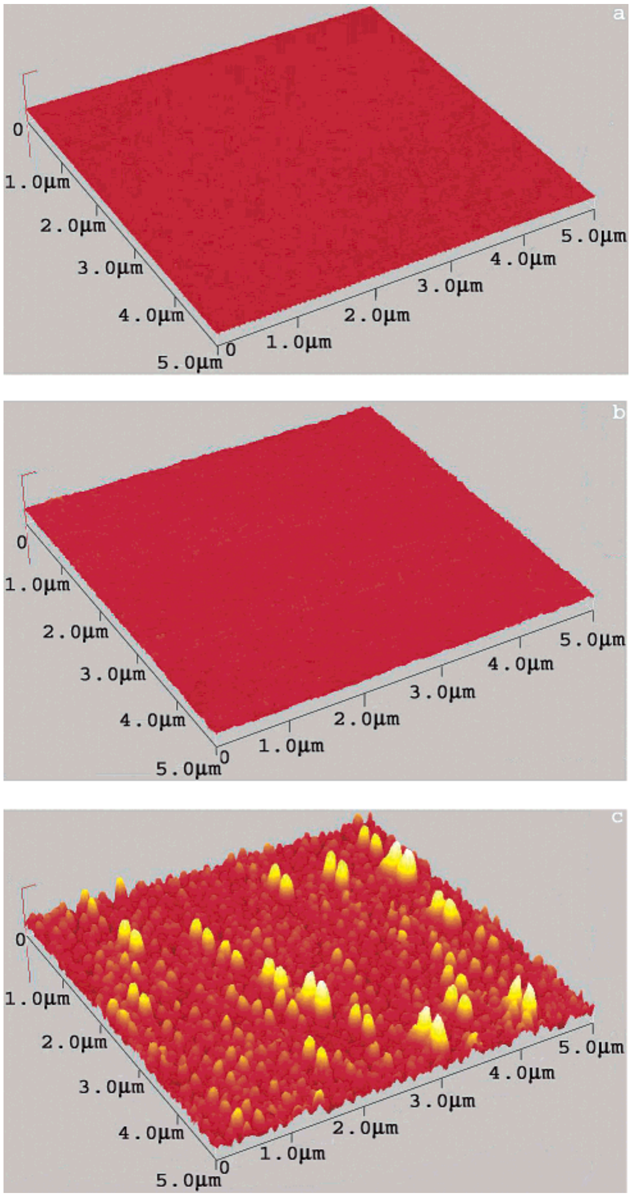


Figure 3. AFM image for the (a) pristine, (b) aniline primed, and (c) PANI grafted Si(100) surface.

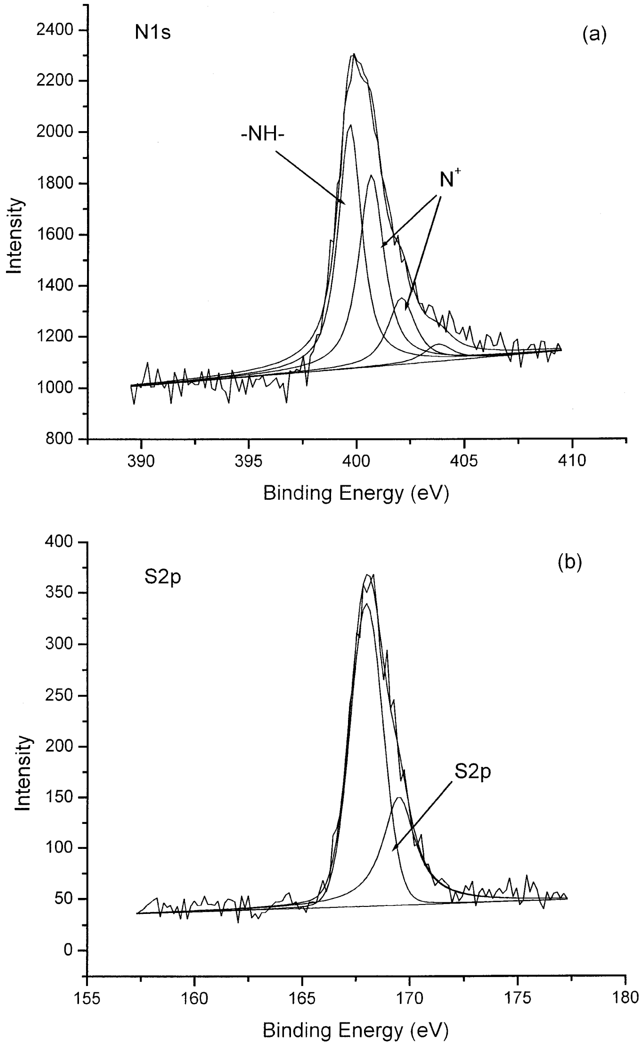
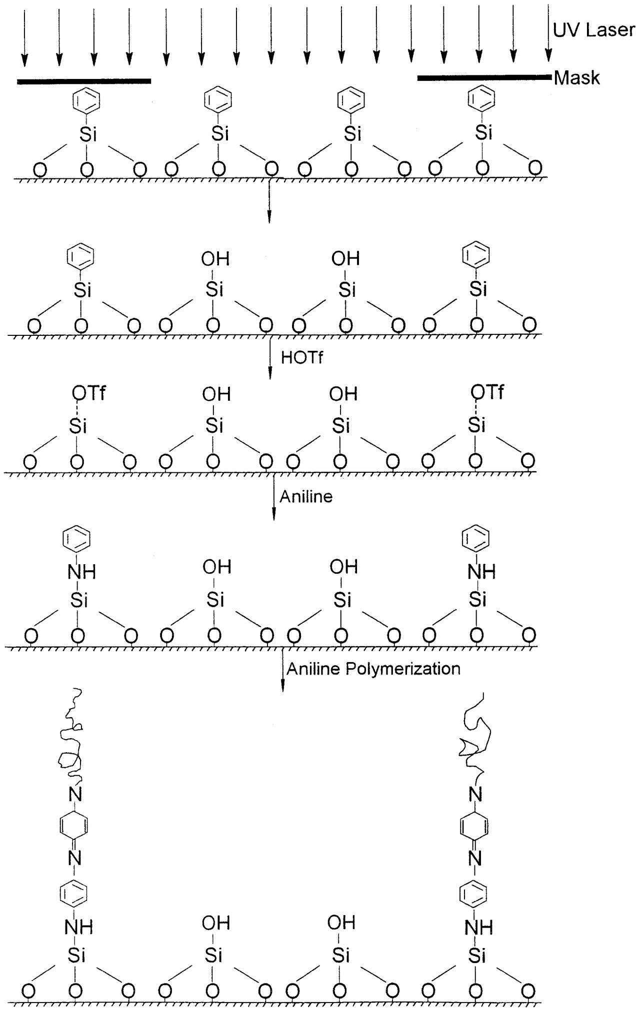


Figure 4. (a) N 1s and (b) S 2p core-level spectra for the surface grafted PANI after protonation with H_2SO_4.

easily observed. The sizes of most PANI aggregates are between 150 and 200 nm in diameter, and the aggregates are closely packed. The PANI layer has a mean height of 32 nm, which coincides with the ellipsometry result, and a surface roughness rms = 3.87 nm. It should be emphasized that a much higher regularity in the morphology was observed for the PANI grafted using the present method than for the physically deposited PANI films, the latter having a rms of 10.2 nm for a film thickness of 34 nm.

Protonated State of the Grafted PANI on the Silicon Surface. The successful grafting of the PANI chains was additionally confirmed by the significant increase in the surface conductivity and changes of XPS core-level spectra after protonation with a 0.5 M H_2SO_4 solution. Like the homopolymer, the EM base of PANI-aniline-SAM-silicon surface can be reprotonated with an acidic solution. Figure 4a,b presents the XPS analysis of N 1s and S 2p core-level spectra of PANI-aniline-SAM-silicon surface after doping with H_2SO_4. Comparing the N 1s core-level spectrum (Figure 2b) to that of the reprotonated PANI-aniline-SAM-silicon surface (Figure 4a), one can notice that the $-N=$ groups ($BE = 398.2$ eV) were replaced after protonation by positively charged nitrogens ($BE = 400.9$ and 402.2 eV). Similarly, the protonation of the EM base form of the aniline homopolymer also occurred preferentially at the imine group.[28] The above change in the curve-fitted N 1s spectra, combined with the strong S 2p signal, allowed one to conclude that the EM base grafted on the silicon surface was effectively reprotonated by H_2SO_4 and that the reprotonation of the grafted PANI chains is not unlike that of the homopolymer. Regarding the conductivity of the grafted PANI in the protonated state, the surface resistance measured by the four-probe method changed from the insulation state of the pristine silicon wafer to a surface resistance of 2.96 kΩ/area (with the area 1 cm wide and 0.2 cm long) for the grafted PANI after protonation. Both the ellipsometry measurements and the AFM surface morphology analysis provided an average thickness of 35 nm for the PANI grafted on the silicon surface. On the basis of this value, one can obtain a surface conductivity of 23 S/cm. The bulk conductivity of the protonated PANI films is, in general, of the order of 1 S/cm. As shown by the AFM images, the different values can be attributed to the ordered, high-density structure of the surface layer in which the PANI chains are tightly packed. The relatively high conductivity of

Scheme 2. Strategy for Patterned Graft Polymerization of Polyaniline (PANI) on a Silicon Substrate



the grafted PANI makes the present surface modification technique potentially valuable for surface graft polymerization of conductive polymers to various substrates. Finally, it is appropriate to emphasize that the thin layer of grafted PANI chains are covalently bound to the silicon surface and cannot be easily removed by extraction with organic solvents or by peeling tests with Scotch tape.

Patterned Grafted Polyaniline. Until now, the experiments have been carried out with unpatterned PANI. As shown in Scheme 2, patterned PANI can be formed by graft polymerization on preselected areas. It was generated by first patterning a phenylsilane SAM monolayer by the photolithographic technology. Some authors[26a,27b] have shown that a phenylsilane monolayer can be patterned with a deep UV laser or UV light through a lithographic mask. The UV laser/light could efficiently cleave the Si−R bond on the surface and generate SiOH groups in contact with air. We employed this method by first patterning a phenylsilane monolayer with a 263 nm laser through a predesigned lithographic mask. In this case, the Si−phenyl bonds were removed from the irradiated areas, leaving a monolayer of unreacted Si−phenyl in the unexposed regions for further functionalization. Then the reaction of the unexposed phenylsilane with triflic acid and the further exposure to the aniline resulted in a patterned aniline-primed surface. The graft oxidative polymerization of aniline could be achieved by adding an oxidant and aniline solution for polymerization on the aniline-primed areas. The grafted PANI thus formed constitutes a negative of the lithographic mask. Figure 5a presents the SEM image of the patterned PANI after graft polymerization. The white strips represent the grafted PANI area, whereas the black strips the nongrafted areas. A relatively clear boundary between the patterned and nonpatterned areas can be observed in the SEM image. A closer look at the boundaries between the two can be obtained under a higher magnification by AFM (Figure 5b), which demonstrates that this method provides a high line edge acuity of the patterned PANI. With a rich available chemistry for reactions with specified SAMs and the advent of new nanotechnological methods to pattern SAM monolayers at the nanometer scale, this method can provide a strategy for patterning conductive polymers at nanoscale arrays without the need of a photoresist.

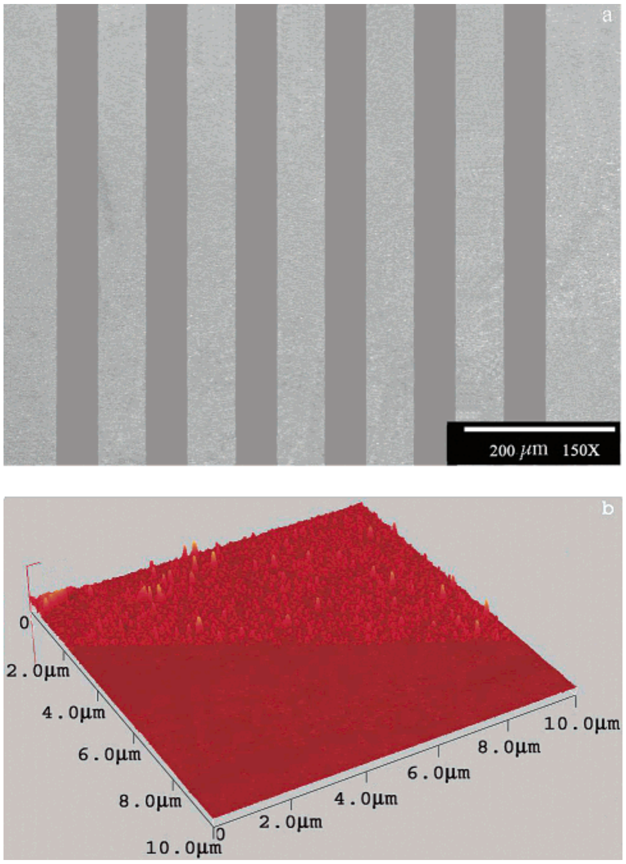


Figure 5. (a) SEM image of the patterned PANI film on a silicon substrate and (b) selected edge area of (a) under AFM.

The surface conductivity through the patterned wires was 21 S/cm (for the surface fraction grafted), a value very near to that determined for the nonpatterned case (23 S/cm). This is not surprising because the width of the wires was large (about 50 μm). As expected, the surface conductivity in the direction normal to the wires was negligible.

Conclusion

A phenylsilane monolayer was first generated by reacting phenyltrichlorosilane with a hydroxylated silicon surface through the self-assembly method, under an inert atmosphere. The SAM layer was photopatterned under an UV laser at 263 nm through a lithographic mask. The as-patterned SAM was allowed to react with triflic acid (HOTf) in order to remove the benzene ring from the SAM layer. The −OTf groups of SAM were substituted with aniline to form an aniline-primed substrate. The aniline sites allowed the further graft polymerization of aniline to generate a patterned conductive polyaniline (PANI). The conductivity through the patterned wires was as large as 21 S/cm, much larger than the usual value of the bulk PANI films (∼1 S/cm). The microscopy experiments revealed that the patterned PANI had a compact structure and a good edge acuity of the patterns. The combination of surface graft polymerization of aniline and photopatterned self-assembly monolayer (SAM) provides a new strategy for patterning the conductive polymers with potential use in the electrical and biomedical fields.

References and Notes

(1) MacDonald, S. A.; Willson, C. G.; Frechet, J. M. J. *Acc. Chem. Res.* **1994**, *27*, 151.
(2) Healy, B. G.; Foran, S. E.; Walt, D. R. *Science* **1995**, *269*, 1078.
(3) Zamborini, F. P.; Crooks, R. M. *Langmuir* **1997**, *13*, 122.
(4) Jeon, N. L.; Choi, I. S.; Whitesides, G. M.; Kim, N. Y.; Laibinis, P. E.; Harada, Y.; Finnie, K. R.; Girolami, G. S.; Nuzzo, R. G. *Appl. Phys. Lett.* **1999**, *75*, 4201.
(5) Crooks, R. M.; Ricco, A. J. *Acc. Chem. Res.* **1998**, *31*, 219.
(6) Mrksich, M.; Whitesides, G. M. *Trends Biotechnol.* **1995**, *12*, 228.
(7) Gosh, P.; Amirpour, M. L.; Lackowski, W. M.; Pishko, M. V.; Crooks, R. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 1592.
(8) Singhvi, R.; Kumar, A.; Lopez, G. P.; Stephanopoulos, G. N.; Wang, D. I. C.; Whitesides, G. M.; Ingber, D. E. *Science* **1994**, *264*, 696.
(9) Chen, C. S.; Mrksich, M.; Huang, S.; Whitesides, G. M.; Ingber, D. E. *Biotechnol. Prog.* **1998**, *14*, 356.
(10) (a) Braun, D.; Brown, A.; Staring, E.; Meijer, E. W. *Synth. Met.* **1994**, *65*, 85. (b) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.
(11) (a) Dodadabalapour, A.; Torsi, L.; Katz, H. E. *Science* **1995**, *268*, 270. (b) Burroughes, J. H.; Jones, C. A.; Friend, R. H. *Nature (London)* **1988**, *335*, 137.
(12) (a) Inganäs, O.; Pei, Q. *Adv. Mater.* **1992**, *4*, 277. (b) Baugman, R. H.; Shacklette, L. W.; Elsenbaumer, R. L.; Plichta, E. J.; Becht, C. In *Molecular Electronics*; Lazarev, P. I., Ed.; Kluwer Academic Publishers: The Netherlands, 1991; p 267.
(13) Lonergan, M. C.; Severin, E. J.; Doleman, B. J.; Beaber, S. A.; Grubbs, R. H.; Lewis, N. S. *Chem. Mater.* **1996**, *8*, 2298.
(14) Chen, L. H.; Jin, S.; Tiefel, T. H. *Appl. Phys. Lett.* **1993**, *62*, 2440.
(15) Kranz, C.; Ludwig, M.; Gaub, H. E.; Schuhmann, W. *Adv. Mater.* **1995**, *7*, 38.
(16) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684.
(17) Beh, W. S.; Kim, I. T.; Qin, D.; Xia, Y. N.; Whitesides, G. M. *Adv. Mater.* **1999**, *11*, 1038.
(18) Chang, S. C.; Bharathan, J.; Yang, Y.; Helgeson, R.; Wudl, F.; Ramey, M. B.; Reynolds, J. R. *Appl. Phys. Lett.* **1998**, *73*, 2561.
(19) Drury, C. J.; Mutsaers, C. M. J.; Hart, C. M.; Matters, M.; de Leeuw, D. M. *Appl. Phys. Lett.* **1998**, *73*, 108.
(20) Bjornholm, T.; Greve, D. R.; Reitzel, N.; Hassenkam, T.; Kjaer, K.; Howes, P. B.; Larsen, N. B.; Bogelund, J.; Jayaraman, M.; Ewbank, P. C.; McCullough, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 7643.
(21) Holdcroft, S. *Adv. Mater.* **2001**, *13*, 1753.
(22) Huang, Z.; Wang, P. O.; MacDiarmid, A. G.; Xia, Y.; Whitesides, G. *Langmuir* **1997**, *13*, 6480.
(23) Ulman, A. *J. Mater. Educ.* **1989**, *11*, 205.
(24) (a) Li, Z. F.; Ruckenstein, E. *Synth. Met.* **2002**, *129*, 73. (b) Li, Z. F.; Ruckenstein, E. *J. Colloid Interface Sci.* **2002**, *251*, 343.
(25) (a) Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074. (b) Tripp, C. P.; Hair, M. L. *Langmuir* **1991**, *7*, 923.
(26) (a) Dulcey, C. S.; Georger, J. H.; Krauthamer, V.; Stenger, D. A.; Fare, T. L.; Calvert, J. M. *Science* **1991**, *252*, 551. (b) Plueddemann, E. P. In *Silane Coupling Agents*; Plenum Press: New York, 1991. (c) Murray, R. W. In *Introduction to the Chemistry of Molecularly Designed Electrode Surfaces*; Murray, R. W., Ed.; Techniques of Chemistry Series; John Wiley and Sons: New York, 1992.
(27) (a) Smith, D. A.; Freed, C.; Bianconi, P. A. *Chem. Mater.* **1993**, *5*, 245. (b) Ingall, M. D. K.; Honeyman, C. H.; Mercure, J. V.; Bianconi, P. A.; Kunz, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 3607. (c) Hrkach, J.; Ruehl, K.; Matyjaszewski, K. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1988**, *29* (2), 112. (d) Matyjaszewski, K.; Chen, Y. L. *J. Organomet. Chem.* **1988**, *340*, 7. (e) Matyjaszewski, K.; Chen, Y. L.; Kim, H. K. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series No. 360; American Chemical Society: Washington, DC, 1988; pp 78−88.
(28) Ray, A.; Asturias, G. E.; Kershner, D. L.; Ritchter, A. F.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1989**, *29*, E145.
(29) Thoden van Velzen, E. U.; Engbersen, J. F. J.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1994**, *116*, 3597.
(30) Petrucci, M. G. L.; Kakkar, A. K. *J. Chem. Soc., Chem. Commun.* **1995**, 1577.
(31) Snauwaert, P.; Lazzaroni, R.; Riga, J.; Werbist, J. J.; Gonbeau, D. *J. Chem. Phys.* **1990**, *92*, 2187.
(32) Trivedi, D. C. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: Chichester, 1997; Vol. 2, p 505.

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