Macromolecules

Article

Oxidative Graft Polymerization of Aniline on Modified Si(100) Surface

Yongjun Chen, , K. G. Neoh, and K. L. Tan

Macromolecules, **2001**, 34 (10), 3133-3141• DOI: 10.1021/ma0008589 • Publication Date (Web): 14 April 2001

Macromolecules is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Articles

Oxidative Graft Polymerization of Aniline on Modified Si(100) Surface

Yongjun Chen, E. T. Kang,* and K. G. Neoh

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 119260

K. L. Tan

Department of Physics, National University of Singapore, Kent Ridge, Singapore 119260

Received May 18, 2000; Revised Manuscript Received February 7, 2001

ABSTRACT: Chemical modification of the argon plasma-pretreated Si(100) surface by UV-induced surface graft polymerization with either glycidyl methacrylate (GMA) or glycidyl acrylate (GA) was carried out. The GA graft polymerized Si substrate was further subjected to coupling reaction with aniline (An) and finally oxidative graft polymerization of An. The composition and microstructure of the graft-polymerized Si(100) surfaces were studied by X-ray photoelectron spectroscopy (XPS) and imaging XPS, respectively. The graft concentrations of the GMA polymer, GA polymer, and An polymer increased with increasing concentration of the respective monomer used for graft polymerization. The graft polymerization efficiency of GA on the Ar plasma-pretreated Si(100) was much higher than that of GMA. Ethanol, when used as a solvent, catalyzed the coupling reaction of the epoxide groups of GA with An and should be of more than 40 vol % in concentration to achieve the optimum effect. The protonation−deprotonation characteristics, interconvertible intrinsic redox states, and metal reduction behavior of the polyaniline (PANI) chains, obtained from subsequent oxidative graft polymerization of An on the modified Si(100) surface, were grossly similar to those of the PANI homopolymer. The resistance of the modified Si(100) surface from consecutive graft polymerization with GA and An was on the order of 10^7 Ω/sq.

Introduction

Considerable attention has been paid to the deposition of functional thin films on silicon surfaces because of the importance of the process to the development of advanced materials for applications ranging from microelectronics to solar cells.[1] The method of chemical vapor deposition (CVD) has been used for synthesizing insulators, conductors, high-temperature superconductors, and diamond thin films on semiconductor surfaces.[2−4] However, the CVD method is used mainly for depositing inorganic and molecular films on silicon surfaces. In many cases during the production of microelectronics devices, the silicon surfaces need to be modified to introduce stable thin films of polymers and organic compounds. For example, the introduction of an organic adhesion promoter on silicon surface to improve its adhesion with dielectric materials, such as polyimides and poly(tetrafluoroethylene), is desirable.[5] The common methods for introducing stable organic films on silicon surfaces include the coupling of highly reactive compounds, such as the silanes,[6,7] and the adsorption of substances having specific polar groups, such as the proteins.[8]

On the other hand, the methods for chemical modification of polymer surfaces are more well-known and have been reviewed recently.[9] The main approaches to chemically modified polymer surfaces are those of wet chemical oxidation, plasma treatment, and attachment of polymer chains. Among the techniques available, surface modification via grafting and graft copolymerization is one of the most promising techniques, as it allows the molecular redesign of most substrate surfaces to impart new and specific functionalities.[10−17]

Recently, polyaniline (PANI) has been of particular interest because of its environmental stability, controllable electrical conductivity, and interesting redox properties associated with the chain nitrogen.[18,19] PANI also exhibits crystallinity and solution- or counterion-induced processability.[20,21] Furthermore, the electrical properties of PANI can be substantially improved through secondary doping[22] and proper molecular matching among the polymer, dopant, and solvent molecules. PANI has potential applications not only in the areas of corrosion protection of metals,[23] light-emitting devices,[24] control of electromagnetic reaction, and the dissipation of electrostatic charges[25,26] but also as biocompatible materials[27,28] and materials for catalysts, electrodes, and sensors.[29,30]

In this study, we report on a novel method for the chemical deposition of the polyaniline onto the Si(100) surface. The method involves initially surface modification of the Ar plasma-pretreated silicon via UV-induced graft polymerization of glycidyl acrylate (GA) or glycidyl methyl acrylate (GMA). The epoxide functional groups of the grafted GA polymer chains on the silicon surface are subsequently reacted with aniline. The silicon surface with the covalently coupled aniline is then subjected to oxidative graft polymerization of aniline to result in a covalently grafted PANI layer.

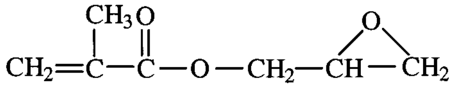
---

* To whom correspondence should be addressed. Fax (65) 779-1936; E-mail cheket@nus.edu.sg.

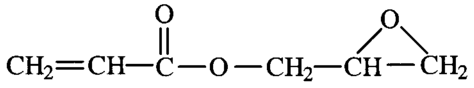
10.1021/ma0008589 CCC: $20.00

Experimental Section

Materials. The single-crystal Si(100) wafers polished on one side and 6 in. in diameter were purchased from Hitachi Inc., Japan. The silicon wafers were sliced into rectangular strips of about 0.5 cm × 1.0 cm in size. To remove the organic residues from the surface, the silicon substrates were cleaned using the "piranha" solution, a mixture of 70% concentrated sulfuric acid and 30% hydrogen peroxide. The cleaned silicon strips were then washed with distilled water and dried under reduced pressure for the subsequent surface modification. The glycidyl methacrylate (GMA) and aniline (An) monomers were obtained from Aldrich Chemical Co. of Milwaukee and were used as received. The glycidyl acrylate (GA) was purchased from Polyscience Inc. and was used as received. The structures of GMA and GA are shown below:



GMA



GA

The solvents, such as 1,4-dioxane, acetone, ethanol, and *N*-methylpyrrolidinone (NMP), and other chemicals were of reagent grade. They were also obtained from the Aldrich Chemical Co. and were used as received.

Plasma Pretreatment and Surface Graft Polymerization. A cylindrical quartz glow discharge cell, model SP-100, manufactured by Anatech Ltd., was used for the plasma pretreatment of the silicon substrate. The glow discharge was generated at a frequency of 40 kHz and a plasma power of 35 W. The pressure in the quartz cell was maintained at ~0.58 Torr of argon while the polymer films were exposed to the glow discharge for 0−60 s. The Ar plasma-pretreated silicon was exposed to air for about 10 min to facilitate the formation of surface peroxides and hydroperoxides for the subsequent UV-induced surface graft polymerization process.[12,31]

The surface modification of silicon by graft polymerization of GMA or GA and aniline was carried out in three steps. The first step involved the UV-induced graft polymerization of GMA or GA on the Ar plasma-pretreated silicon substrate. The second step involved the coupling reaction between the epoxide groups of the graft-polymerized GA and aniline. The last step involved the surface oxidative graft polymerization of aniline on the modified silicon surface via the covalently immobilized aniline sites.

The UV-induced surface graft polymerizations of GMA and GA on the Ar plasma-pretreated Si(100) surfaces were carried out in a Riko rotary model RH 400-10W photochemical reactor, manufactured by Riko Denki Kogyo of Chiba, Japan. The reactor was equipped with a 1000 W high-pressure Hg lamp and a constant temperature water bath. All UV-induced graft copolymerization was carried out at a constant temperature of 28 °C. The Ar plasma-pretreated silicon was immersed in a 1,4-dioxane solution of either GMA or GA in a Pyrex tube. Each reaction mixture was thoroughly degassed before being sealed under a nitrogen atmosphere. It was then subjected to UV irradiation for 15−120 min. After each grafting experiment, the silicon strip was washed with copious amounts of 1,4-dioxane to remove the residual monomer and the adsorbed homopolymer. The GMA or GA graft-polymerized silicon (GMA-*g*-Si or GA-*g*-Si) substrates were then dried under reduced pressure. The epoxide-ring-opening reaction with the aniline (An) monomer was carried out in ethanol solution, containing the GA-*g*-Si substrate and An. The reaction temperature was varied in the range 25−70 °C and the reaction time in the range 2−10 h. The An concentration in ethanol, on the other hand, was varied between 20 and 100 vol %. After the covalent coupling of An to the epoxide group, the silicon substrate was washed thoroughly with copious amounts of NMP to remove the unreacted An monomer. The residual NMP on the An-coupled GA-*g*-Si (An-GA-*g*-Si) substrate was, in turn, removed by washing with ethanol.

The oxidative graft polymerization of aniline via the aniline moiety of the An-GA-*g*-Si substrate was carried out in 0.5 M H_2SO_4 solution containing 0.01−0.2 M aniline and the corresponding amount of $(NH_4)_2S_2O_8$ oxidant to achieve an aniline monomer to oxidant molar ratio of 1:1. The reaction was allowed to proceed at 0 °C for 5 h. The method was thus similar to that reported in the literature for the oxidative homopolymerization of aniline to produce the conductive emeraldine (EM) salt.[32,33] The grafted EM salt on the silicon surface was converted to the neutral EM base form by immersing and equilibrating the substrate in copious amounts of doubly distilled water. The surface-modified silicon was subsequently immersed in a large volume of NMP (a good solvent for EM base) for at least 24 h with continuous stirring to remove the adhered and physically adsorbed EM base polymer. During the washing process, the NMP solvent was changed every 8 h. The polyaniline (PANI)-grafted silicon surface was further washed with distilled water to remove the residual NMP before being dried under reduced pressure (the PANI-An-GA-*g*-Si surface). The EM state of the grafted PANI on the Si(100) surface was reduced to the LM state by exposure to hydrazine for 1 h, followed by thoroughly rinsing with distilled water, before being dried under reduced pressure.[32,33] For the electroless deposition of Pd metal, the PANI-An-GA-*g*-Si surface with the PANI in its LM state was immersed in the palladium nitrate solution (100 mg dm^{-3} Pd(II) ions in 0.05 M HNO_3) for 10 min. After removal from the Pd nitrate solution, the Pd laden Si substrate was rinsed thoroughly with deionized water before being dried under reduced pressure.

Characterization of the Surface-Modified Silicon. The graft-modified silicon surfaces were characterized by X-ray photoelectron spectroscopy (XPS), imaging XPS, and conductivity measurements. XPS measurements were made on a Kratos Analytical AXIS HSi 165 spectrometer with a Mg Kα X-ray source (1253.6 eV photons). The X-ray source was run at a reduced power of 150 W (15 kV and 10 mA). The EM samples were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level spectra were obtained at the photoelectron takeoff angle (α, with respect to the sample surface) of 90°. The pressure in the analysis chamber was maintained at 10^{-8} Torr or lower during each measurement. To compensate for surface charging effects, all binding energies were referenced to the C 1s hydrocarbon peak at 284.6 eV. In peak synthesis, the line width (full width at half-maximum or fwhm) of Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak area ratios and were accurate to within ±10%. The chemical maps of the graft-modified silicon surfaces were obtained from the Kratos analytical AXIS HSi 165 spectrometer with a monochromatized Al Kα X-ray source (1486.6 eV photons). The range scanned was from −0.3 to +0.3 mm at 60 lines and 60 points resolution.

The conductivity of the graft-modified silicon surface was measured by the two-probe method, using a Hioki model 3265 digital electrometer. For each conductivity value reported, at least three sample measurements were averaged.

Results and Discussion

The processes of surface modification of silicon by argon plasma treatment, UV-induced graft polymerization with GA (or GMA), reactive coupling of the epoxide functional groups of the grafted GA polymer with aniline, and finally oxidative graft polymerization of aniline via the surface-bonded aniline moieties are shown schematically in Figure 1. Each process is described in detail below.

UV-Induced Surface Graft Polymerzations of GA and GMA on the Ar Plasma-Pretreated Si Surfaces: GA-*g*-Si and GMA-*g*-Si Surfaces. The

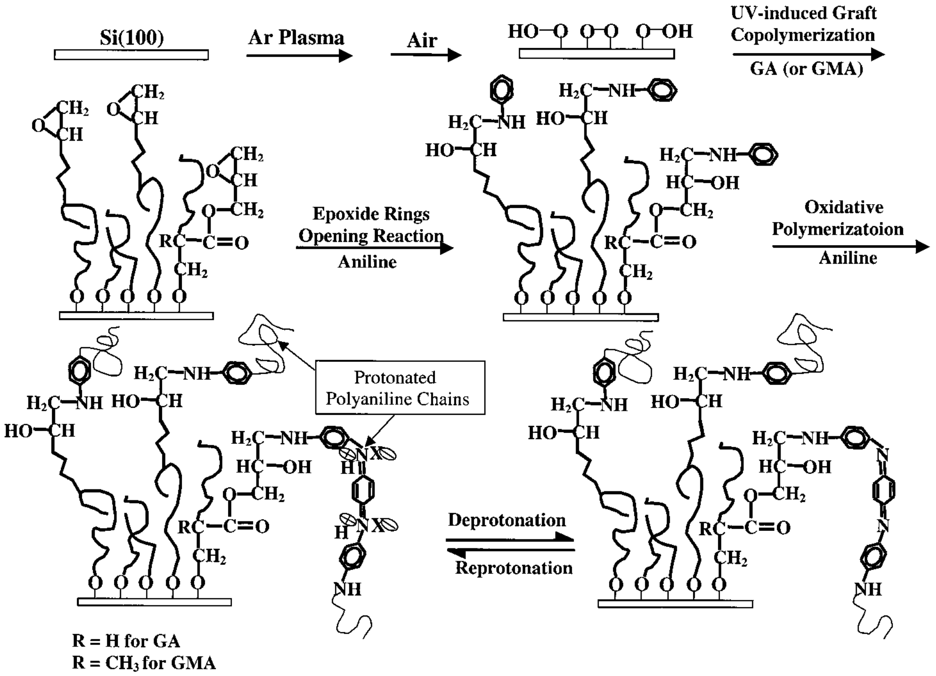


Figure 1. Schematic representations of the chemical deposition processes and the surface structures of the silicon substrates with grafted GA (or GMA) and aniline polymers.

effect of Ar plasma pretreatment under similar experimental conditions on the surface composition of the silicon substrate has been reported earlier, and the optimum Ar plasma pretreatment time is between 10 and 20 s.[31] The glow discharge results in the formation of surface activated Si species. The subsequent exposure of the Ar plasma-pretreated surface to air causes oxygen to be incorporated onto the silicon surface, leading to surface oxidation and the formation of peroxide and hydroperoxide species. The peroxide and hydroperoxide species can readily initiate the surface free radical polymerization in a mechanism generally proposed for the UV-induced surface graft polymerization.[12,31,34]

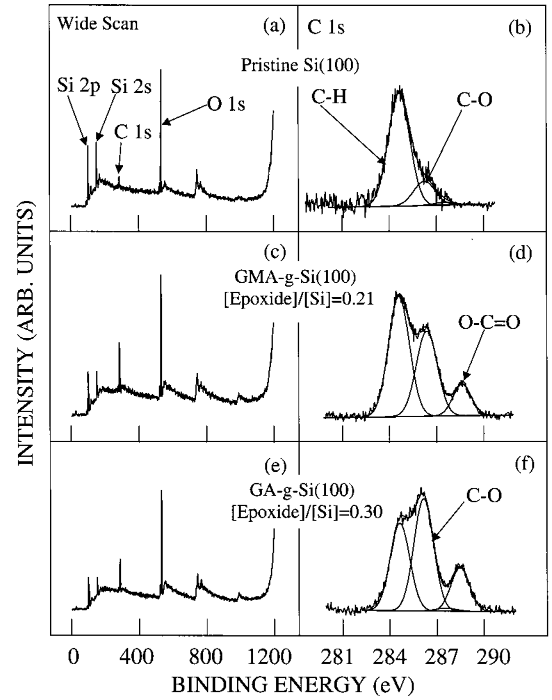


Figure 2. Wide scan and C 1s core-level spectra of the pristine Si(100) surface (a, b), 10 s Ar plasma-pretreated Si(100) surface after the UV-induced graft copolymerization in 20 vol % GMA solution for 1.5 h (c, d), and 15 s Ar plasma-pretreated Si(100) surface after the UV-induced graft copolymerization in 20 vol % GA solution for 15 min (e, f).

Figure 2 shows the respective wide scan and C 1s core-level spectra of the pristine Si (100) surface (parts a and b), the 10 s argon plasma-pretreated silicon surface after the UV-induced graft polymerization in 20 vol % GMA solution for 1.5 h (parts c and d), and the 15 s argon plasma-pretreated silicon surface after the UV-induced graft polymerization in 20 vol % GA solution for 15 min (parts e and f). Parts a and b in Figure 2 reveal the presence of trace amounts of organic contaminant on the pristine Si surface. After graft polymerization, the presence of surface-grafted GMA and GA polymers can be deduced from the three C 1s peak components with binding energies (BE's) similar to those of the glycidyl homopolymers,[35] viz., 284.6 eV for the *C*−H species, 286.2 eV for the *C*O species, and 288.7 eV for the *C*OO species. The graft concentration can be defined in this case as the [epoxide]/[Si] ratio, or the equivalent [*C*OO]/[Si] ratio, and derived from the *C*OO spectral component to Si 2p core-level spectral area ratio, as each GMA or GA molecule has one *C*OO species and one epoxide unit. The graft concentrations of the above GMA-*g*-Si and the GA-*g*-Si surfaces are 0.21 and 0.30, respectively. After graft polymerization, the presence of the GA and GMA polymers on the Si surfaces has resulted in an increase in the C 1s core-level signal intensity and a decrease in the Si 2p core-level signal intensity, as shown in the wide scan spectra of Figure 2c,e. Comparison of parts c and e of Figure 2 reveals that the intensity of the Si 2p signal in Figure 2e is lower than that in Figure 2c. The observation is consistent with the difference in graft concentrations (0.21 vs 0.30 for the two Si surfaces). The *C*H:*C*O:*C*OO peak area ratio for the GMA graft-polymerized surface (Figure 2d) is about 4.3:3.0:1, which differs somewhat from the *C*H:*C*O:*C*OO peak area ratio of 3:3:1 for the GMA homopolymer. Thus, part of the *C*H component in Figure 2d may have been contributed by carbon

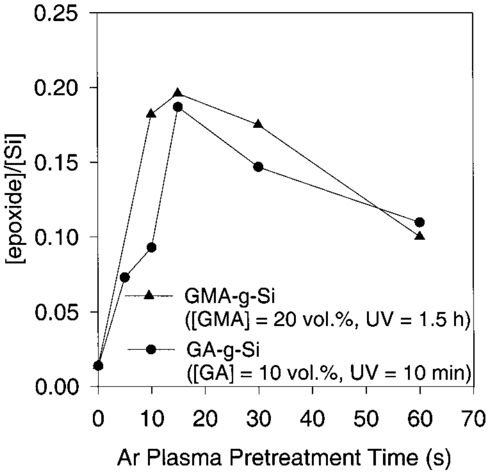


Figure 3. Effect of the Ar plasma pretreatment time of the Si(100) substrate on the graft concentration, expressed as the [epoxide]/[Si] ratio of the GA and GMA polymer.

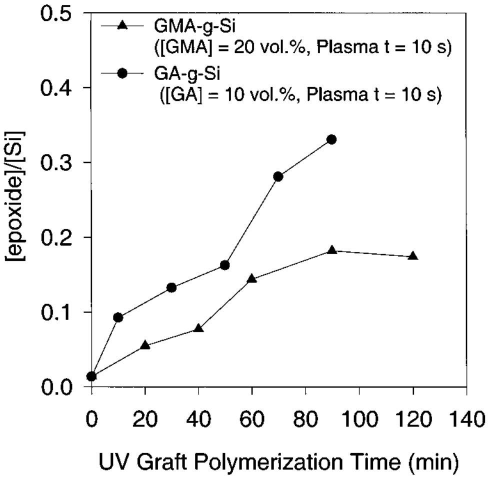


Figure 4. Effect of UV-induced graft copolymerization time on the graft concentration, expressed as the [epoxide]/[Si] ratio of the GA and GMA polymer.

signal from the pristine Si surface. On the other hand, the *C*H:*C*O:*C*OO peak area ratio for the GA graft-polymerized surface (Figure 2f) is about 2.1:2.7:1, which is fairly close to the theoretical ratio of 2:3:1 dictated by the chemical structure of the GA polymer. The composition of the GA-*g*-Si surface thus suggests that the surface of silicon is covered to a large extent by the grafted GA polymer.

Figure 3 shows the effect of Ar plasma pretreatment time of the silicon substrate on the graft concentrations of the GMA and GA polymers. The graft concentration of each polymer increases with increasing Ar plasma pretreatment time of the silicon substrate. Increasing the Ar plasma pretreatment time results in more activated sites on the silicon surface. The increase in active sites, in turn, leads to the formation of more peroxide and hydroperoxide species, upon exposure to air, for the subsequent UV-induced surface graft polymerization. However, when the Ar plasma pretreatment time is greater than 15 s, the graft concentrations for both polymers decrease with increasing Ar plasma pretreatment time. It has been reported previously that prolonged plasma or corona treatment of polymer surfaces does not result in the introduction of a large amount of oxygen atoms or peroxides during the subsequent atmospheric exposure.[12] A similar phenomenon has been observed for the argon plasma-treated Si(100) surface.[31] The optimum peroxide concentration was found to be at the argon plasma treatment time between 10 and 20 s. Thus, the optimum graft concentration observed for each polymer at the Ar plasma pretreatment time of about 15 s coincides with the optimum peroxide concentration on the Si surface. The decrease in the graft concentration observed at the Ar plasma pretreatment time above 15 s is probably due to the fact that the active species formed initially on the Si surface have been partially removed by the etching effects of the plasma upon increasing the plasma treatment time. Figure 4 shows the effect of UV graft polymerization time on the graft concentration of the GMA and GA polymers for the 10 s Ar plasma-pretreated silicon surfaces. The graft concentrations for both the GMA and GA polymers increase with increasing UV graft polymerization time, albeit not at the same rate.

From the data in Figures 3 and 4, it can be concluded that the graft polymerization efficiency of GA is much higher than that of GMA. In Figure 3, although the GA monomer concentration is lower that for GMA (10 vol % vs 20 vol %) and the UV graft polymeriation time for GA is much shorter than that for GMA (10 min vs 1.5 h), the graft concentration of the GA polymer is still comparable to that of the GMA polymer. In Figure 4, the graft concentration of the GA polymer is everywhere higher that that of the GMA polymer even though the GA monomer concentration is lower than the GMA monomer concentration (10 vol % vs 20 vol %). At the GA monomer concentration of 20 vol % or above and UV graft polymerization time of 30 min, excessive homopolymerization in the reaction mixture prevents the recovery of the Si substrate. The difference in the graft polymerization efficiency between the GA and GMA probably arises from the difference in their chemical structures. The GMA molecule is sterically more hindered toward addition polymerization due to the presence of disubstituted vinyl group and is thus expected to polymerize with lower efficiency.

Based on the observed effects of Ar plasma pretreatment time, monomer structure, monomer concentration, and UV graft polymerization time on the graft concentration, the GA-*g*-Si substrates prepared under the optimum conditions of 15 s of Ar plasma pretreatment time, 20 vol % GA monomer concentration, and 15 min of UV graft polymerization time are used for the subsequent coupling reaction with aniline. Under this set of optimum conditions, the graft concentration, expressed as [epoxide]/[Si] ratio, is about 0.3, as shown in Figure 2e,f.

Figure 5 shows the chemical (elemental) maps of the pristine Si (100) surface (parts a and b) and the GA-*g*-Si surface (parts c and d) within an area of 0.3 mm × 0.3 mm. The C 1s and Si 2p XPS core-level signals were used to obtain these maps. For the pristine silicon surface, it can be seen from Figure 5a,b that the surface appears to be generally homogeneous in composition. The minor nonuniformity in Si distribution is probably due to the different extents of oxidation throughout the Si surface and the presence of residual organic contaminants. The presence of the latter is consistent with the presence of a weak carbon signal on the surface of the pristine silicon, as shown in Figures 2b and 5a. When the silicon surface is graft polymerized with GA, the intensity of the C 1s component increases, while that of the Si 2p component decreases substantially, as shown in parts c and d of Figure 5, respectively.

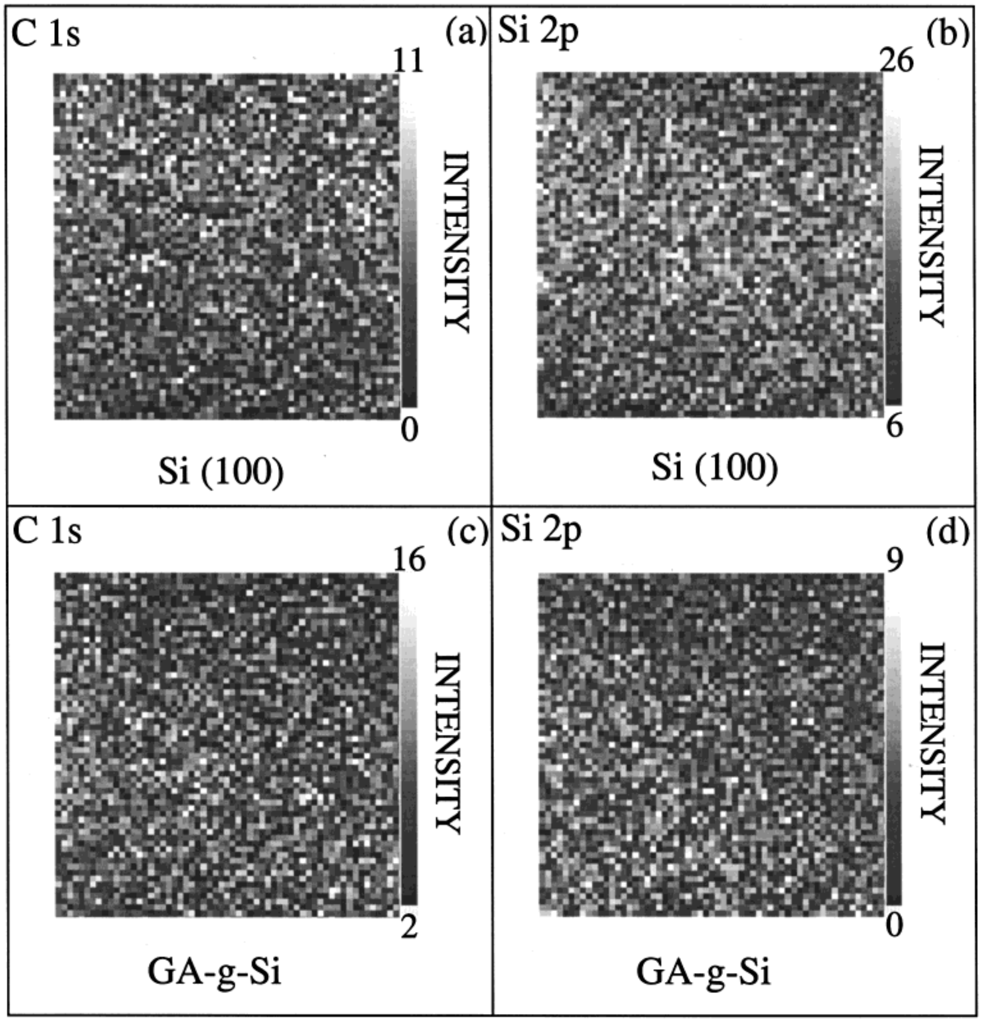


Figure 5. C 1s and Si 2p chemical maps in a 0.3 mm × 0.3 mm area of the pristine Si(100) surface (a, b) and the GA-*g*-Si surface ([epoxide]/[Si] = 0.3) (c, d).

Reactive Coupling of Aniline with the Epoxide Moieties of the Grafted GA Polymer: An-GA-*g*-Si Surface. The GA graft-polymerized silicon surface can be further functionalized through reactions with amines, including the less reactive aromatic amine, such as aniline (An). The reaction is allowed to proceed in ethanol since alcohols can act as catalysts in the ring-opening reaction of the epoxides.[36] Figure 6 shows the respective C 1s and N 1s spectra of the GA-*g*-Si surface after reactive coupling with An in pure aniline (parts a and b) and in a 60 vol % ethanol solution of An (parts c and d). The coupling reaction was allowed to proceed at 30 °C for 4 h. The extent of reaction can be expressed as the [N]/[Si] molar ratio, determined from the corrected N 1s and Si 2p core-level spectral area ratio. The XPS results in Figure 6 indicate that the coupling reaction is greatly affected by the presence of ethanol as a solvent. In the absence of ethanol, the extent of the coupling reaction is reduced by almost half, despite the use of pure aniline. This phenomenon is consistent with the fact that alcohol can promote the ring-opening reaction of the epoxides.[37] Furthermore, the coverage of the GA-*g*-Si substrate surface by the coupling reaction with aniline leads to a decrease in the relative signal intensities of the *C*O and *C*OO species, as shown in Figure 6a,c, in comparison to those in Figure 2f. Moreover, the N 1s core-level spectra in Figure 6b,d suggest that the reaction between the epoxide groups and aniline involves only the primary amine. The coupled amine functional groups probably do not undergo further reaction with the epoxide groups, as the N 1s core-level spectra are dominated by the *N*H peak

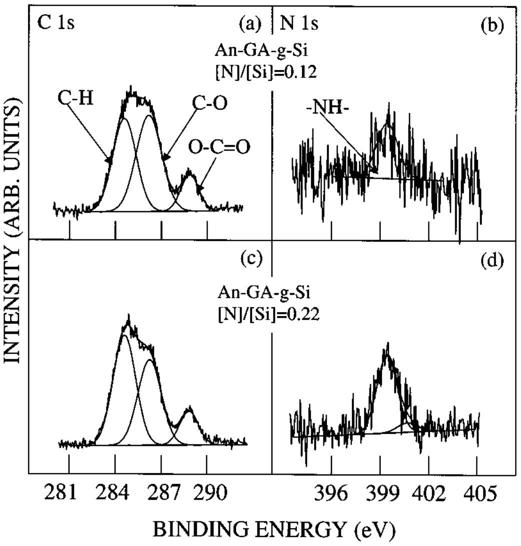


Figure 6. C 1s and N 1s core-level spectra of the GA-*g*-Si surface ([epoxide]/[Si] = 0.3) after reaction with aniline at 30 °C for 4 h in pure An (a, b) and in 60 vol % ethanol solution of aniline (c, d).

Table 1. Effect of Temperature, Aniline Monomer Concentration, and Reaction Time on the Coupling Reaction between GA and Aniline[a]

temp (°C)[b]	[N]/[Si]	aniline monomer concn (vol %)[c]	[N]/[Si]	coupling reaction time (h)[d]	[N]/[Si]
25	0.11	35	0.13	2	0.37
40	0.30	50	0.14	4	0.40
50	0.31	60	0.22	6	0.41
60	0.35	80	0.13	8	0.42
70	0.38	100	0.12	10	0.42

[a] Coupling reaction of aniline with the epoxide groups of GA on the GA-*g*-Si surface (graft concentration or [epoxide]/[Si] = 0.3). The extent of coupling reaction, expressed as the [N]/[Si] mole ratio, was determined from the curve-fitted N 1s and Si 2p core-level spectral area ratio. [b] Other reaction conditions: aniline monomer concentration = 20 vol %, coupling reaction time = 4 h. [c] Other reaction conditions: temperature = 30 °C, coupling reaction time = 4 h. [d] Other reaction conditions: temperature = 60 °C, aniline concentration = 60 vol %.

component at the BE of about 399.4 eV.[37] The phenomenon probably has resulted from the presence of a high concentration of aniline, which contains primary amine, in the reaction mixture and the fact that the reactivity of the primary amine toward the epoxide is higher than that of the secondary amine.

The effect of aniline concentration on the extent of the coupling reaction between the epoxide groups of the GA polymer and aniline is shown in Table 1. For coupling reaction carried out at the temperature of 30 °C for 4 h on the GA-*g*-Si surface with an [epoxide]/[Si] ratio of 0.3, the [N]/[Si] ratio does not change appreciably when the aniline concentration is increased from 20 to 60 vol %. On the other hand, however, when the aniline concentration is increased to above 60 vol %, the [N]/[C] ratio begins to decrease. The solvent effect becomes less important at ethanol concentration below 40 vol %. The effect of temperature and reaction time on the extent of the coupling reaction between the epoxide groups of the GA polymer and aniline is also summarized in Table 1. Thus, the extent of the reaction, expressed as the [N]/[Si] ratio, increases with increasing temperature. At temperatures above 60 °C, the effect of temperature on the extent of the reaction diminishes. Furthermore, as the boiling point of ethanol is only about 78 °C, the highest reaction temperature chosen for the coupling reaction in this study is 70 °C. For the effect of reaction time on the extent of the coupling reaction, the reaction was carried out at the temperature of 60 °C and the aniline concentration of 60 vol % on the GA-*g*-Si surface with an [epoxide]/[Si] ratio of 0.3. The extent of the coupling reaction, expressed as the [N[/[Si] ratio, increases only marginally at reaction time above 2 h. This result indicates that the reaction is not limited by the rate of diffusion of aniline to the epoxide groups of the GA polymer, and all the epoxide functional groups probably have been consumed.

Based on the observed effects of the experimental variables on the extent of the coupling reaction between the epoxide groups of the grafted GA polymer and aniline, a set of optimum conditions for achieving the maximum extent of the coupling reaction appears to be 60 °C for the reaction temperature, 60 vol % for the aniline concentration, and 6 h for the reaction time. Based on the above reaction conditions, the extent of the coupling reaction, expressed as the [N]/[Si] ratio, is about 0.41. The pendant aniline groups on the surface of An-GA-*g*-Si serve as sites for the subsequent covalent anchoring of the polyaniline chains onto the silicon substrate.

Oxidative Graft Polymerization of Aniline on the An-GA-*g*-Si Surface: PANI-An-GA-*g*-Si Surface. Oxidative graft polymerization of aniline were carried out on the An-GA-*g*-Si surface which had a [N]/[Si] ratio of about 0.41. The high surface concentration of the immobilized aniline units will help to promote the subsequent oxidative graft polymerization of aniline. Figure 7a–c shows the respective C 1s, N 1s, and Si 2p core-level spectra of the An-GA-*g*-Si surface after the oxidative graft polymerization in 0.5 M H_2SO_4 containing 0.05 M aniline. The surface-grafted polyaniline (PANI) salt has been deprotonated by equilibrating in copious amounts of distilled water to covert the PANI salt to its neutral emeraldine (EM) base form, as protonation–deprotonation in PANI is an equilibrium process.[32] The C 1s, N 1s, and Cl 2p core-level spectra of the PANI-An-GA-*g*-Si surface after reprotonation by 1 M $HClO_4$ (protonation level or [Cl]/[N] = 0.45) are shown in Figure 7d–f. The graft concentration is defined as the number of aniline repeat units per substrate Si atom (within the probing depth of the XPS technique) and can be expressed as the [N]/[Si] molar ratio. The N 1s core-level spectrum of the deprotonated PANI-An-GMA-*g*-Si surface in Figure 7b shows predominantly the presence of the quinonoid imine (=N– structure) and benzenoid amine (–NH– structure). The two species correspond to peak components with BE's at about 398.2 and 399.4 eV, respectively.[37] The presence of about equal proportion of the imine and amine nitrogen in the N 1s core-level spectrum of the deprotonated surface is consistent with the intrinsic redox state of the EM base form ([=N–]/[–NH–] ratio ~ 1) of PANI.[37] The residual high BE tail in the N 1s spectra probably has originated from the surface oxidation products or weak charge-transfer complex oxygen.[38] Comparison of the N 1s core-level spectrum in Figure 7b to that of the reprotonated PANI-An-GA-*g*-Si surface in Figure 7e suggests that the grafted EM base on the Si surface can be effectively reprotonated by $HClO_4$, as indicated by the disappearance of the –N= component and the appearance of the corresponding proportion of the positively charge nitrogen. For the EM base form of the aniline homopolymer, protonation occurs preferentially at the imine units.[32] Thus, the deprotonation–reprotonation behavior of the grafted PANI chains on the Si surface is not unlike that of the aniline homopolymer.

Figure 8 shows the increase in the graft concentration of PANI with increasing aniline concentration used for the oxidative graft polymerization. When the aniline concentration is above 0.05 M, the increase in graft concentration becomes moderate. The PANI graft concentration ([N[/[Si] ratio) on the An-GA-*g*-Si surface for oxidative graft polymerization carried out in 0.20 M aniline can reach about 3.8. The substantially enhanced [N]/[Si] ratio over that of the starting An-GA-*g*-Si substrate, which has a [N]/[Si] of 0.41, confirms the oxidative graft polymerization of aniline on the An-GA-*g*-Si surface. The process is shown schematically in Figure 1.

The successful grafting of the PANI chains is further confirmed by the preservation of their deprotonation–reprotonation behavior and electrical properties. Figure 8 also shows the resistance of the PANI-An-GA-*g*-Si surface after reprotonation by 1 M $HClO_4$. Generally, the surface resistance decreases with increasing aniline

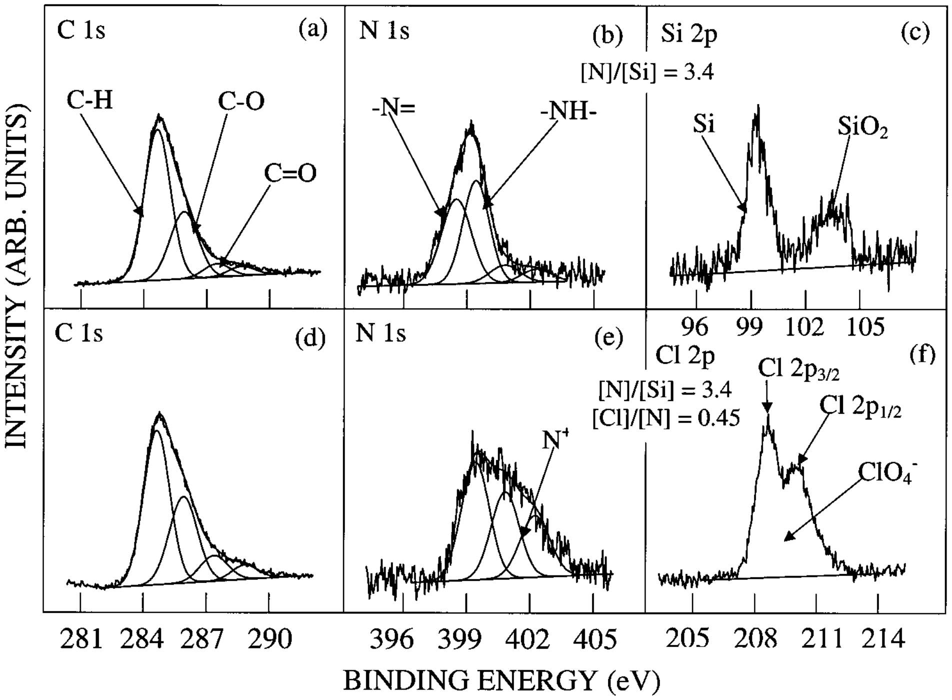


Figure 7. C 1s and N 1s core-level spectra of an An-GA-*g*-Si surface ([N]/[Si] = 3.4) after oxidative graft polymerization in 0.05 M aniline solution, followed by deprotonation with distilled water (a, b), and the C 1s, N 1s, and Cl 2p core-level spectra for the corresponding surface after reprotonation by $HClO_4$ (c, d).

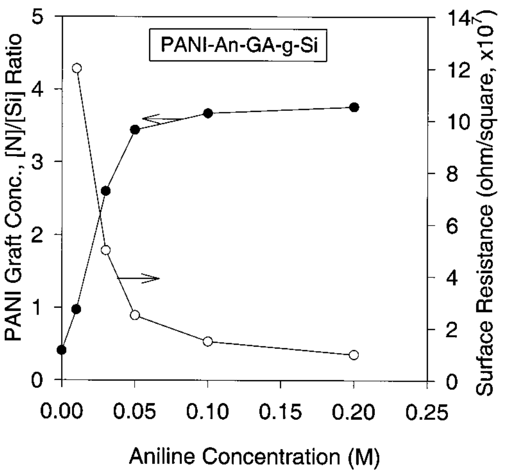


Figure 8. Effect of aniline monomer concentration used during the oxidative graft polymerization on the graft concentration of PANI, expressed as the [N]/[Si] ratio, on the PANI-An-GA-*g*-Si surface and on the corresponding surface resistance.

concentration (and thus the graft concentration of PANI). At the aniline concentration of 0.2 M used for the oxidative graft copolymerization, the surface resistance is about 10^7 Ω/sq. The bulk conductivity of the protonated PANI films, on the other hand, is on the order of 1−10 S/cm.[38] The relation between surface resistance (R_s) and bulk resistivity (ρ) is given by $R_s = \rho/t$, where t is the thickness of the grafted PANI film. Thus, using 7.5 nm (the probing depth of the XPS technique in an organic matrix)[39] as the approximate thickness of the grafted aniline polymer layer, the bulk resistivity is on the order of 1 Ω·cm, which is equivalent to a bulk conductivity value (σ) on the order of 1 S/cm, as $\sigma = 1/\rho$. The preservation of equivalent bulk conductivity of PANI after graft polymerization on Si surface makes the present surface modification technique potentially valuable for antistatic applications and in shielding of electromagnetic interference (EMI). Furthermore, the surface resistance of the PANI-An-GA-*g*-Si can be changed by varying the protonation level since the deprotonation−reprotonation behavior of the grafted PANI is not unlike that of the PANI homopolymer.[40] Moreover, the chemical states and physical properties of the PANI grafted on the Si surface are also similar to those of the aniline homopolymer, as shown by the data in Figure 7. Finally, although the surfaces of the PANI-An-GA-*g*-Si samples are grafted with a layer of PANI, the Si signal is still discernible, indicating that the polymer layer is only in the order of the sampling depth of the XPS technique (~7.5 nm in an organic matrix).[39]

The EM base of the grafted PANI on the Si(100) surface can also be readily reduced to the leucoeraldine (LM) state. Parts a and b of Figure 9 show respectively the C 1s and N 1s core-level spectra of the PANI-An-GA-*g*-Si surface after reduction by hydrazine. The N 1s core-level spectrum of the reduced PANI-An-GA-*g*-Si surface is dominated by the −NH− peak component at the BE of about 399.4 eV,[40] as shown in Figure 9b. The residual imine species may be attributed to the incomplete reduction of the imine nitrogen of EM to the amine nitrogen by NH_2NH_2, while the residual high BE component above 400 eV may have resulted, at least in part, from surface oxidation products or weak charge-transfer complexed oxygen and is consistent with the reactive nature of most conjugated polymer surfaces.[40]

The fact that PANI can exist in a large number of interconvertible intrinsic oxidation states suggests that by coupling the metal reduction process in acid solution to an increase in the intrinsic oxidation state of the polymer and the subsequent reprotonation and reduction of the oxidized polymer in the acid medium, spontaneous and sustained reduction of certain metal ions to their elemental form can be achieved.[41,42] Parts c and d of Figure 9 show the respective N 1s and Pd 3d XPS core-level spectra for the fully reduced PANI-An-

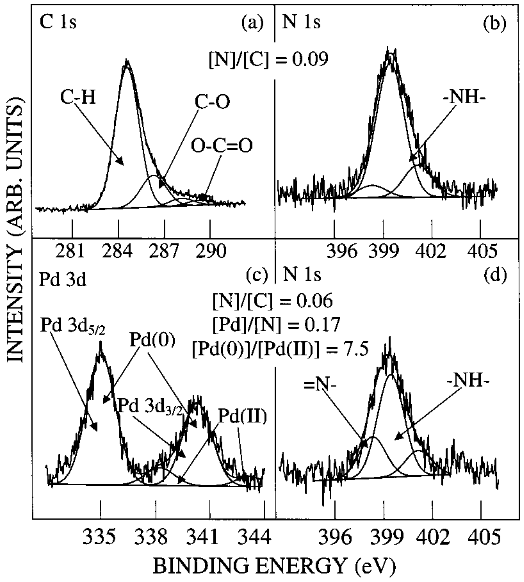


Figure 9. C 1s and N 1s core-level spectra of the LM state of the grafted PANI on the Si(100) surface after immersed in NH_2NH_2 for 1 h (a, b) and N 1s and Pd 3d core-level spectra of the corresponding surface after equilibrating in 100 mg dm^{-3} $Pd(NO_3)_2$ nitric acid solution for 10 min (c, d).

GA-*g*-Si surface after equilibrating in a palladium nitrate acid solution containing initially 100 mg dm^{-3} of Pd ion for about 10 min. Comparison of parts d and b of Figure 9 suggests that there is an increase in the proportion of the imine nitrogen after the metal uptake. The result is consistent with an increase in the intrinsic oxidation state of the grafted PANI in its LM state upon metal reduction. The Pd 3d core-level spectrum in Figure 9c can be curve-fitted with a major and a minor spin−orbit split doublet. The major doublet with the BE's for the Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ peak components lying at about 335 and 340 eV, respectively, are assigned to the Pd(0) species.[43] The minor doublet with the BE's for the Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ peak components lying at about 338.2 and 343.5 eV, respectively, are assigned to the Pd^{2+} ion.[43] Thus, the ability of the reduced PANI-An-GA-*g*-Si surface to become coupled with the metal reduction process is identical to that of the fully reduced LM state of the aniline homopolymer.[40−42]

The valence band photoemission spectra of protonated PANI samples have been studied by ultraviolet photoelectron spectroscopy (UPS).[44] Comparing the observed spectra with the band calculations,[45−47] the spectra contain structural features at the BE around 3.5 eV for the π band, at around 8 eV for the π and σ band, and 13.5 eV for the σ band. Figure 10 shows the XPS valence band spectra from 0 to 20 eV for the deprotonated (part a) and reprotonated (part b) PANI-An-GA-*g*-Si surfaces. The corresponding spectra for the deprotonated and reprotonated EM base of the aniline homopolymer are shown in parts c and d of Figure 10, respectively. Although the finite spectral intensity at the Fermi level (E_F) is small, it can still be detected for the protonated PAN-An-GA-*g*-Si surface and the protonated EM homopolymer. However, the emission intensity at E_F is not detectable for the deprotonated PANI-An-GA-*g*-Si surface and EM base homopolymer. The origin of the density of states near E_F is the polaron band, as no finite intensity is expected near E_F in the case of bipolarons.[45−48] The relatively weak spectral intensity at E_F for the protonated PANI-An-GA-*g*-Si surface and protonated EM homopolymer corresponds to the much localized electronic state with a high degree of disorder. As the photoemission spectrum at E_F provides information on the state of electronic localization in conducting polymers, the valence band results in Figure 10 suggest that the state of electronic localization in the grafted PANI chains on the modified Si surface is not unlike that of the aniline homopolymer.

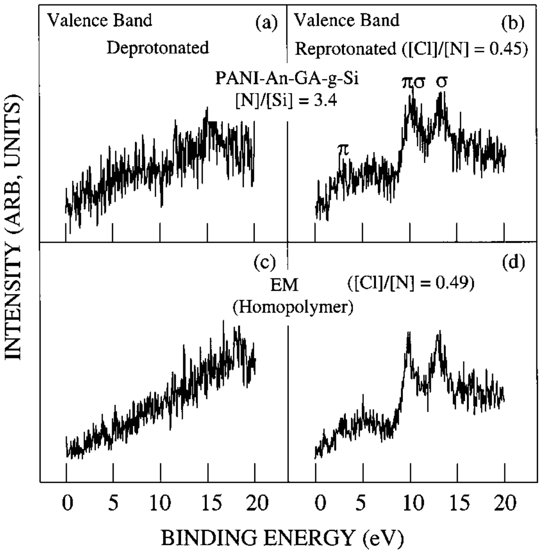


Figure 10. Valence band spectra (0−20 eV) for the deprotonated and reprotonated states of the PANI-An-GA-*g*-Si surface ([epoxy]/[Si] = 3.4) (a, b) and the EM base homopolymer (c, d).

Finally, it is appropriate to emphasize that the graft polymerized aniline chains are covalently tethered onto the Si surface. The grafted PANI chains cannot be removed by extraction with organic solvents. The chemical deposition of the aniline polymers with well-preserved intrinsic structures and oxidation states on the Si substrate as a result of surface molecular design make the present method a viable and promising approach to the preparation of electroactive surface structure and molecular composites.

Conclusion

Argon plasma-pretreated Si(100) surfaces were subjected to surface modification via UV-induced graft polymerization with GMA and GA (the GMA-*g*-Si and GA-*g*-Si surfaces, respectively). The epoxide groups of the grafted GA chains were reactively coupled with aniline (the An-GA-*g*-Si surface) and then subjected to oxidative graft polymerization of aniline (the PANI-An-GA-*g*-Si surface). The composition and microstructure of the graft-polymerized Si surfaces were characterized by XPS and imaging XPS, respectively. The extent of the coupling reaction between the epoxide ring in the grafted GA chain and aniline increased with increasing temperature and reaction time. Ethanol, the solvent used for the coupling reaction, served as the catalyst to promote the coupling reaction when present in more than 40 vol %. When the An-GA-*g*-Si surfaces were subjected to the oxidative polymerization of aniline, the graft concentration increased with increasing aniline concentration. The intrinsic oxidation states, protonation−deprotonation behavior, metal reduction ability, electrical conductivity, and electronic/valence structures of the aniline polymer were preserved in the PANI chains covalently tethered on the Si surface.

References and Notes

(1) Jasinski, J. M.; Gates, S. M. *Acc. Chem. Res.* **1991**, *24*, 9.
(2) Ahmed, W.; Ahmed, E.; Hitchman, M. L. *J. Mater. Sci.* **1995**, *30*, 4115.
(3) Lee, M. S.; Bent, S. F. *J. Phys. Chem. B* **1997**, *101*, 9195.
(4) Chen, Q. J.; Chen, Y.; Yang, J.; Lin, Z. D. *Thin Solid Films* **1996**, *274*, 160.
(5) Sacher, S. *Prog. Surf. Sci.* **1994**, *47*, 273.
(6) Xia, L. Q.; Jones, M. E.; Maity, N.; Engstrom, J. R. *J. Chem. Phys.* **1995**, *103*, 1691.
(7) Xu, J. Z.; Choyke, W. J.; Yates, J. T. *J. Phys. Chem. B* **1997**, *101*, 6879.
(8) Liebmannvinson, A.; Lander, L. M.; Foster, M. D.; Brittain, W. J.; Vogler, E. A.; Majkrzak, C. F.; Satija, S. *Langmuir* **1996**, *12*, 2256.
(9) Ranby, B. In *Current Trends in Polymer Photochemistry*; Allen, N. S., Edge, M., Bellobono, J. R., Selli, E., Eds.; Ellis Horwood: New York, 1995.
(10) Uyama, Y.; Kato, K.; Ikada, Y. *Adv. Polym. Sci.* **1998**, *137*, 1.
(11) Kang, E. T.; Neoh, K. G.; Tan, K. L.; Liaw, D. J. In *Adhesion Promotion Technique*: *Technological Application*; Mittal, K. L., Pizzi, A., Eds.; Marcel Dekker: New York, 1999; Chapter 10.
(12) Suzuki, M.; Kishida, A.; Iwata, H.; Ikada, Y. *Macromolecules* **1986**, *19*, 1804.
(13) Kang, E. T.; Zhang, Y. *Adv. Mater.* **2000**, *12*, 1481.
(14) Kang, E. T.; Tan, K. L.; Kato, K.; Uyama, Y.; Ikada, Y. *Macromolecules* **1996**, *29*, 6872.
(15) Clark, D. T.; Dilks, A.; Shuttleworth, D. In *Polymer Surfaces*; Clark, D. T., Feast, W. J., Eds.; Wiley: New York, 1978; Chapter 9, p 185.
(16) Penn, L. S.; Wang, H. *Polym. Adv. Technol.* **1994**, *5*, 809.
(17) Kang, I.-K.; Kwon, B. K.; Lee, J. H.; Lee, H. B. *Biomaterials* **1993**, *14*, 787.
(18) Amano, K.; Ishikawa, H.; Kobayashi, A.; Satoh, M.; Hasegawa, E. *Synth. Met.* **1994**, *62*, 229.
(19) Tan, K. L.; Kang, E. T.; Neoh, K. G *Polym. Adv. Technol.* **1994**, *5*, 171.
(20) Nicolau, Y. F.; Djurado, D. *Synth. Met.* **1993**, *55*−*57*, 394.
(21) Angelopoulous, M.; Asturius, G. E.; Ermer, S. P.; Ray, A.; Scherr, E. M.; MacDiarmid, A. G.; Akhtar, M.; Kiss, Z.; Epstein, A. J. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 151.
(22) MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *65*, 103.
(23) Ahmad, N.; MacDiarmid, A. G. *Synth. Met.* **1996**, *78*, 103.
(24) Chen, S. A.; Chuang, K. R.; Chao, C. L.; Lee, H. T. *Synth. Met.* **1996**, *82*, 207.
(25) Trivedi, D. C.; Dhawan, S. K. In *Polymer Science Contemporary Themes*; Sivaram, S., Ed.; Tata McGraw-Hill: New Delhi, 1991; Vol. II, p 746.
(26) Joo, J.; Wu, C. Y.; Benatar, A. Jr.; Faisst, C. F.; Zegarski, J.; MacDiarmid, A. G. In *Intrinsically Conducting Polymers: An Emerging Technology*; Aldissi, M., Ed.; Kluwer Press: Dordrecht, 1993; p 165.
(27) Chen, Y. J.; Kang, E. T.; Neoh, K. G.; Wang, P.; Tan, K. L. *Synth. Met.* **2000,** *110*, 47.
(28) Wang, C. H.; Dong, Y. Q.; Sengothi, K.; Tan, K. L.; Kang, E. T. *Synth. Met.* **1999**, *102*, 1313.
(29) Heeger, A. J.; Yang, Y.; Westerweele, E.; Zhang, C.; Cao, Y.; Smith, P. In *The Polymeric Materials Encyclopedia: Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 5500.
(30) MacDiarmid, A. G.; Yang, L. S.; Huang, W. S.; Humphrey, B. D. *Synth. Met.* **1987**, *18*, 393.
(31) Zhang, J.; Cui, C. Q.; Lim, T. B.; Kang, E. T.; Neoh, K. G.; Lim, S. L.; Tan, K. L. *Chem. Mater.* **1999**, *11*, 1061.
(32) Ray, A.; Asturias, G. E.; Kershner, D. L.; Ritchter, A. F.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1989**, *29*, E145.
(33) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Adv. Polym. Sci.* **1993**, *106*, 135.
(34) Wu, S. Y.; Kang, E. T.; Neoh, K. G.; Tan, K. L. *Macromolecules* **1999**, *32*, 186.
(35) Wang, T.; Kang, E. T.; Neoh, K. G.; Tan, K. L.; Cui, C. Q.; Lim, T. B. *J. Adhes. Sci. Technol.* **1997**, *11*, 679.
(36) Rozenberg, B. A. *Adv. Polym. Sci.* **1986**, *75*, 73.
(37) Kang, E. T.; Neoh, K. G.; Tan, T. C.; Khor, S. H.; Tan K. L. *Macromolecules* **1990**, *23*, 2918.
(38) Trivedi, D. C. In *Handbook of Organic Conductive Molecules and Polymers;* Nalwa, H. S., Ed.; John Wiley & Sons: Chichester, 1997; Vol. 2, p 505.
(39) Tan, K. L.; Woon, L. L.; Wong, H. K.; Kang, E. T.; Neoh, K. G. *Macromolecules* **1993**, *29*, 2832.
(40) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci.* **1998**, *23*, 277.
(41) Ting, Y. P.; Neoh, K. G.; Kang, E. T.; Tan, K. L. *J. Chem. Technol. Biotechnol.* **1994**, *59*, 31.
(42) Kang, E. T.; Ting, Y. P.; Neoh, K. G.; Tan, K. L. In *The Polymeric Materials Encyclopedi: Synthesis, Properties and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 5496.
(43) Moulder, J. F.; Stickler, W. F.; Sobol, P. E.; Bomben, K. D. In *Handbook of X-Ray Photoelectron Spectroscopy*; Chastain, J., Ed.; Perkin-Elmer: Eden Prairie, MN, 1992; pp 86 and 119.
(44) Sakamoto, H.; Itoh, M.; Kachi, N.; Kawahara, T.; Mizoguchi, K.; Ishii, H.; Miyahara, T.; Yoshioka, K.; Masubuchi, S.; Kazama, S.; Matsushita, T.; Sekiyama, A.; Suga, S. *J. Electron Spectrosc.* **1998**, *92*, 159.
(45) Bredas, J. L.; Themans, B.; Andre, J. M. *J. Chem. Phys.* **1983**, *78*, 6137.
(46) Bredas, J. L.; Themans, B.; Fripiat, J. G.; Andre, J. M. *Phys. Rev.* **1984**, *B29*, 6761.
(47) Stafstrom, S.; Bredas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1987**, *59*, 1464.
(48) Lazzaroni, R.; Logdlund, M.; Stafstrom, S.; Salaneck, W. R.; Bredas, J. L. *J. Chem. Phys.* **1990**, *93*, 4433.

MA0008589