

Chemical Modification of Silicon (100) Surface via UV-Induced Graft Polymerization

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Modification of argon plasma-pretreated single-crystal silicon wafer surface via UV-induced graft polymerization with various functional monomers, such as acrylamide (AAM), *N,N*-diamethylaminoethyl methacrylate (DMAEMA), and 2,2,2-trifluoroethyl acrylate (TFEA), was achieved. The modified Si(100) surfaces were characterized by X-ray photoelectron spectroscopy (XPS), imaging XPS, atomic force microscopy (AFM), and water contact angle measurements. The graft polymerization was affected by plasma pretreatment time and UV irradiation time. XPS results suggest that mild and brief plasma treatment is sufficient to cause surface oxidation and to generate sufficient peroxides and hydroxyl peroxides for the subsequent UV-induced graft polymerization in the presence of a vinyl monomer. Prolonged plasma treatment and the accompanying overoxidation of the silicon surface have an adverse effect on the graft polymerization. For all the cases investigated, the XPS results revealed that the grafted polymers form a thin layer with a thickness of 5 nm or less on the silicon surface. The AAM and TFEA graft-polymerized surfaces were uniform in morphology. However the DMAEMA graft-polymerized surface exhibited structural domains. Contact angle measurements further indicated that the silicon surface could be selectively made hydrophilic or hydrophobic through the proper choice of monomers used for graft polymerization.

Introduction

The deposition of thin films onto various silicon surfaces has attracted considerable attention due to its importance to the development of advanced materials for applications ranging from microelectronics to solar cells.¹ During the past 2 decades, chemical vapor deposition (CVD) has quickly become one of the most important techniques for synthesizing insulators, conductors, diamond thin films, and high-temperature superconductors on semiconductor surfaces.^{2–8} More

recently, even C-60 film has been successfully coated onto a silicon surface using this method.⁹ However, CVD methods can only be used for depositing inorganic and molecular organic films on silicon surfaces. In many cases during the production of microelectronics devices, silicon surfaces need to be modified to introduce stable thin films of organic compounds. For example, modification of silicon surfaces via the introduction of organic thin films to improve adhesion toward dielectric materials, such as polyimide and poly(tetrafluoroethylene) (PTFE), is desirable.¹⁰ However, there is still no suitable method for introducing stable thin films of most common organic compounds on silicon surface till now, except via the reaction with some highly active compounds, such as silanes,^{11–16} or by the adsorption of some specific

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substances having strong polar groups, such as proteins.¹⁷

It has been demonstrated that modification of polymer surfaces can be performed through graft copolymerization under relatively mild conditions for a number of conventional polymers, such as polyolefins,^{18–20} polyesters,^{21–23} fluoropolymers,^{24–25} and conjugated polymers,^{26,27} when their surfaces are pretreated with high-energy radiation, plasma glow discharge, corona discharge, ozone exposure, or UV irradiation. The chemical methods of surface modification of polymers have been reviewed recently.²⁸ Among these methods, surface graft polymerization has the ability to introduce specific functional groups in desirable quantity onto the polymer surface via the proper choice of the monomers and reaction condition without affecting the bulk properties. The surface-modified polymer substrates can be further functionalized through protein and enzyme immobilization.²⁹ Their improved hydrophilic and adhesion properties after graft polymerization have also been of recent interest.³⁰ A recent study has also reported the generation of monolayers of polymer molecules on solid substrates by using self-assembled monolayer of initiator.³¹

In the present work, we report on a detailed study of graft polymerization of some functional monomers onto single-crystal silicon substrates using an UV irradiation method. Before graft polymerization, the silicon surface was pretreated with argon plasma discharge to introduce active species for the initiation of graft polymerization. The monomers used were acrylamide (AAm), *N,N*-diamethylaminoethyl methacrylate (DMAEMA), and 2,2,2-trifluoroethyl acrylate (TFEA). The graft-polymerized silicon surfaces were studied by angle-resolved X-ray photoelectron spectroscopy (XPS), imaging XPS, and atomic force microscopy (AFM).

Experimental Section

Materials. Single-crystal silicon wafers, Si(100), polished on one side and 6 in. in diameter were supplied by Hitachi,

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Inc., Japan. The monomers used for graft polymerization, viz., AAm, DMAEMA, and TFEA, were obtained from Aldrich Chemical Co. The AAm monomer was purified by recrystallization while the DMAEMA and TFEA monomers were purified by vacuum distillation before use. All other chemicals and solvents were of reagent grade and were also purchased from Aldrich Chemical Co. They were used as received without further purification.

Plasma Treatment and Graft Polymerization. The silicon wafers were cut into rectangular strips of about 2.0 cm \times 3.0 cm in size for the grafting experiments. To remove all the organic residues from the surface, the silicon substrates were cleaned using "piranha" solution, a mixture of 70% concentrated sulfuric acid and 30% hydrogen peroxide. The silicon substrates were immersed in piranha solution for a period of 30 min at 60 $^{\circ}$ C. The piranha-treated substrates were then immersed in doubly distilled water for 10 min and subsequently rinsed with the doubly distilled water a minimum of five times. The effect of the piranha treatment on the silicon surface was studied by multiple treatments of a wafer with the piranha solution. Its surface roughness after each treatment was measured with AFM. No significant change in surface roughness was found.

The plasma treatment of the silicon substrates was performed between two horizontal parallel plate electrodes of 7 cm \times 13 cm in area in a glow discharge quartz reactor (Model SP100 Plasma System), manufactured by Anatech Co. Ltd. The plasma power supply was set at 32 W at a frequency of 40 kHz. The substrate was placed on the bottom electrode with the Si(100) surface exposed to the glow discharge at an argon pressure of about 0.58 Torr for a predetermined period of time. The plasma-pretreated silicon surface was subsequently exposed to the atmosphere for about 30 min to allow the formation of peroxide and hydroxyl peroxide species for the subsequent graft polymerization experiment.¹⁸ As the glow discharge chamber was purged thoroughly with a continuous argon stream before ignition, the contribution of residual air or water vapor in the chamber would be negligible, if at all.

For graft polymerization, the Ar plasma-pretreated silicon substrate was placed in a Pyrex tube containing 20 mL of 10% (wt/wt) monomer solution and 5 mL of 0.053 mM riboflavin. The AAm and DMAEMA monomers were dissolved in doubly distilled water while TFEA was dissolved in 1,4-dioxane. After purging with purified argon for about 30 min, the reaction mixture was sealed with a silicon stopper. It was then kept at 30 $^{\circ}$ C during irradiation by UV from a 1000 W high-pressure mercury lamp in a Riko RH400-10W rotary photochemical reactor (manufactured by Riko Denki Kogyo of Chiba, Japan) for a predetermined time. The riboflavin in the monomer solution consumes the dissolved oxygen in the monomer solution in a photochemical reaction.³² After the grafting experiment described above, the silicon substrate with surface grafted AAm or DMAEMA polymer was removed from homopolymer solution and washed thoroughly with doubly distilled water. It was then subjected to repeated rinsing and soaking in a gently stirred water bath for at least another 24 h to remove the residual homopolymers. In the case of the surface graft polymerized with TFEA, acetone was used to remove the homopolymer under the same vigorous conditions.

Surface Characterization. The topography of the surfaces of pristine and graft-modified silicon substrates was examined in a Nanoscope III atomic force microscope (AFM) using the contact mode. The average roughness (R_a) of the substrate surface was calculated directly from the AFM image.

The chemical compositions of the surfaces were determined by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed on a VG ESCALAB MKII spectrometer using a nonmonochromatized Mg K α X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The silicon substrates were mounted on the standard sample studs by means of double-sided adhesive tape. The core-level signals were obtained at photoelectron takeoff angles of 20 $^{\circ}$ and 75 $^{\circ}$ (α values,

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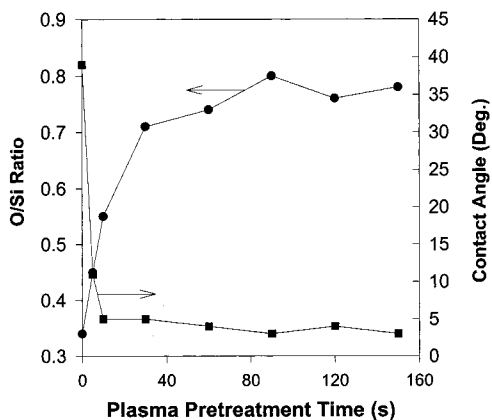


Figure 1. Changes in O/Si atomic ratios and contact angles of a silicon surface as a function of plasma treatment time.

with respect to the sample surface). The X-ray source was run at a reduced powder of 120 W (12 kV and 10 mA). The pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower during each measurement. All binding energies (BEs) were referenced to the neutral C1s peak at 284.6 eV. Surface elemental stoichiometries were determined from core-level peak area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to $\pm 5\%$. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries. The chemical maps of the graft-modified silicon surfaces were obtained using an imaging XPS technique from a VG ESCA 220 i-XL spectrometer. A nonmonochromatized Mg K α X-ray source was used and the maximum resolution was about 50 μm .

Static water contact angles were measured at 25 °C and 60% relative humidity by the sessile drop method, using a 3- μL water droplet in a telescopic goniometer (Ramè-Hart, Model 100-0-230). The telescope with a magnification power of 23 \times was equipped with a protractor of 1° graduation. For each sample, at least five measurements on different surface locations were averaged.

Results and Discussion

The changes in the O/Si atomic ratio and the contact angle of the Si(100) surface as a function of the Ar plasma treatment time under the present glow discharge conditions are shown in Figure 1. The O/Si ratio was determined from the sensitivity factor-corrected O1s and Si2p core level peak area ratios obtained at a photoelectron takeoff angle (α) of 75°. An increase in the O/Si ratio and a decrease in the water contact angle were observed upon increasing the Ar plasma treatment time. These results are similar to those reported previously that the O/C ratios of the polymer surfaces increase with Ar plasma treatment time.³³ It can be seen clearly that the O/Si ratios increase rapidly with Ar plasma treatment time up to a treatment time of about 30 s. After that, the ratio approaches an asymptotic value. It has been reported previously that prolonged plasma or corona treatment of polymer surfaces does not result in the introduction of a larger amount of oxygen atoms or peroxides during the subsequent atmospheric exposure.^{18,34} Since the chemical properties of silicon resemble those of carbon, it can be deduced

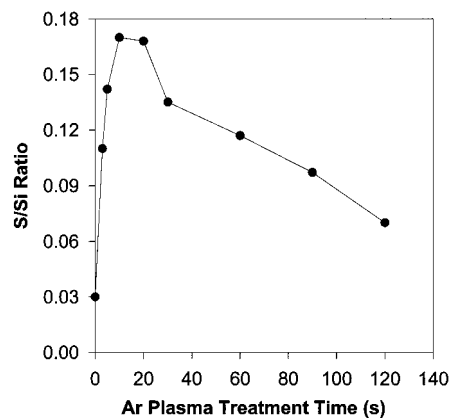
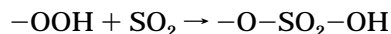


Figure 2. Surface peroxide concentration of the Ar plasma-treated silicon surface as determined from XPS analysis after derivatization with SO₂.

that Ar plasma treatment of silicon surface, followed by atmospheric exposure, can also introduce some active oxygen species, such as the Si–O and Si–O–O species. The introduction of polar groups as a result of plasma treatment also gives rise to a more wettable surface, as indicated by the contact angle data in Figure 1.

Plasma has been used extensively for the treatment of silicon wafers, mainly for surface cleaning and etching. The idea behind the utilization of the plasma is the creation of a very reactive gas environment enclosed in a vacuum. Surfaces in contact with the plasma experience interactions that may result in sputtering and chemical reactions caused by the highly reactive radicals, low-energy ions, and electrons created in the plasma. To ascertain the fact that the Ar plasma treatment can introduce peroxides on the silicon surface, the peroxides formed on silicon upon Ar plasma exposure were quantified by XPS after the reaction with SO₂. Peroxides and hydroxyl peroxides react readily with SO₂ via the following mechanism:^{35,36}



The dependence of the peroxides concentration, or the S/Si atomic ratios, on the Ar plasma treatment time of the Si surface is shown in Figure 2. It is obvious that the dependence of the peroxides concentration on the Ar plasma treatment time is not monotonic. Under the present glow discharge conditions, the optimum concentration of peroxides was achieved at an Ar plasma treatment time between 10 and 20 s. Thus, prolonged plasma exposure does not result in a continuous enhancement of the peroxides concentration on the silicon surface. From the comparison of the data in Figures 1 and 2, it can be seen that the amount of peroxides decreases sharply with the Ar plasma treatment time for plasma treatment time greater than 20 s, even though the O/Si ratio continues to increase beyond this treatment time. Thus, continuous exposure of the active species created during the initial stage of plasma treatment probably has resulted in the further alteration of these active species. Alternatively, the active species formed initially may have been partially re-

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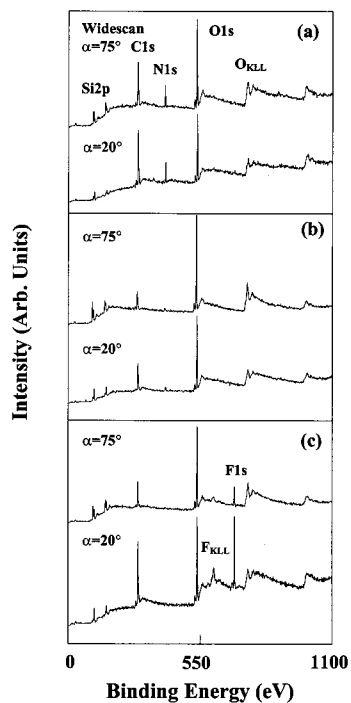


Figure 3. XPS widescan spectra at the two takeoff angles (α) of 20° and 75° , for a 10-s Ar plasma-pretreated silicon surface after graft polymerization with (a) AAm, (b) DMAEMA, and (c) TFEA.

moved by the etching effects of the plasma treatment upon increasing the plasma treatment time. The continuous increase in surface oxygen concentration at plasma treatment time above 20 s (Figure 1) would suggest an alteration in the nature of the active species, as the oxygen species were incorporated after the atmospheric exposure. This postulation is also consistent with the earlier finding that plasma treatment not only can introduce peroxides onto the silicon surface but also oxidizes the surface.³⁷ Furthermore, the relatively high S/Si ratio, as revealed by XPS, may indicate the contribution of other oxidized silicon species in the reaction with SO_2 .

Figure 3 shows the XPS widescan spectra at the two takeoff angles of $\alpha = 20^\circ$ and 75° , for a 10 s Ar plasma-pretreated silicon surface after graft polymerization with AAm, DMAEMA, and TFEA. The UV graft polymerization time was kept at 30 min for all samples. A much higher N1s/Si2p or F1s/Si2p core-level signal intensity ratio is observed at the more surface glancing $\alpha = 20^\circ$ than at $\alpha = 75^\circ$, indicating that the graft layer is restricted to the outermost surface of the silicon substrate. This phenomenon differs from that observed on polymer surfaces in which graft polymerization takes place on the outermost surface but the graft chains can migrate or diffuse into the subsurface layer of polymer substrate, resulting in a restructured surface.^{25,38} The lack of surface restructuring is consistent with the more ordered and rigid structure of the single-crystal silicon surface.

Figure 4 shows the C1s core-level spectra of the pristine silicon wafer surface (Figure 4a), and the 10-s

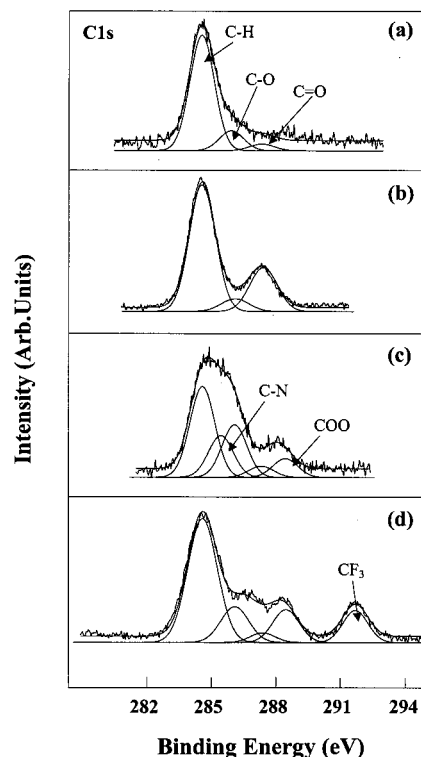


Figure 4. XPS C1s core-level spectra of (a) a pristine silicon surface and a 10-s Ar plasma-pretreated silicon surface after being (b) graft polymerized with AAm, (c) graft polymerized with DMAEMA, and (d) graft polymerized with TFEA.

Ar plasma-pretreated silicon surface after graft polymerized with AAm (Figure 4b), DMAEMA (Figure 4c), and TFEA (Figure 4d). The UV graft polymerization time was kept at 30 min for all samples. Although prior to plasma treatment and graft polymerization, the silicon wafer surfaces were cleaned by washing thoroughly with the piranha solution, there still existed some surface carbon contamination, as shown in Figure 4a. The C1s spectrum of the pristine silicon surface contains a major peak component at the binding energy (BE) of 284.6 eV, associated with the neutral carbon species, and two minor components with BEs at 286.2 and 287.9 eV, attributable to the C–O and C=O species, respectively. The total surface carbon concentration is about 5% of that of silicon. As this C/Si ratio is substantially lower than the O/Si and S/Si ratios after the plasma treatment, the peroxides and oxygenated species on the silicon surface are mainly associated with the silicon atoms, although it is probable that some of them may be associated with the carbon atoms. Once the silicon surface has been graft polymerized with AAm, the C=O species undergoes a sharp increase in intensity arising from the C=O groups in AAm units. After the plasma-pretreated silicon substrate was subjected to UV graft polymerization with DMAEMA, the C1s core level spectrum was curve-fitted with five peak components with BEs at 284.6 eV for the C–H species, 285.9 eV for the C–N species, 286.2 eV for the C–O species, 287.9 eV for the C=O species, and 288.7 eV for the COO species.³⁹ On the other hand, for silicon surface graft polymerized with TFEA, the C1s spectrum can also be curve-fitted with five peak components, corre-

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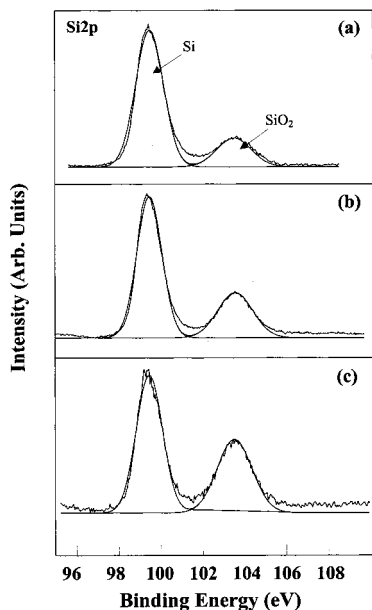


Figure 5. XPS Si2p core level spectra of (a) a pristine silicon surface, (b) the silicon surface after 10 s of Ar plasma treatment, and (c) the 10 s Ar plasma-pretreated silicon surface after UV graft polymerized with AAm.

sponding to the C–H, C–O, C=O, COO, and CF₃ species, respectively. The peak area ratio for the C–H, C–O, COO, and CF₃ species is fairly close to the theoretical ratio of 3:1:1:1, based on the chemical structure of TFEA.

Parts a, b, and c of Figure 5 show, respectively, the Si2p core-level spectra of the pristine silicon surface, the 10-s Ar plasma treated silicon surface, and the 10-s Ar plasma treated silicon surface after 30 min of UV-induced AAm graft polymerization. In addition to the elemental Si species at the BE of 99.5 eV, SiO₂ is also detected at the BE of 103.6 eV.⁴⁰ The SiO₂/Si ratio increased after the silicon wafer surface was subjected to Ar plasma treatment, as shown in Figure 5b, indicating the presence of surface oxidation of the Si atoms upon Ar plasma treatment. The SiO₂/Si ratio increased further when the Ar plasma treated silicon surface was graft polymerized with AAm. This phenomenon is attributable to the fact that the grafted AAm polymer layer on the outermost surface of silicon can effectively reduce the probing depth of the XPS technique, resulting in the reduced signal intensity of the elemental Si species relative to that of the SiO₂.

Figure 6 shows the changes in N/Si or F/Si ratios as a function of the UV graft polymerization time when the 10-s Ar plasma-pretreated silicon surfaces are graft polymerized with AAm, DMAEMA, and TFEA. The N/Si and F/Si ratios are directly related to graft densities. The N/Si or F/Si ratios increase with UV irradiation time, albeit not to the same extent, in all the three cases. The graft concentration of the AAm polymer was higher than that of DMAEMA or TFEA polymer at the same extent of UV irradiation. Between 0 and 60 min of UV graft polymerization time, the N/Si and F/Si ratios increase rapidly and approach an asymptotic value after 60 min.

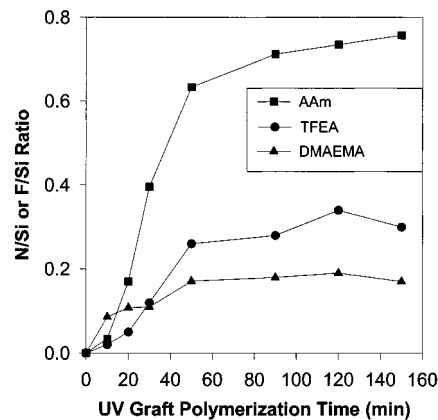


Figure 6. The changes in N/Si or F/Si atomic ratios as a function of UV graft polymerization time when the silicon surface was graft polymerized with AAm (●), DMAEMA (■), and TFEA (▲).

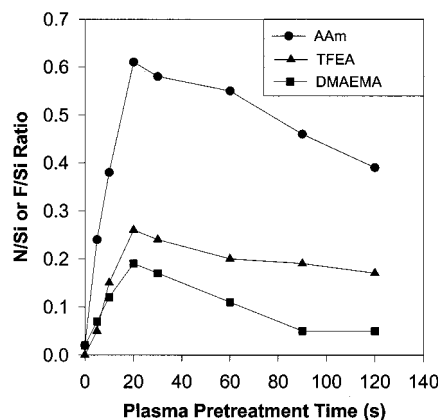


Figure 7. The changes in N/Si or F/Si atomic ratios as a function of the Ar plasma pretreatment time of the Si substrate when the silicon surface was graft polymerized with AAm (●), DMAEMA (■), and TFEA (▲).

Figure 7 shows the N/Si and F/Si ratios as a function of the Ar plasma pretreatment time of the silicon substrate. Thus, prolonged plasma treatment does not result in the continuous increase in graft concentration. The highest graft concentration was achieved at a plasma treatment time between 10 and 20 s. This result is entirely consistent with the optimum peroxide concentration observed at the same extent of plasma treatment in Figure 2. It also provides further support for the peroxide-initiated mechanism proposed for the present UV-induced surface graft polymerization.

Figure 8 shows the dependence of water contact angle on the graft concentration (expressed in terms of the UV graft polymerization time) for the silicon surfaces graft polymerized with the three kinds of monomers. The plasma pretreatment time for each substrate was fixed at 10 s, and the graft concentrations correspond to those shown in Figure 6. Due to its high grafting efficiency, the contact angle of AAm graft-polymerized surface is almost independent of the UV irradiation time after 30 min, probably because of the complete coverage of the silicon surface by the AAm polymer. In the cases of DMAEMA or TFEA graft-polymerized surface, the contact angle approaches an asymptotic value only after 80 min of UV graft polymerization. Compared with the pristine silicon, the silicon surface became more hydrophilic when graft polymerized with AAm and became

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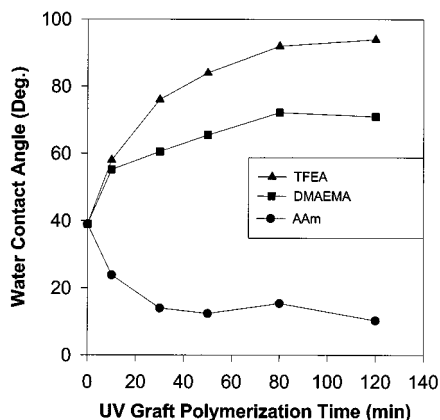


Figure 8. The changes in water contact angle of the silicon surface graft polymerized with (●) AAm, (■) TFEA, and (▲) DMAEMA as a function of the UV graft polymerization time.

more hydrophobic when graft polymerized with DMAEMA and TFEA. The contact angle of the TFEA polymer-grafted silicon surface exceeds 90° after 80 min of UV graft polymerization, indicating the formation of a highly hydrophobic silicon surface. It is interesting to observe that the DMAEMA graft-polymerized silicon surface yielded a more hydrophobic surface than the pristine wafer surface, although both the DMAEMA monomer and the polymer are soluble in aqueous medium. In fact, the DMAEMA polymer is soluble in water at 25 °C. However, its water solubility is somewhat limited, as it contains both hydrophilic and hydrophobic moieties. The lower critical solution temperature (LCST) of the polymer is around 55 °C.⁴¹ The advancing and receding contact angles of the DMAEMA graft-polymerized silicon surface are 81° and 29°, respectively. These contact angles are very similar to those measured from the spin-coated DMAEMA polymer film, which are 85° and 26°, respectively. The hysteresis in contact angle thus suggests the presence of a “submerged” hydrophilic character for the surface.⁴² This phenomenon is probably due to the fact that the hydrophobic moieties of the DMAEMA polymer tend to orient themselves toward the outermost surface, while the hydrophilic moieties tend to orient themselves toward the oxidized silicon substrate surface. Ar plasma treatment can also result in a very hydrophilic surface, as shown in Figure 1. However, the plasma-induced hydrophilic surface is not stable, as indicated by the fact that the water contact angle recovers gradually in about 1 or 2 weeks. For the graft-modified silicon surface, the water contact angle does not change appreciably with time because the grafted polymer chains on the silicon surface are much more stable than the active species introduced by the plasma treatment alone.

Figure 9 shows the XPS image of the pristine Si(100) surface with an area of 1 mm × 1 mm. The Si2p signal at BE of 99.3 eV for pure silicon was used to obtain this surface element map. From this image, it can be seen that the pristine silicon surface appears generally homogeneous. However, minor nonuniform silicon distribution can also be detected, as indicated by the contrast of the two regions in the figure. The nonuni-

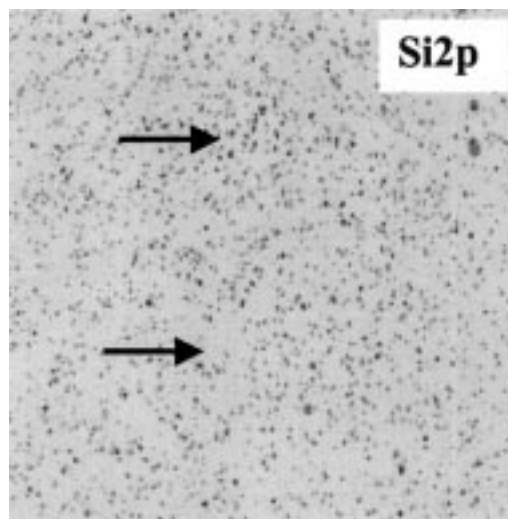


Figure 9. The scanning XPS derived Si2p chemical map of the pristine silicon surface with the scan size of 1 mm × 1 mm.

formity is probably due to different extents of surface oxidation.

Figure 10 shows the XPS images of the graft-modified silicon surfaces. The image size was also about 1 mm × 1 mm. The XPS core level signals of N1s, F1s, and Si2p were used to obtain these elemental maps. The N1s image of the AAm graft-polymerized silicon surface (Figure 10a) and the F1s image of the TFEA graft-polymerized surface (Figure 10e) clearly show that the AAm polymer and the TFEA polymer form fairly uniform graft layers on the silicon surfaces. From the corresponding silicon maps of these two surfaces (parts b and f, respectively, of Figure 10), it can also be deduced that the distribution of silicon is rather uniform. Although the surface was grafted with a layer of polymer, the silicon signal is still well-resolved, indicating that the polymer layer is thinner than the sampling depth of XPS. This result is also consistent with those of Figure 3.

When the silicon surface was graft polymerized with DMAEMA, regions with higher nitrogen concentration can be observed from both the nitrogen map and the silicon maps (parts c and d, respectively, of Figure 10 and indicated by the arrows; the images were taken at the same position of the sample), suggesting that the DMAEMA polymer forms domain structures on the silicon surface, which is quite different from those of the AAm and TFEA graft-polymerized surfaces.

The average roughness (R_a) in a 1 μm × 1 μm surface region for the single crystal silicon wafer is about 0.05 nm, as revealed by AFM images. After 10 s of Ar plasma treatment, there are only minor changes to the surface morphology. The surface became slightly rougher (R_a ~0.07 nm), probably as a result of surface oxidation. Upon graft polymerization with AAm or TFEA, the grafted polymer forms a uniform layer on the silicon surface, even though the surface roughness becomes greater than that of the pristine surface. The graft polymerization was carried out with 1 h of UV irradiation on a 10-s Ar plasma-pretreated silicon surface. The R_a in a 1 μm × 1 μm area is 0.21 nm for the AAm graft-polymerized silicon surface and 0.35 nm for the TFEA graft-polymerized surface. Thus the TFEA graft-poly-

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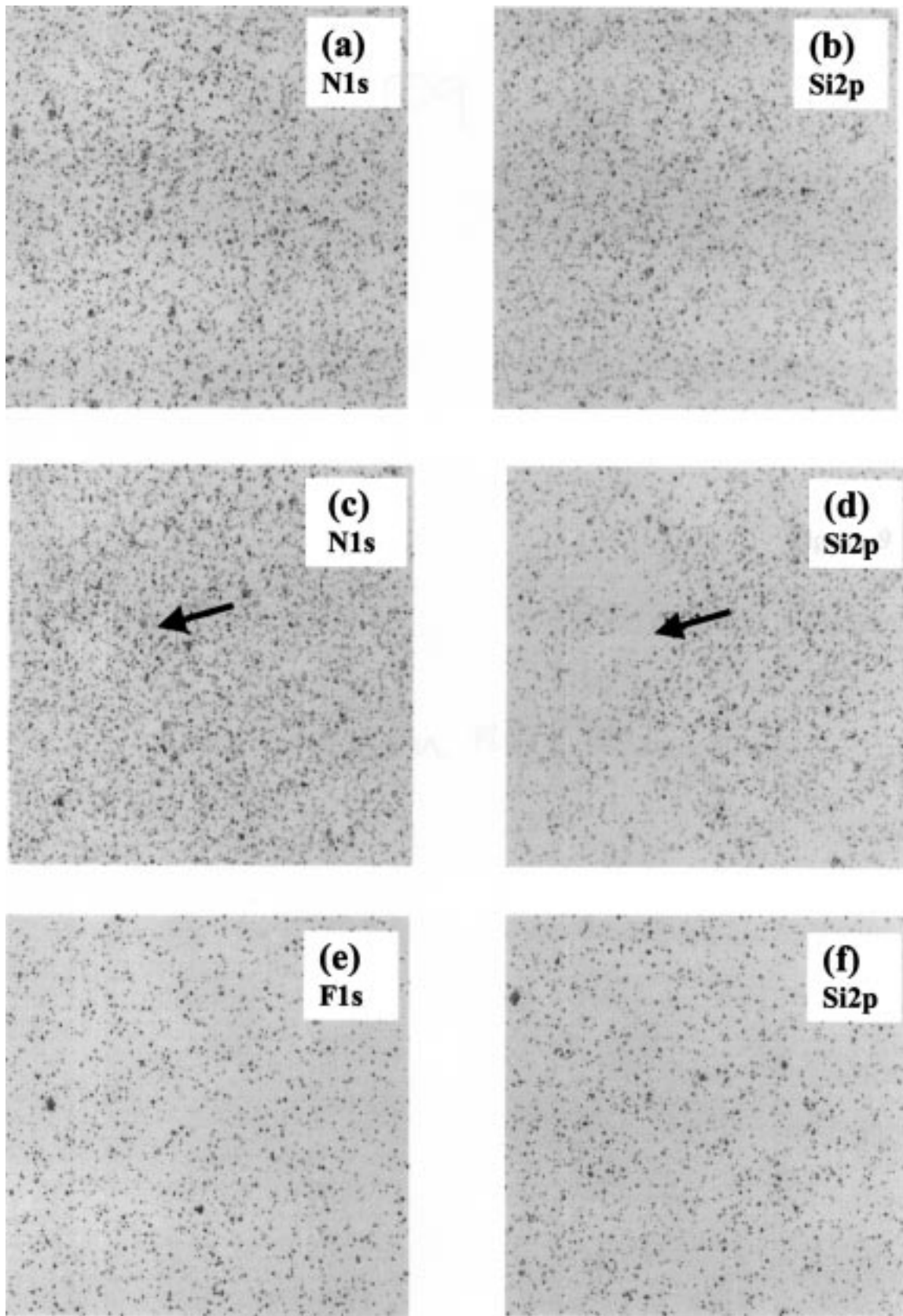


Figure 10. The scanning XPS derived chemical map in a $1\text{ mm} \times 1\text{ mm}$ area of the graft-modified silicon surfaces: (a, b) the N1s and Si2p chemical maps of an AAm graft-polymerized surface, (c, d) the N1s and Si2p chemical maps of a DMAEMA graft-polymerized surface, and (e, f) the F1s and Si2p chemical maps of a TFEA graft-polymerized surface.

merized silicon surface has a rougher surface than that of the AAm graft-polymerized surface, though it has a lower graft density (Figure 6).

The DMAEMA graft-polymerized silicon surface, on the other hand, has quite a different surface morphology from those of AAm and TFEA graft-polymerized sur-

faces. This surface is rougher than either the AAm or the TFEA graft-polymerized surface. The surface also shows domain structures with domain size ranging from about 0.5 to 1.0 μm . The much smaller particles are probably associated with contaminants and cannot be avoided easily since the DMAEMA polymer is a polymer electrolyte with positive charges and the DMAEMA graft-polymerized surface will have a high tendency to adsorb contaminants under normal condition owing to electrostatic interaction. In fact, previous studies have reported that the DMAEMA graft-copolymerized polymer surfaces have a positive ζ potential and undergo strong electrostatic interaction toward other oppositely charged surfaces.^{43,44} The formation of domain structure on DMAEMA polymer-grafted silicon surfaces is probably due to the fact that the DMAEMA polymer is an ionic polymer with positive charges that can result in strong inter- or intrachain interactions. Such small domains can also aggregate to form a larger structure. The domain structure as revealed by AFM is consistent with the chemical structure of the surface observed in the XPS images of Figure 10.

Conclusion

Single crystal silicon surfaces, when pretreated with Ar plasma, have been found to be susceptible to UV-

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induced graft polymerization with AAm, DMAEMA, and TFEA. The graft polymerization was affected by both the plasma pretreatment time of the Si substrate and the UV graft polymerization time. XPS results show that mild and short plasma treatment, followed by atmospheric exposure, can generate sufficient peroxides and other oxygen functionalities. The former greatly facilitates the subsequent graft polymerization in the presence of UV irradiation. Prolonged plasma treatment, on the other hand, has an adverse effect on the efficiency of graft polymerization due to the overoxidation of the surface. The XPS results suggest that the grafted polymers form a thin layer with a thickness 5 nm or less on the outermost silicon surface. The AAm and TFEA graft-polymerized surfaces are uniform in chemical structure and in morphology. However, the DMAEMA graft-polymerized surface exhibits domain structures in the surface morphology. Contact angle measurements reveal that the hydrophilicity or hydrophobicity of the silicon surface can be considerably enhanced by graft polymerization with appropriate functional monomers.

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