

XPS and AFM characterization of the self-assembled molecular monolayers of a 3-aminopropyltrimethoxysilane on silicon surface, and effects of substrate pretreatment by UV-irradiation

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The self-assembled (SA) molecular monolayers of a 3-aminopropyltrimethoxysilane (3-APTS) on a silicon (111) surface, and the effects of ultraviolet (UV) pre-treatment for substrates on the assembling process have been studied using XPS and atomic force microscopy (AFM). The results show that the SA 3-APTS molecules are bonded to the substrate surface in a nearly vertical orientation, with a thickness of the monolayer of about 0.8–1.5 nm. The SA molecular monolayers show a substantial degree of disorder in molecular packing, which are believed to result from the interactions of amine tails in the silane molecules used with surface functionalities of the substrates, and the oxygen-containing species from the ambient. UV irradiation for silicon substrates prior to the self-assembly reaction can enhance the assembly process and hence, significantly increase the coverage of the monolayer assembled for the substrates. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: XPS; AFM; self-assembly; 3-aminopropyltrimethoxysilane; UV-irradiation

Introduction

To grow high-quality, high-coverage, self-assembled (SA) molecular mono-/multilayers on metal or inorganic semiconductor substrates, e.g. gold, silver, silicon or germanium substrates, is an important issue in manufacturing functional materials. These promising technologies have been finding a broad range of applications in many areas of research and engineering, e.g. surface modification and functionalization of materials,^[1,2] development of biomedical devices and biosensors, and fabrication of molecular/nanoelectronic and photonic devices, etc.^[3–6] In particular, it has been broadly investigated in fabricating nanosize or molecular-size electronics devices based on these systems. Up until now, a large variety of such SA molecular monolayer-substrate systems have been explored and investigated. In these systems, the self-assembling molecules and the substrates can be either organic or inorganic. Because the surface properties of these systems are determined ultimately by the exposed functionalities of the assembling molecules, materials with various surface functions can be designed and produced based on these technologies. Much attention has been paid to the self-assembly of organo-silanes on silicon-based substrates, i.e. elemental silicon and silicon oxides.^[4,7] In these systems, the self-assembly processes can be carried out in either vapor or liquid phase. The self-assembling molecules in the mono- or multimolecular layers obtained attach to the silicon substrates by forming covalent Si–O bonds with the substrates. This bonding is well stable and robust over a wide range of temperature.^[4,8]

However, like other types of SA systems, the organo-silane SA layers grown on the silicon substrates are, in most cases, containing a substantial proportion of various forms of imperfections,

e.g. vacancies, impurities, incomplete bonding between the SA molecules and the substrate, abnormally oriented SA molecules, and unexpected interactions between the SA molecules, etc.^[7,9] The presence of these imperfections limits significantly the application of this novel technology to industry. Thus, efforts have been paid in investigation of the formation mechanisms of the imperfections in the SA layers, as well as in seeking new techniques for improving the order in molecular arrangement of the SA layers. It is well known that self-assembly processes can be influenced by many factors coexisting during the processes. Of these, the surface properties of the substrates and the chemical reactivity of all the functionalities contained in the SA molecules are believed to affect the quality and the coverage of the SA layers most significantly. Thus, to optimize the surface properties of the substrates and minimize the undesirable intermolecular interactions between the SA molecules, and between these molecules and the substrates, are of great interest for research in these areas. Among those mostly used self-assembly agents on silicon-based substrates, 3-aminopropyltrimethoxysilane (3-APTS) has been chosen often

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for surface passivation, protection and hydrophobisation for silicon and silicon-oxide materials, as well as for the study of the general mechanisms of the self-assembly processes. These SA systems have been finding their applications in electronics and energy industries.

In this work, the properties of the SA molecular layers of a 3-aminopropyltrimethoxysilane on an *n*-type doped silicon (111) single-crystal substrate have been studied using XPS and atomic force microscopy (AFM). The effects of the surface pretreatment for substrates on the SA processes are investigated. In the results, the 3-APTS molecules are bonded to the substrates in a vertical orientation, with the thickness of the SA monolayers well matching the length of the APTS molecules. A substantial proportion of the silane molecules in the SA monolayer obtained can interact with the gaseous species present in the ambient, or with the functionalities on the surface of the substrate. With these interactions, new surface moieties can be formed, which contribute to imperfect packing within the SA monolayers. Ultraviolet (UV) irradiation of the silicon substrates prior to the SA processes can improve significantly the coverage of the SA layers formed on the substrates.

Experimental

Most of the chemicals used, i.e. 3-aminopropyltrimethoxysilane (purity 95%), toluene (purity 95%), and hydrofluoric acid (water solution, concentration 40%), were supplied from Fisher Scientific UK, Ltd (Loughborough, UK). The silicon substrates used were cut from a commercially supplied, *n*-type doped single-crystal, (111) oriented silicon wafer. The UV irradiation was carried out using a model 42 UV-ozone cleaner, manufactured by Jelight Company Inc. (USA), with the duration of the irradiation set by a continuously changeable digital timer. The UV treatment time for the substrates was taken to be typically 20 s. The XPS data were acquired using an Axis Hsi XPS system manufactured by Kratos analytical, equipped with a charge neutralizer for minimizing the sample charging effects. The XPS machine has an energy resolution of better than 0.5 eV. The base pressure of the analysis chamber during the analysis was kept to be constantly lower than 5.0×10^{-9} mbar. The Al $K\alpha$ line (1486.6 eV) was selected for excitation during the data acquisition. The AFM images were obtained using a model CSPM4000 scanning probe system, Benyuan Nano-instrument Ltd., Guangzhou, China. The machine is controlled by an SPM Console software, with an associated Imager version 4.60 software for image processing. Besides the conventional surface imaging, the machine was also equipped with a nanofabrication system operated in either thermoelectrical mode or mechanical vector-scratching mode, with the fabrication pattern predesigned using the computer software. The AFM images shown here were all obtained under contact-scanning mode.

The silicon substrates were firstly immersed in a chemical solution prepared by 1:1 v/v mixing of a 40% ammonia-ethyl alcohol solution with a 40% hydrogen peroxide-water solution, kept in the solution for 10 min at about 70 °C, and then rinsed with deionized (DI) water. The substrates were then immersed in a 5% hydrofluoric acid-DI water solution for 5 min to strip off the native oxides.^[10,11] Afterwards, these treated substrates were silanized either just after the treatment, or after further irradiation by UV. Silanization was carried out at room temperature by immersing the pretreated substrates in toluene containing 3-APTS with a

Table 1. XPS elemental quantification results obtained for all the samples studied. The C/O and the Si/O ratios are also shown in two right-hand-side columns

| | UV treat. time (sec.) | Atomic concentration (%) | | | | | |
|--------------|--------------------------|--------------------------|------|-------|------|------|------|
| | | C 1s | O 1s | Si 2p | N 1s | C/O | Si/O |
| Before | 0 | 44.6 | 17.9 | 37.5 | – | 2.49 | 2.09 |
| silanization | 20 | 38.9 | 22.4 | 38.8 | – | 1.74 | 1.73 |
| After | 0 | 46.2 | 27.4 | 13.2 | 13.2 | 1.68 | 0.48 |
| silanization | 20 | 57.0 | 17.3 | 15.4 | 10.3 | 3.29 | 0.89 |

concentration of an order of several milli-Mole/l. The duration for the silane treatment was normally chosen to be 14 or 20 h. After silanization, the samples were then sonicated in a methanol bath for 10 min and blow dried.

Results and Discussion

The XPS survey scan (not shown) for the bare substrates, both before and after UV treatment, shows strong C 1s, O 1s, Si 1s, and Si 2p signals. After silanization, the N 1s signal emerges in addition to these other signals, showing that a 3-APTS layer has been introduced on the sample surface. Table 1 shows the XPS quantification results obtained for the as-etched silicon substrates, the UV-irradiated substrates, and both silanized samples on these substrates. The duration used for the hydrofluoric-acid etching for these samples was 5 min. It was found that a substantial amount of carbon and oxygen still remains on the surfaces of these etched samples, which cannot be removed completely by simply extending the HF etch time. UV irradiation following the HF stripping for the silicon substrates was found to decrease remarkably the C/O and the Si/O ratios at the surface of the substrates. This shows the photoinduced oxidation and oxygenation effects occurring at the surfaces of the substrates upon the treatment used. On the other hand, great differences are also shown by the silanized samples grown on these differently prepared substrates. More carbon and less oxygen are found for the silane monolayers coated on the UV-irradiated substrates than those coated on the as-etched substrates. On the basis of the data shown here, the C/O ratio of the 3-APTS monolayers coated on the UV-irradiated substrate is 3.29, in apparent contrast to 1.68 for that coated on the as-etched substrate. This indicates that UV-irradiation can significantly change the surface properties for the silicon substrates used, and therefore, affect the self-assembly processes conducted later thereon. The larger C/O ratio shown by the 3-APTS monolayers prepared on the UV-treated substrates represents a surface layer, richer in carbon in comparison to that prepared on the as-etched samples. These surface carbons are believed to indicate the presence of a monolayer of silane molecules formed on the substrates. Thus, the larger C/O ratio associated with samples on the UV-irradiated substrates shows that the surfaces of these samples are more covered by an SA monolayer compared to those on the as-etched substrates, i.e. pretreatment for silicon substrates by UV irradiation can dramatically enhance the self-assembly processes conducted later on these pretreated substrates.

The Si 2p and the O 1s spectra for the samples, both before and after silanization, are shown in Fig. 1. From the top to the bottom, the spectra lines for the as-etched substrate, the UV-irradiated substrate, the SA layer on the as-etched substrate,

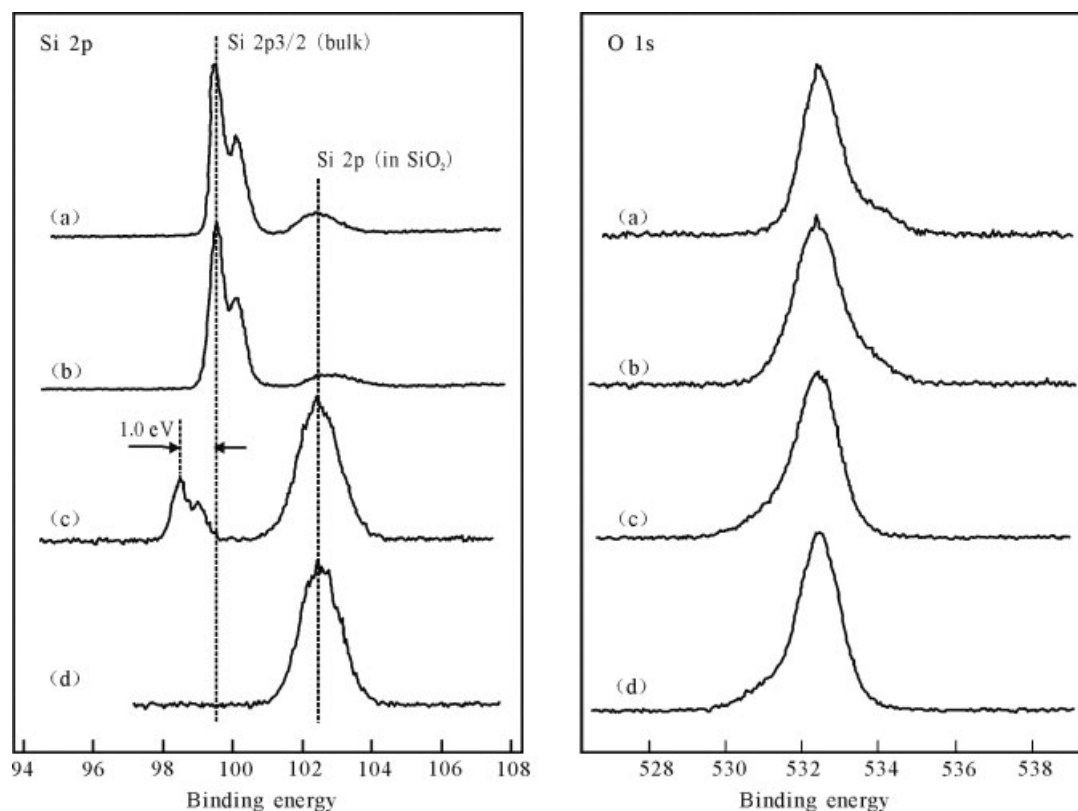


Figure 1. Si 2p (left panel) and O 1s (right panel) XPS regions for: (a) the as-etched substrate; (b) the UV-irradiated substrate; (c) the SA layer on the as-etched substrate; and (d) the SA layer on the UV-irradiated substrate.

and the SA layer on the UV-irradiated substrate are shown one after another. The oxygen signals for both substrates, i.e. the first two spectra lines, are asymmetric, with a small shoulder appearing to the high-energy side of the main peak. Here, in terms of line shape, the O 1s spectrum for the UV-irradiated substrate is slightly broadened compared to that for the as-etched substrate. The broadening of the former is contributed by those oxygen species introduced to the substrate surface during UV irradiation, which result from the reactions of the ambient oxygen-containing entities with the Si–H sites present on the HF-treated silicon surface. These surface functionalities newly formed, favor the formation of the Si–O–Si-type bonding between the substrate and the hydrolyzed silane molecules, which will be introduced on the substrate via the self-assembly processes conducted later. This, therefore, reflects the assistant effects of substrate pretreatment by UV for the SA processes studied here. On the other hand, the Si 2p spectra for these two substrates both have a strong doublet with the Si $2p_{3/2}$ peak located at about 99.6 eV, and a much weaker signal centered at about 102.4 eV. Of these, the doublet is assigned to the bulk silicon, and the other peak is contributed from the residual native SiO_2 , which still remains at a substantial amount after the HF treatment used.^[12,13]

More apparent differences are found between the spectra for the silanized samples. As shown by the spectrum lines (c) and (d), the oxide component in the Si 2p region for both silanized samples increases dramatically, showing the presence of the Si–O bonding formed after silanization. In the spectra for the sample prepared on the as-etched substrate, a small doublet associated with the bulk silicon still remains but, interestingly, shifts to 98.6 eV, i.e.

1.0 eV lower than its binding energy shown before silanization. In contrast, the spectrum for the sample prepared on the UV-irradiated silicon substrate does not show this component (line (d) in the figure). These differences in the Si region suggest that the as-etched silicon surface was not covered completely by the silane monolayer assembled. This is in contrast to the sample grown on the UV-irradiated substrate. These results again show that UV-irradiation can enhance the surface oxidation for the silicon surface exposed after the HF treatment. Indeed, UV light can cleave the Si–H bonds present on the HF-treated silicon surface,^[14–16] and activates the reactive surface sites therein. This then leads to a more complete oxidation for the irradiated silicon surface in comparison to the unirradiated silicon.

The 1.0 eV decrease in binding energy for the Si 2p signal of the bulk Si appearing in the spectrum line (c) may indicate a repinning effect of the Fermi level as the terminating hydrogen atoms are removed during the SA reaction. These effects have been demonstrated in both theory and experiment. In case of the *n*-type doped H-passivated silicon, as used in this work, this repinning effect of the Fermi level causes a decrease in the binding energies of the bulk Si because the removal of the terminating hydrogen creates a large number of dangling bonds at the Si surface, and hence, introduces many surface electronic states. However, this energy shift observed here is slightly larger than that observed by Thornton *et al.* for the Si (100) surface.^[10,17] Further investigations are still needed for the mechanisms causing this energy shift.

The curve-fitting digraphs for the C 1s, N 1s and O 1s spectra for the samples, both before and after silanization, are shown in Fig. 2. In all the three panels, from top to bottom, the spectra lines shown are, in turn, for the unsilanized substrates, the silanized

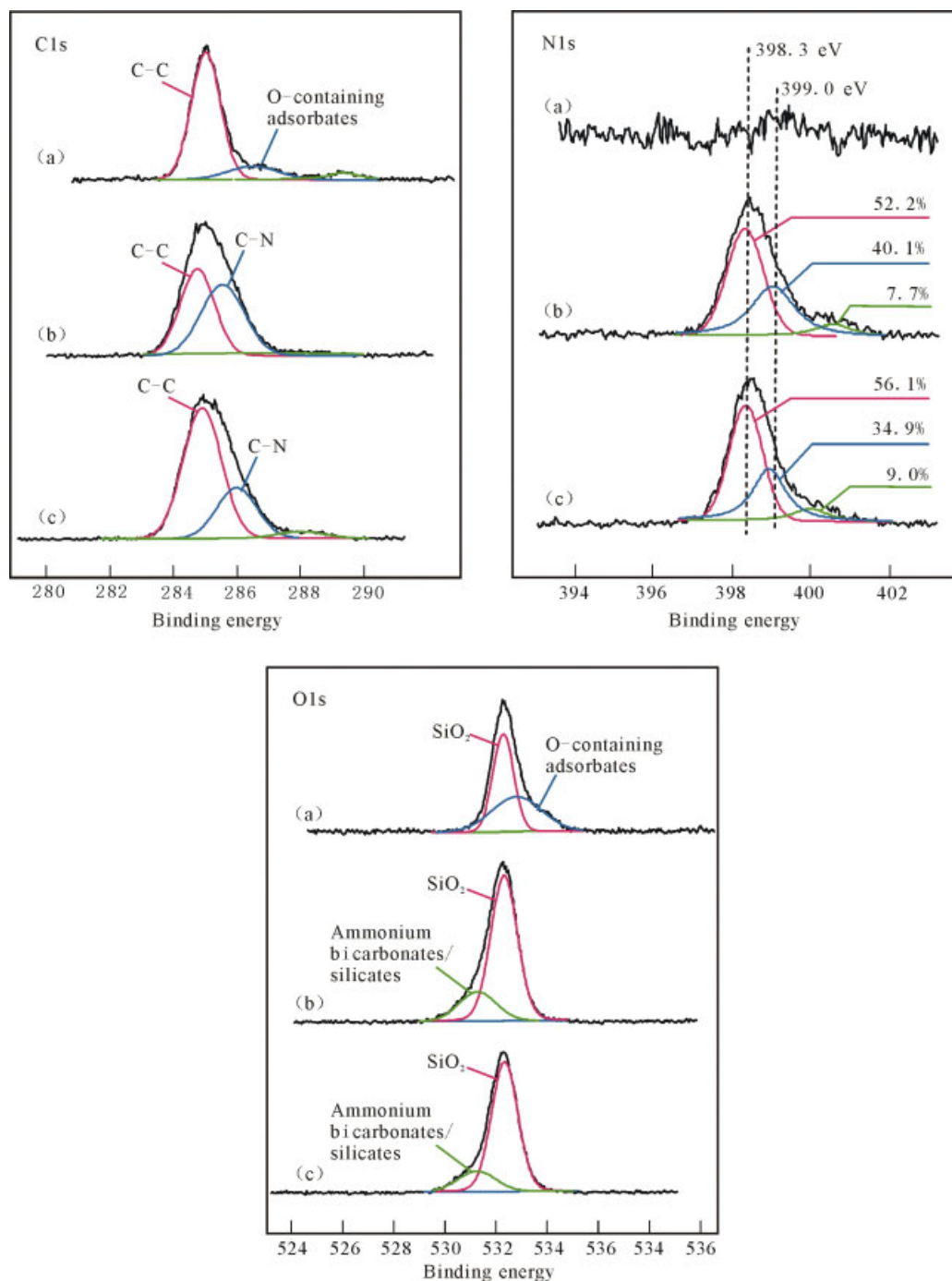


Figure 2. Curve-fitting digraphs for C 1s (top left panel), N 1s (top right panel), and O 1s (bottom panel) XPS regions for: (a) the as-etched substrate; (b) the SA layer on the as-etched substrate; and (c) the SA layer on the UV-irradiated substrate. For the silanized samples, the proportions of all the nitrogen species found are shown by the numbers in the figure (digraphs (b) and (c) in the top right panel).

sample on the as-etched substrate, and the silanized sample on the UV-irradiated substrate. In all the three C 1s spectra shown in the top left panel, the primary carbon peak at 284.6 eV represents the backbone and the methyl carbons in the organic surface adsorbates. In the case of the silanized samples, this peak is, in the main, contributed from the 3-APTS monolayer present on the samples' surfaces. Other species that may also contribute to this peak may include the residue toluene solvent possibly remaining following silanization. However, this contribution is not significant

because a characteristic peak for toluene, i.e. the $\pi \leftrightarrow \pi^*$ shakeup C 1s signal expected to appear at about 290.1 eV is not visible here. This shows that little residue toluene solvent has remained on the surfaces of these samples after sonicated in ethanol following silanization, and thus, does not contribute significantly to the XPS signal. Indeed, for most SA systems having been investigated so far, the solvents chosen for growing the SA layers in liquid mode may be adsorbed physically to the substrates, but this adsorption occurs at only a much lower level in comparison to that the

adsorbates selected do, which are chemisorbed robustly thereon. Thus, the finish of the surface obtained after the SA growth procedures designed is predominantly covered by the expected SA molecules.^[18]

The small carbon component at 286.6 eV for the unsilanized substrates is attributed to the oxidized carbon species which are bonded, more likely chemically, to the adsorbate surface oxygen. This component does not appear in the spectra for the silanized samples. Instead, the spectra for both these latter samples contain another broad peak in the range of binding energy 285.6–286.0 eV. This new carbon peak is believed to assign to the C–NH₂ moieties present in the 3-APTS molecules introduced by silanization. The broadening of this peak may be caused by the interaction of the amine end groups in the 3-APTS with the surface groups of the substrates.^[7] This is also evidenced by the apparent asymmetric broadening of the N 1s spectra shown in the top right panel. Here, the N 1s spectra for the silanized samples can be generally fitted by three components, i.e. the primary peak at 398.3 eV, and two smaller peaks at 399.0 eV and around 400.2 eV. The strong primary peak is associated with the free amine, and the other two weaker peaks may show the species formed by the reaction of the amine tails of the 3-APTS molecules with some other electronegative entities present. As suggested by others, the hydroxyls at the surface of the Si substrate, and the carbon dioxide and water from the ambient are most probably involved in such reactions.^[19] In these reactions, the end amines in the 3-APTS are oxidized into their protonated forms, with the binding energy of the N 1s signal associated shifted upwards to a higher value.^[20,21] The most probable products of these reactions may be the ammonium bicarbonate and ammonium silicate groups. Here, the presence of these protonated amine species show that the 3-APTS monolayer grown contained a substantial degree of disorder. A proportion of the 3-APTS molecules grafted on the substrates are believed to be abnormally oriented. The backbone chain of these molecules may even bend down towards the substrate with their amine ends bonded to the substrate via forming ammonium silicate moieties. Beside this, reversely oriented bonding is also possible,^[19,22] where the amine end, rather than the silane end of the 3-APTS are bonded to the substrate via the chemical-reaction mechanisms mentioned above, or van der Waals interactions.^[23]

Indeed, a complete coverage of H-termination, or hydroxylation for Si surfaces, is in general difficult to obtain by wet surface treatment.^[24–26] In the results shown here, the 399.0 and the 400.2 eV components for the monolayers assembled on the UV-irradiated substrates are relatively weaker in intensity and narrower in full-width-at-half-maximum (FWHM) in comparison with those monolayers assembled on the as-etched substrates. This shows that UV pretreatment for the silicon substrates used favours a more ordered packing of the silane molecules in the self-assembly processes which follows on the treated substrates.

In the O 1s region shown in the bottom panel in Fig. 2, the main peak located at 532.2 eV is contributed either from the silicon oxides layer on the bare substrate, or from the Si–O–Si moieties for the silanized samples. In the top spectra line for the bare substrate, the broad additional component to the higher-energy side of the primary peak, centered around 532.8 eV, represents a variety of oxide species present, possibly including various oxygen-containing organic surface adsorbates and surface hydroxyls. In contrast, in the other two spectra lines for the silanized samples, i.e. the spectrum lines (b) and (c), this higher-binding-energy oxygen component disappears

and is replaced by another new peak located at a binding energy of 531.2 eV, to the lower-energy side, i.e. the other side of the primary peak. This new oxygen signal is believed to associate with the oxygen contained in the ammonium bicarbonate and ammonium silicate groups, formed via the reactions between the amino groups with the ambient carbon dioxide and the surface groups on the substrate. These oxygen species are more electronegative than those in the Si–O bonds present in the silicon dioxide and the silicone materials. Again, the presence of these additional oxygen species in the silane monolayer assembled show also a certain degree of imperfect packing of the assembling molecules in the monolayer formed.

The surface topography for both the uncoated and coated samples were imaged using AFM. Figure 3 shows three 8 μm × 8 μm images taken of these samples. The native surface of the silicon sample used (Fig. 3(a)) is generally flat in atomic scale except for a population of pores appearing in places with a number density of approximately 8000/μm². The Root-Mean-Square (RMS) roughness, as measured by the AFM system used, is ~0.85 Å. After being etched by HF solution, the native silicon oxide layer was removed with extension of the treatment time. Figure 3(b) and (c) show the images taken for the silicon substrates treated for 2 and 5 min, respectively. The topography of the 2-min-treated substrate is believed to show a substantial amount of incompletely etched native silicon oxides remaining with patches of the revealed bulk silicon beneath. The histogram plot obtained from this image shows a two-peak structure with a shoulder appearing to the lower-height side of the main peak. Here, this second peak corresponds to the level of the exposed bulk silicon, whereas the main peak represents the top surface of the remaining silicon oxides. In contrast, the 5-min-etched substrate shows a completely exposed silicon surface over the image area, with only one single peak appearing in its histogram plot. On the other hand, the RMS roughness for these etched surfaces, as calculated based on these two images shown is ~13.1 Å for the 2-min-etched substrate, and ~1.7 Å for the 5-min-etched substrate. This indicates that the substrate surface with the incompletely stripped silicon oxides is much rougher than that of the completely exposed silicon.

Figure 4 shows the AFM images obtained for the silanized samples. Here, the images 4(a) and (b) (again, 8 μm × 8 μm in size) are for the samples silanized for 3 and 20 hours, respectively. The trough shown in Fig. 4(a) is typically found on the samples silanized for this duration. This is believed to show the areas of the silicon substrate still exposed with the other areas around having been coated by a monolayer of the 3-APTS molecules. These areas are found to contract as the time of silanization treatment is further extended. The surface of the 20-h silanized sample, shown in Fig. 4(b), has much smaller such uncovered silicon areas. In this image, these areas have been reduced to narrow linear troughs, whereas the further extended SA monolayers have covered the other areas. The line profiles taken along the straight lines indicated in the respective images in Fig. 4(a) and (b) show that the layer thickness of the 3-APTS monolayers obtained here are 0.8–1.5 nm. This is in agreement with the length of the 3-APTS molecules deposited in a nearly vertical orientation on substrates.^[4,27] However, in this study, it was found difficult to obtain a complete coverage of the substrates used by the 3-APTS by extending the time of the self-assembly reaction. This indicates that the SA molecules grafted in different areas of the substrate surface have possibly different orientations. Indeed, previous work

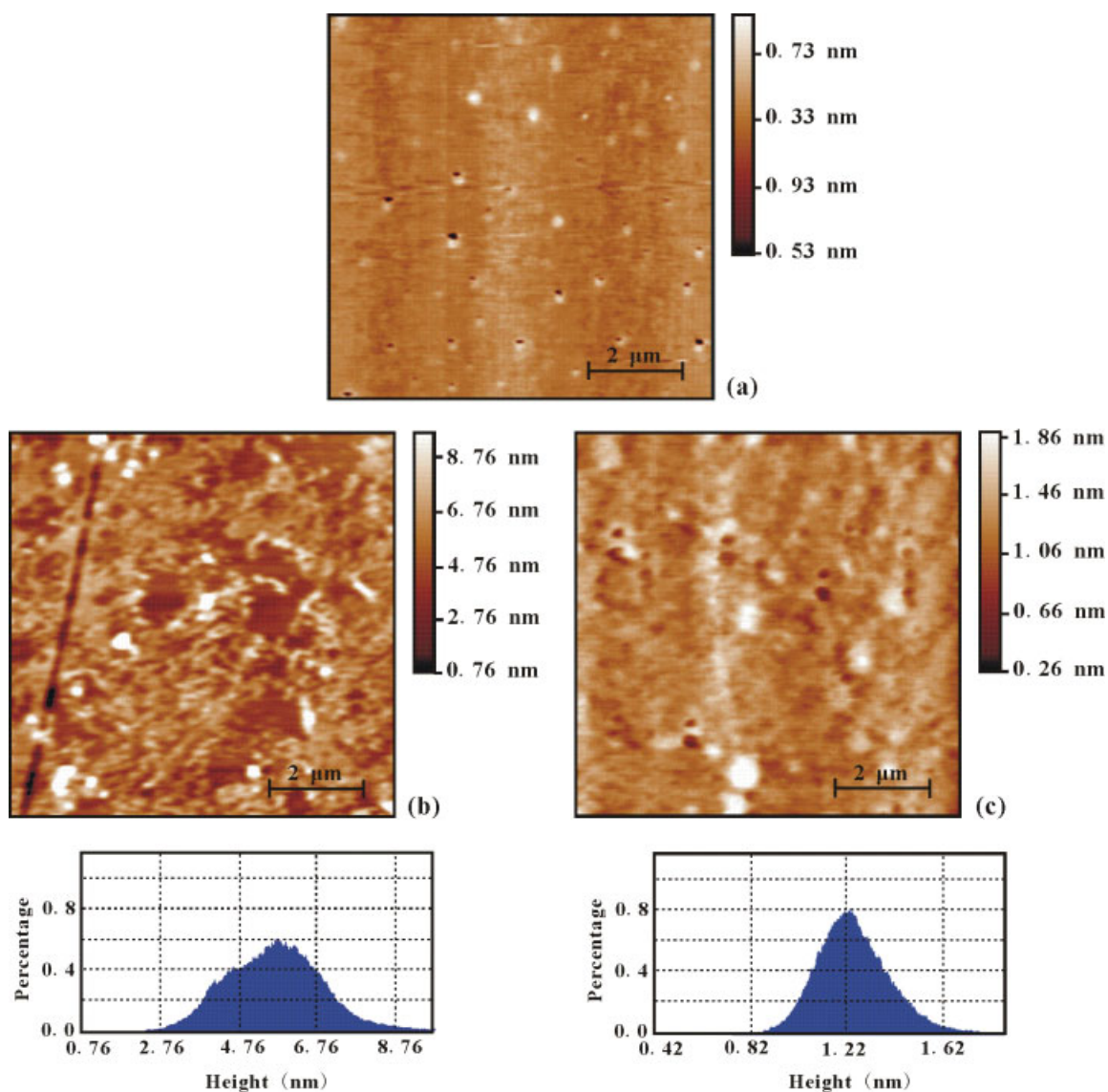


Figure 3. Three $8\ \mu\text{m} \times 8\ \mu\text{m}$ AFM images for both, the uncoated and the coated samples. These are: 3(a) the as-supplied silicon substrate; 3(b) the silicon treated in HF solution for substrates 2 min; and 3(c) the substrates treated in HF for 5 min. The histograms for the last two images are also shown below the respective images.

has shown that the SA molecules grafted in most cases have their axes forming an angle, though small generally, with the surface normal of the substrates rather than perpendicular exactly to the surface. Thus, those SA molecules grafted on different areas of the substrate surface may take different azimuthal angles. This then leads to a mismatch in molecular orientation at the boundaries between the SA layers formed in different areas of the substrate surface. Further grafting of the SA molecules at these boundaries is relatively unlikely to occur since it results in a relatively higher free energy. For this reason, these boundaries between adjacent areas of the SA monolayers are still visible following an extended duration of the SA reaction. Within the linear troughs are the exposed surface areas of the substrate. Figure 4(c) shows an AFM image zoomed into a smaller area ($1\ \mu\text{m} \times 1\ \mu\text{m}$) in a SA region in Fig. 4(b). This image shows undulations of the surface with a RMS roughness of $5.8\ \text{\AA}$. This indicates a relatively poorer flatness for an SA monolayer, reflecting a degree of local disorder in these areas.

Conclusions

The surface properties and compositions of the SA molecular monolayer of a 3-APTS on an *n*-type doped silicon (111) single crystal substrate, and the effects of pretreatment for substrates by UV irradiation on the SA processes have been studied using XPS and AFM. The SA layers of 3-APTS on the silicon substrates obtained show a substantial degree of disorder which is believed to result from intermolecular interactions between the SA molecules and the undesirable binding of the amino groups to the silicon substrates. Chemical reactions of the exposed amino groups with carbon dioxide from air are also possible. UV irradiation of the substrate surface prior to the SA processes can improve remarkably the coverage of the SA layers formed on the silicon substrates.

Acknowledgements

This work was supported by the Advanced Research Grant Program for Returning Scholars, the State Ministry of Human Resources of

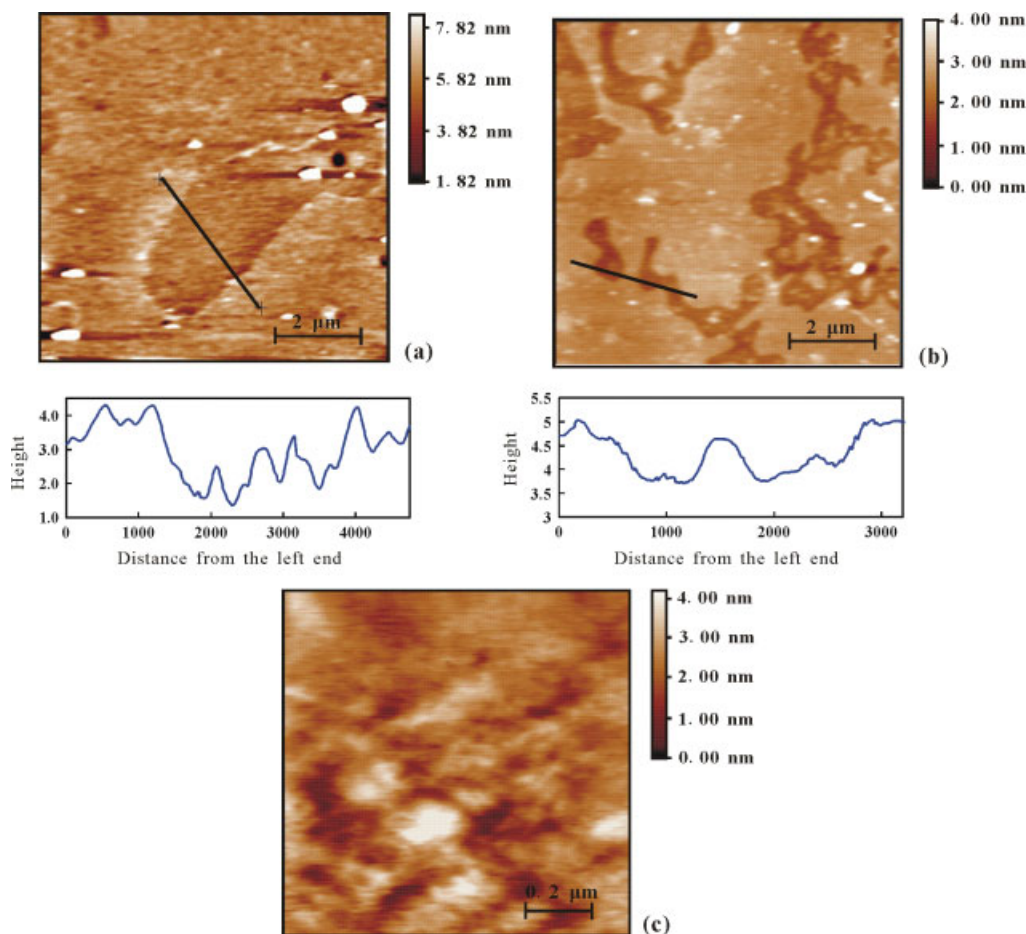


Figure 4. AFM images obtained for the silanized samples. Images 4(a) and (b) ($8 \mu\text{m} \times 8 \mu\text{m}$ in size) are for the samples silanized for 3 h and 20 h. 4(c) shows a zoomed area ($1 \mu\text{m} \times 1 \mu\text{m}$ in size) selected in image 4(b). The boxes below 4(a) and (b) show the line-profiles along the straight line taken as indicated in the respective images.

China. The work also received support from a research funding unit of the local government of Beijing, China. Thanks are also given to Ms Susan Osbeck and Mr He Liang at the Faculty of Engineering of the Robert Gordon University, UK, for their assistance for some experiments.

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