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Self-assembling of cyano- and carboxyl-terminated monolayers using short-chain alkylsiloxane

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ABSTRACT

A simple method was developed for the preparation of cyano- and carboxyl-terminated alkylsiloxane monolayers on the hydroxylated surface of the SiO_2/Si substrate through using adsorption and hydrolysis reaction of a short-chain 2-cyanoethyl triethoxysilane [$(CH_3CH_2O)_3SiCH_2CH_2CN$]. The contact angle and the X-ray photoelectron spectroscopy (XPS) measurements have proved that the cyano terminal group indeed formed on the substrate and was transformed into the carboxylic terminal group after hydrolysis. The ellipsometry shows the presence of an intact monolayer with thickness of around 0.7 nm before and during the hydrolysis reaction. The surface morphology was observed with atomic force microscopy (AFM) imaging. Those all indicate that uniform and ordered self-assembled monolayers (SAMs) were formed on the substrate.

1. Introduction

SAMs are being increasingly investigated for applications in chemical, biological and micro electro mechanical systems by modifying chemical properties of the surfaces [1]. According to the International Technology Roadmap for Semiconductors (ITRS), 2007 edition [2], the barrier thickness for copper wiring should be less than 2 nm in the next 10 years. Therefore, the conventional physical vapor deposited (PVD) Ta, TaN or TaN/Ta layers will not meet this requirement. Many researches proved that the SAMs can obtain perfect barrier performance at the thickness below 2 nm [3–5]. It might be a promising alternative of traditional diffusion barriers for copper in the ultra large scale integrated (ULSI) circuit.

Many device wiring structures are required to withstand high temperatures (about 400 °C) during fabrication. Singh et al. [6] reported that the cyanide-functionalized mesoporous silica (MPS) films are stable up to 500 °C in vacuum, N_2, and air ambient. In the work of Ganesan et al. [5], they found that the carboxyl-terminated SAM at the Cu/SiO_2 interface increase the copper diffusion-induced device failure time by a factor of 12 compared to the interfaces without a barrier. Therefore, the cyano- and carboxyl-terminated SAMs would be the available diffusion barriers for copper interconnects.

First of all, these two kinds of SAMs should be well prepared in order to achieve this purpose. The fabrication of these SAMs has been studied by some researchers using long-chain alkylsiloxane. Cyano-terminated monolayer was deposited on the glass substrate by using a 16-carbon, trichlorosilyl surfactant (synthesized from ω-hexadecenyl bromide) as a dilute solution in dicyclohexyl by Balachander and Sukenik [7]. It can also be easily prepared by ω-cyano alkyl trichlorosilane [8]. Carboxyl-terminated SAM on silica substrate is difficult to be produced since the silane derivative in this case would have polar moieties at both ends and make it difficult to develop a uniform monolayer on the surface. It can be produced by chemical oxidation of a deposited vinyl-terminated SAM as described by Wasserman et al. [9]. Recently, Hallen and Hallen [10] developed a method for the preparation of carboxyl-terminated alkylsiloxane monolayers on silicon using the ozonolysis and hydrolysis of 10-undecenyl trichlorosilane self-assembled monolayers. They achieved contact angles of 0° on receding and around 16° on advancing with ellipsometry showing a uniform monolayer. Carboxyl-terminated SAM can also be developed by converting cyano to carboxylic terminal [11]. However, since the feature size of the metal-oxide-semiconductor (MOS) is shrinking so quickly that the preparation of SAMs using short-chain alkylsiloxane molecules to act as diffusion barriers of copper connection will be more promising. Here, we present the results of the synthesis of cyano-terminated SAM using short-chain 2-cyanoethyl triethoxy silane [$(CH_3CH_2O)_3SiCH_2CH_2CN$] on the hydroxylated surface of the SiO_2/Si substrates and the transformation of the cyano terminal functional group to the carboxylic terminal group by hydrolysis reaction. The morphology and microstructure of the SAMs were characterized by various analysis techniques, such as contact angle measurement (CA), ellipsometry, X-ray photoelectron spectroscopy (XPS), Fourier

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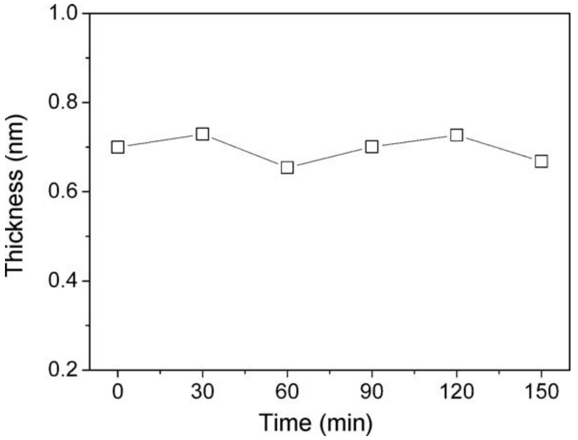

Fig. 1. Thickness change of CN-SAM versus hydrolysis time in a 50:50 (v/v) solution of 15% hydrochloric acid and deionized water at 75 °C.

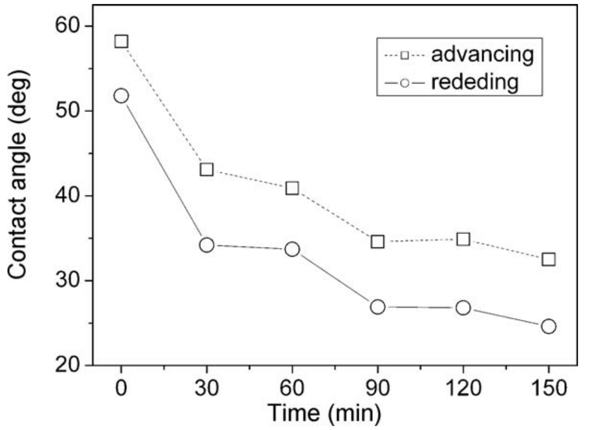

Fig. 2. Contact angles' changes of CN-SAM versus hydrolysis time during the hydrolysis reaction.

transform infrared spectroscopy (FT-IR) and atomic force microscopy (AFM). The chemical vapor deposition of copper films on the hydroxylated SiO_2/Si substrates coated with the cyano- and carboxyl-terminated SAMs as diffusion barriers will be discussed in a continuing work.

2. Experimental

2.1. Preparation of SAMs

The substrates used in the experiments were *n*-type Si (1 0 0) wafers. With the preparation method used in our previous work [12], the surface of silicon dioxide on the silicon substrate is terminated with hydroxyl groups [13,14]. Then the SAMs of cyano terminal functional group were wet chemically absorbed onto the substrate from a 5 mM solution of 2-cyanoethyl triethoxysilane (97%, Sigma–Aldrich, America) in toluene for 6 h, then rinsed with toluene and deionized water, and dried with a stream of nitrogen.

The cyano terminal groups of the SAMs were transformed into carboxylic terminal groups by hydrolysis reaction. The substrate with cyano groups were cleaned, dried, and annealed at 150 °C for about 2 h, then immersed into a 50:50 (v/v) solution mixture of 15% hydrochloric acid and deionized water maintained at 75 °C for

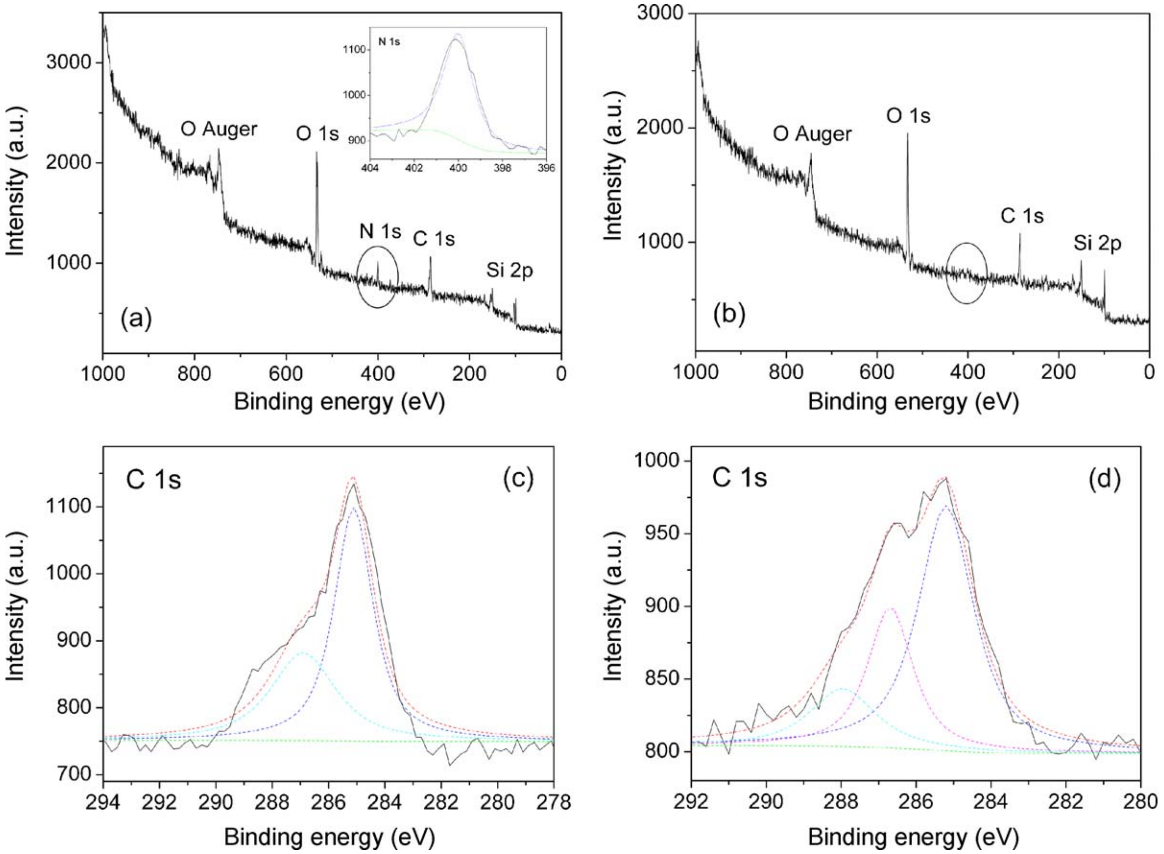

Fig. 3. XPS spectra of the prepared SAMs. (a) The full scale spectrum of the SAM with cyano terminal group before hydrolysis, with the N 1s XPS spectrum inserted; (b) the full scale spectrum of cyano-terminated SAM after hydrolysis in hydrochloric acid solution for about 90 min; (c) and (d) the C 1s XPS spectra of cyano-terminated SAM before and after hydrolysis respectively.

at least 90 min [11]. After the reaction, the samples were rinsed with deionized water and then blown dry with nitrogen.

2.2. Measurements and analysis

2.2.1. Contact angle goniometry

The contact angles were measured by using a CA system (OCA15 plus, Dataphysics, Germany). The advancing contact angles were determined by placing a drop of water from a syringe, advancing the periphery of the drop by adding more liquid, withdrawing the syringe, and measuring the advancing contact angles within 30 s of application of the droplet. The receding contact angles were measured by withdrawing part of the liquid from the drop and measuring the angle. The temperature of the measurements was not controlled and varied between 22 °C and 26 °C. The values reported are the average of at least three different points of each sample and have a maximum error of 1°.

2.2.2. Spectroscopic ellipsometry

Ellipsometry measurements were carried out in a M-2000V instrument (J. A. Woollam Co., Inc., USA). For each sample preparation, the polarization parameters (Δ and Ψ) were measured at five arbitrarily chosen spots on the substrates. The refractivity of the SAMs was considered as 1.43, the incident wavelength was 632.8 nm and the incident angle was 65°, 70 ° and 75°.

2.2.3. X-ray photoelectron spectroscopy

The surface analysis of the samples was explored with XPS (OMICRON, Germany) employing CAE mode (50 eV) and anodes of Mg Kα with radiation at 1253.6 eV. The full scale spectra were scanned one time while the spectra for N 1s and C 1s were scanned 20 times. The energy resolution is about 0.8 eV for full scale XPS measurement and 0.13 eV for the peak position of N 1s and C 1s. The charging correction for binding energy shift was carried out by referencing the Si 2p peak at 103.4 eV. Spectral analysis includes a linear background abstraction and peak separation by using XPS peak fitting program (XPSPEAK version 4.1).

2.2.4. Fourier transformation infrared spectroscopy

FT-IR measurements of the monolayers were carried out by using a Nicolet Nexus 470 FT-IR (Thermo Nicolet, USA). ATR method was used to detect surface samples and three different points of each sample were detected. For each spectrum 200 scans in the range 4000–400 cm^{-1} were recorded, resolution 4 cm^{-1}. The background was scanned with the cleaned hydroxylated surface of the SiO$_2$/Si substrate.

2.2.5. Atomic force microscopy

AFM (NanoScope IVa Controller, Vecco, USA, contact mode, Si$_3$N$_4$ probe, k = 0.06 N/m) was used to investigate the surface morphology of the samples, and the samples were evaluated without any pretreatment. Nanoscope software v6.11 was used to analyse the experimental results.

3. Results and discussion

3.1. Surface structure of the SAMs

When dipped in 5 mM of 2-cyanoethyl triethoxysilane in toluene solution for 6–8 h, the advancing contact angle of water on SiO$_2$/Si substrates modified with cyano functional group is about 50 ± 2°, and the receding contact angle is around 42 ± 2°, which is much smaller than the value of 72 ± 2° previously reported in reference [7]. But after annealed at 150 °C for about 2 h, it reaches a steady value of 58 ± 2° for advancing and 52 ± 2° for receding contact angle, which is in good agreement with reference [8] [glass/Si(CH$_2$)$_3$CN, 56 ± 2°] but not agrees with 72°. This is because there are only two methylene groups in our system, according to Wasserman et al. [9], the water contact angle drops dramatically when the chains are very short. It suggests that the annealing treatment is necessary because the SAMs are not stable enough under the hydrolysis reaction condition as mentioned above [11].

The thickness of the samples is measured using spectroscopic ellipsometry before and after modification with the SAMs. Before modification, the thickness of the oxide layer on the silicon substrate is 3.02 nm which is the average value over five points on the sample with the fluctuation of 0.02 nm. After modification with the cyano-terminated monolayer, the thickness of the sample reaches 3.72 nm, with an increase of 0.70 nm. That is to say the thickness of the cyano-terminated SAM is about 0.70 nm. The film thickness has no remarkable changes with the hydrolysis time increasing, as shown in Fig. 1, which indicates that the effects of hydrolysis time of cyano-terminated SAM on ellipsometric measurements under this hydrolysis condition are very small and the SAMs are not damaged.

With the hydrolysis time increasing, the film thickness has no obvious changes, however, the contact angles' changes can easily be observed (as shown in Fig. 2). In this process, the contact angle decreases with the increase of hydrolysis time and it has no obvious declination when the time reaches 90 min. After hydrolysis for approximately 90 min, the contact angle drops from 58° to 35°. As one knows, the value of 35° is the typical contact angle of carboxyl-terminated SAM with higher density [5]. Therefore, it could be understood that the cyano terminal functional groups are completely changed into the carboxylic terminal groups via hydrolysis reaction for about 90 min.

Several parameters such as the immersing time and the concentration of the reagents were varied to find the procedures

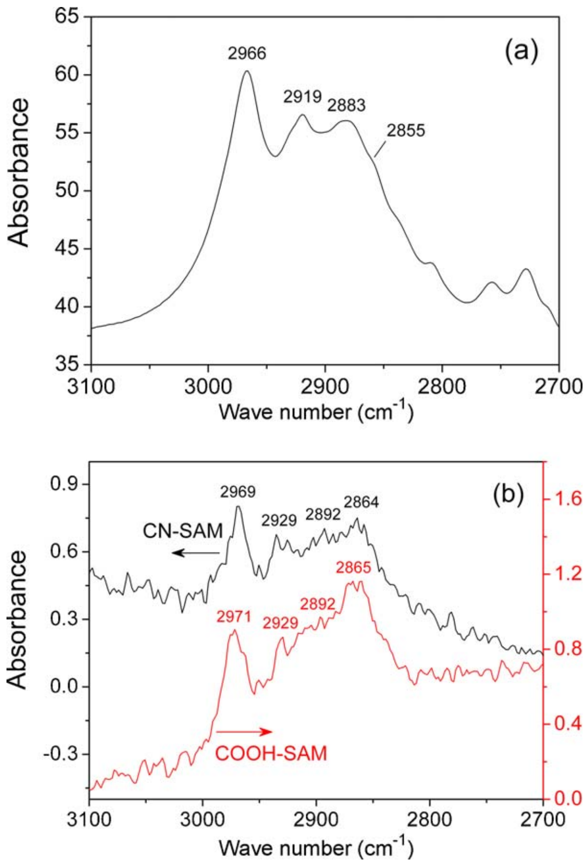

Fig. 4. FT-IR spectra of the different samples. (a) The liquid 2-cyanoethyl triethoxy silane; (b) the cyano- and carboxyl-terminated SAMs.

for the best quality of the SAMs. Taking the cyano-terminated SAM as an example, with the immersing time ranging from 0.5 h to 24 h and the concentration of 2-cyanoethyl triethoxysilane in toluene solution changed from 1 mM to 50 mM, the water contact angle of the monolayer goes up at the beginning, and then reaches a steady value after 6 h with 5 mM concentration of 2-cyanoethyl triethoxysilane. Even though increasing the immersing time and the concentration can get the uniform monolayers, longer time and higher concentration intend to form multilayers or self-polymerization, which makes it difficult to clean the monolayers. After assembling, the monolayers adsorb onto the substrate through the Si–O–Si bond, which more easily hydrolyses in basic environment. Therefore, we considered the acidic hydrolysis method in the next hydrolysis reaction for the preparation of carboxyl-terminated SAM. As reported, Vogel et al. [15] hydrolyzed the isocyanate group of γ-isocyanatopropyl triethoxy silane monolayers with a hydrochloric acid solution (5 mol/L in water) for 2 h. Here, we chose a milder hydrolysis condition assisted with heating up to 75 °C to reduce the damage of the monolayers assembled.

From the above analysis, we can conclude that a 0.70 nm SAM with cynao terminal group is formed onto the hydroxylated surface of the SiO_2/Si substrate after dipped in 5 mM of 2-cyanoethyl triethoxysilane in toluene solution for 6–8 h with the advancing contact angle of 58°, and it has been changed into carboxyl-terminated SAM through a hydrolysis reaction for about 90 min with the advancing contact angle of 35° and without peeling off from the substrate surface under the reaction conditions.

3.2. Microstructures of the SAMs

Fig. 3(a) and (b) shows the full scale XPS spectra of the substrates functionalized with cyano-terminated SAM before and after hydrolysis respectively. It was found that before hydrolysis [see Fig. 3(a)], there is a peak centered at 400 eV attributed to N 1s [5,16], and the N 1s XPS spectrum is inserted in Fig. 3(a). However, after the hydrolysis, that peak disappears [see Fig. 3(b)]. These results suggest that, after self-assembling, the cyano-terminated SAM indeed formed on the substrate, and then the cyano terminal groups disappear after the hydrolysis reaction.

The C 1s XPS spectra are shown in Fig. 3(c) and (d) which refer to before and after hydrolysis respectively. As shown in Fig. 3(c), there are two subbands in the spectrum of C 1s before hydrolysis:

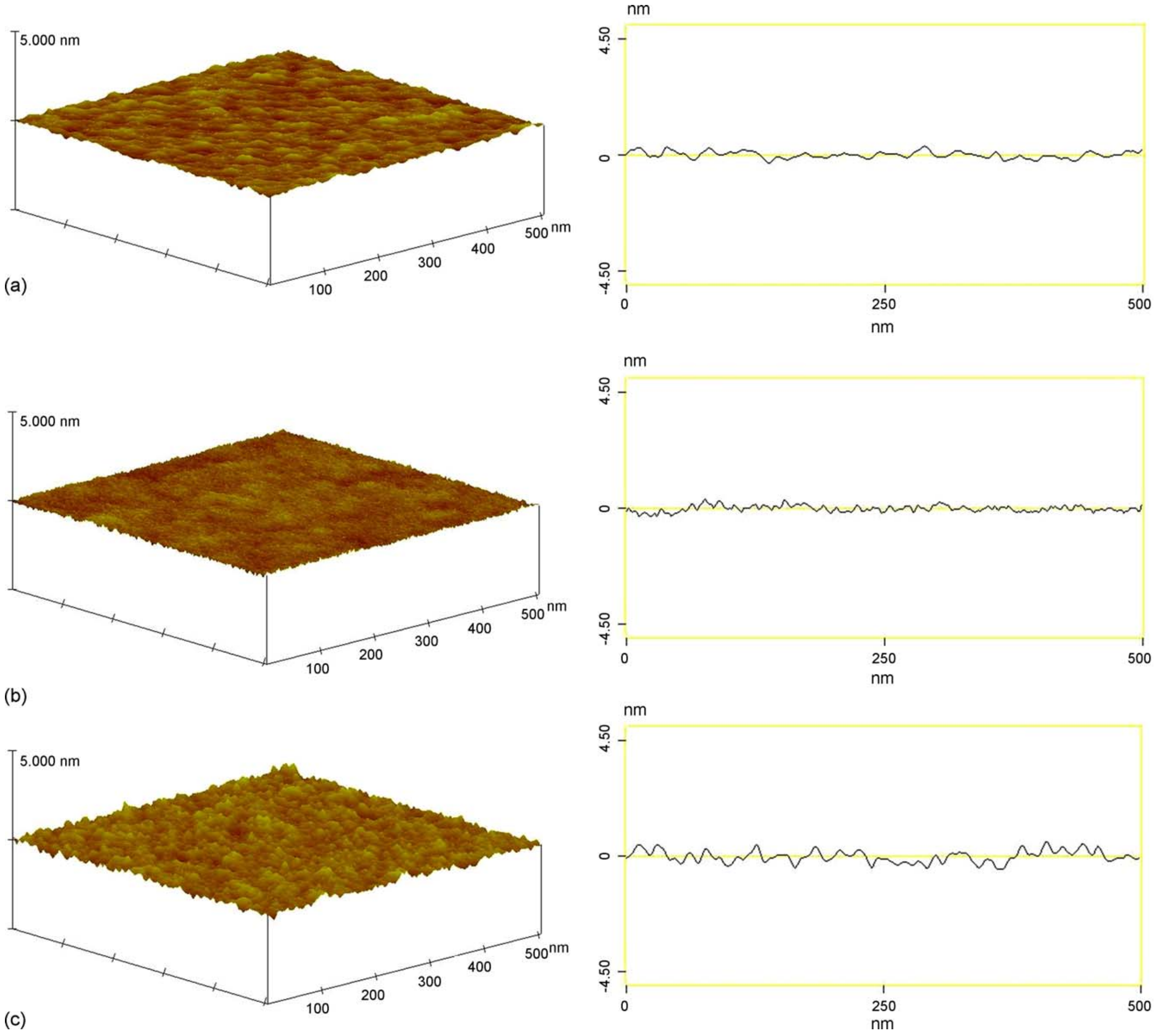

Fig. 5. AFM images of the surface (left) and the section analysis (right). (a) The hydroxylated surface of the SiO_2/Si substrate just after cleaning; (b) cyano-terminated SAM; (c) carboxyl-terminated SAM.

one centered at 285.1 eV arising from C–H species, and another centered at 286.7 eV due to C–O/C≡N bonds [16,17]. After hydrolysis, as shown in Fig. 3(d), a new peak around 288 eV appears, which is assigned to the C=O of the carboxylic group [17,18]. It also supports the conclusion of contact angle analysis that the cyano terminal functional group changed into the carboxylic terminal group through the hydrolysis reaction.

The XPS spectra give us the information of the chemical composition for the surface, and the molecular order and packing analysis is performed by infrared (FT-IR) measurement. Herein, the spectra of the C–H stretching modes in the region 2700–3100 cm^{-1} are used to characterize the average conformational ordering of the monolayers. Fig. 4(a) shows the FT-IR spectrum of the pure liquid 2-cyanoethyl triethoxysilane. The C–H stretching bands at 2919 cm^{-1} and 2855 cm^{-1} are assigned to asymmetric and symmetric stretching mode of methylene, respectively. The peak frequency values shift to 2929 cm^{-1} and 2864 cm^{-1} for the cyano and carboxylic terminal groups modified substrates respectively [see Fig. 4(b)]. Like the methylene group, the frequency values of the methyl stretching bands center at 2966 cm^{-1} and 2883 cm^{-1} in the liquid, and shift to 2969/2971 cm^{-1} and 2892 cm^{-1} respectively for the SAMs, which is in accordance with the literatures [19,20]. By comparing the intensity of symmetric stretching bands, it could easily find that, the methyl peak at 2883 cm^{-1} for liquid sample shifts and diminishes when modified with SAMs, and the methylene peak becomes apparent at 2864 cm^{-1} for the SAM samples. In general, the FT-IR intensity for the SAM samples diminishes compared to the liquid sample, but the intensity of the methyl stretching bands decreases more with respect to that of the methylene group after assembling on the substrates. This experimental result shows that the ethoxy groups of 2-cyanoethyl triethoxysilane react with the surface hydroxyl groups through the hydrolysis of CH_3CH_2–O–Si bonds. It indicates that the monolayers connected with the hydroxylated surface of the SiO_2/Si substrate through Si–O–Si bonds are well oriented. Three points for parallel measurements are randomly chosen for each sample and the results are close to each other, therefore, the samples are considered to be close-packed with SAMs completely covered.

3.3. Morphology of the SAMs

Fig. 5 shows the AFM images of the surface (left) and the section analysis (right) of the substrates before [Fig. 5(a)] and after coating with the cyano-terminated SAM [Fig. 5(b)], and after hydrolysis reaction [Fig. 5(c)]. The roughness information is obtained by the Nanoscope software v6.11 and the values are 0.199 nm, 0.324 nm and 0.365 nm, respectively. It is observed that the surface roughness of the cyano- and carboxyl-terminated SAMs [as shown in Fig. 5(b) and (c), respectively] is almost the same and it has a clear increase in contrast to the surface of clean SiO_2. It indicates that the surface of cyano- and carboxyl-modified SiO_2/Si substrates are covered with a well ordered monolayer and the hydrolysis reaction does not damage the morphology of the SAMs.

4. Conclusion

In conclusion, the cyano-terminated SAM has been prepared via the adsorption of a short-chain 2-cyanoethyl triethoxysilane onto the hydroxylated surface of the SiO_2/Si substrates and modified into the carboxyl-terminated SAM through simple hydrolysis reaction. The group change is identified by the contact angle, ellipsometric measurements and the XPS spectra. The morphology of the monolayer before and after hydrolysis of the cyano terminal group has been characterized by AFM as well. This method seems to be useful for the preparation of the copper diffusion barrier at the thickness below 2 nm.

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