



## Hydrophobic to hydrophilic transition of HF-treated Si surface during Langmuir–Blodgett film deposition

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### ABSTRACT

HF-treated Si surface, which is hydrophobic in nature and quite stable in air and inside pure water, can become completely hydrophilic during nickel arachidate Langmuir–Blodgett film growth. Such transition is clearly evident from the structures of films deposited by different number of strokes and can be understood by considering partial oxidation of Si surface inside subphase water and further or complete oxidation in air, in presence of Ni head-groups. Attached Ni head-groups weaken the nearby Si–Si covalent bonding and easily oxidize those Si atoms. Depending upon the amount of those head-groups and its distribution, oxidation or transition can even complete.

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### 1. Introduction

Si, which is largely used in different device fabrications, is perhaps the mostly investigated semiconductor material. The surface of such Si is one of the key players in deciding the growth and stability of interesting structures on it [1,2]. The surface of Si can be passivated by terminating the surface dangling bonds [3] through different pretreatment. Wet chemical reaction is one such simple pretreatment process, which can not only restore contamination free surface in ambient conditions [4–6] but also modify the surface free energy or polar–nonpolar (hydrophilic–hydrophobic) nature of the surface [2,7–12]. Information about the nature and stability of such terminated Si surface can be obtained [12] by growing Langmuir–Blodgett (LB) film [13,14] on it and determining the structure of the LB film [12,15–18] using X-ray reflectivity (XRR) [19,20] and atomic force microscopy (AFM) [21] techniques and can be verified using contact angle [22] and/or X-ray photoelectron spectroscopy (XPS) [23] measurements. This information is very important in understanding the attachment of different organic, metal–organic and biological systems with the Si surface, which is required for the development of chemical and biological sensors, combining semiconductor electronics with biomolecular recognition elements [24–26].

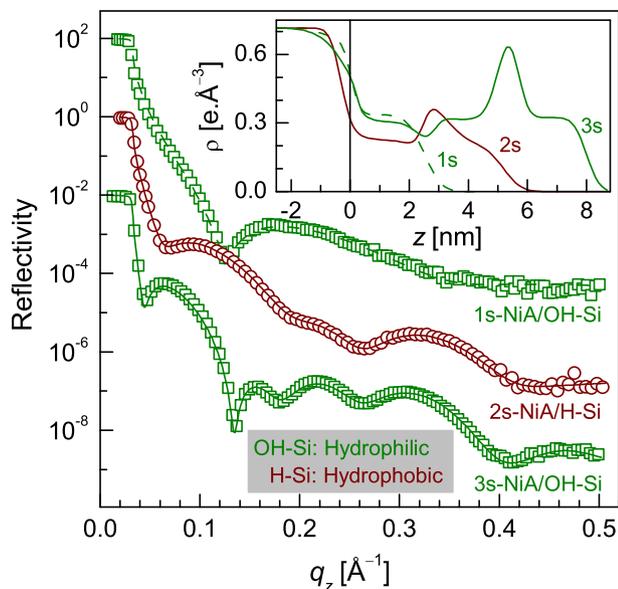
H-terminated Si surfaces are most often used as the starting substrate for further processing for biological, energy and micro-electronic applications [27]. From our previous study of nickel arachidate (NiA) LB films [12], it is clear that the H-terminated Si surface, prepared through HF treatment, is hydrophobic in nature

and is quite stable in ambient condition as well as in pure water. This is evident from the growth of symmetric monolayer (SML) structure of NiA on Si by two (down–up) strokes of deposition [12], which is repeated here in Figure 1. The nature (hydrophobic–hydrophilic) and stability of such passivated or terminated surface may be different in different environments [26,28,29], depending upon the humidity of air [30–32], the amount of dissolved oxygen in water [33–35] and the presence of metal impurity [36–39] on the passivated surface, as these can lead to the growth of oxide layer with time on the surface by desorbing the H-atom [2,40]. It is well known that completely oxide cover or OH-terminated Si surface is hydrophilic in nature [8,9] and is very stable. This is also very much evident from our previous study [12], namely from the growth of asymmetric monolayer (AML) structure and AML/SML structure of NiA on Si by single (up) stroke and three (up–down–up) strokes of deposition, respectively and is presented in Figure 1 for clarity. Now the questions are, what happens to the H-terminated Si surface, which is hydrophobic in nature, when subjected to different environments? Is it possible to transform it completely to hydrophilic, especially during nanolayer deposition and growth? Or is it possible to see the strain effect near hydrophobic/hydrophilic interface due to the partial transformation as observed for Br-terminated Si surface [12]?

Here, we have tried to find out the answers to some of these questions. For that, NiA LB films on HF-treated Si substrates are deposited in different strokes by keeping the substrates in subphase water having different pH with or without Ni metal ions and for different time. The structures of the LB films are then investigated using XRR and AFM techniques, which indicate that complete hydrophobic to hydrophilic transition of HF-treated Si substrate is indeed possible through certain pathway of environments. The

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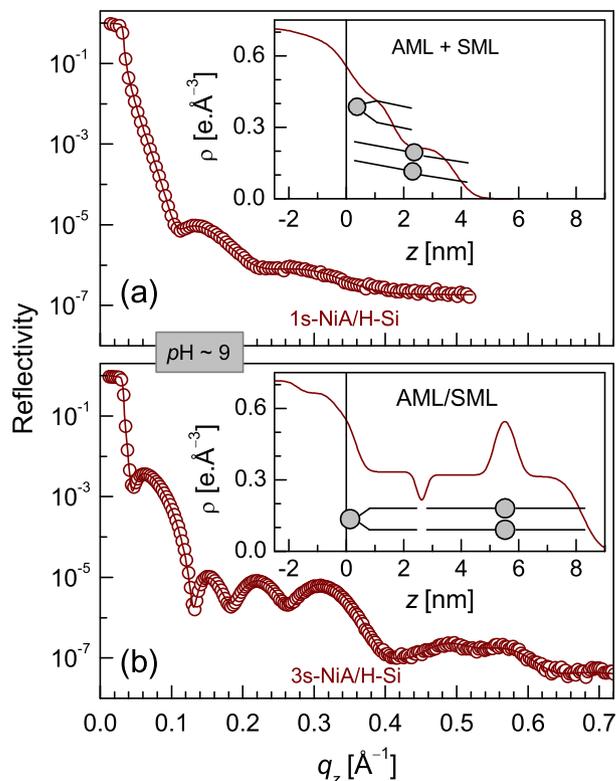
**Figure 1.** XRR data (symbol) and analyzed curves (solid line) of NiA LB films on OH-terminated Si substrates deposited by one and three strokes, and on H-terminated substrate deposited by two strokes. Insets: corresponding EDPs showing the natural hydrophilic and hydrophobic natures of the OH- and H-terminated Si substrates, respectively [12].

mechanism behind such complete transition, which essentially took place through partial transition (or oxidation) at each environment, is verified using contact angle and XPS measurements.

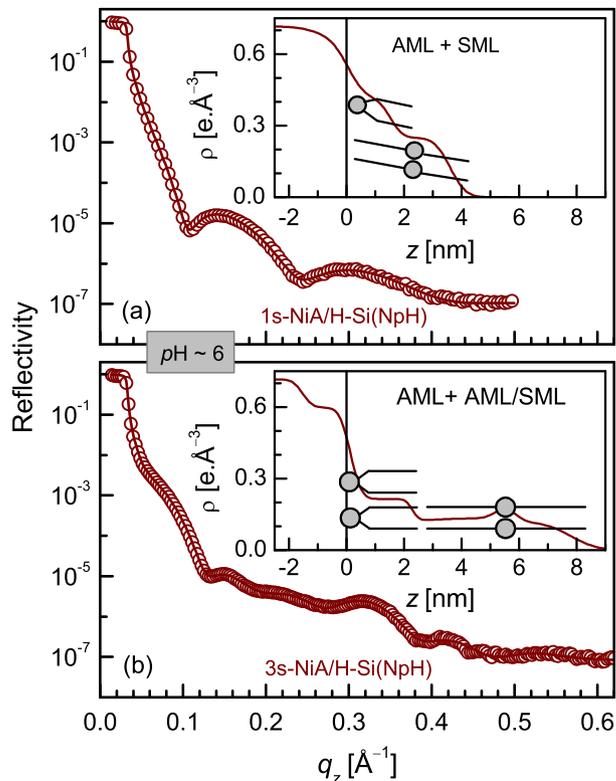
## 2. Experiment

The details about the preparation of NiA LB films on Si substrates are discussed before [12]. In brief, arachidic acid [ $\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$ , Sigma, 99%] molecules were spread from a 0.5 mg/ml chloroform (Aldrich, 99%) solution on Milli-Q water (resistivity 18.2 M $\Omega$  cm) containing nickel sulphate ( $\text{NiSO}_4 \cdot 2\text{H}_2\text{O}$ , Merck, 99%) in a Langmuir trough (Apex Instruments). The pH of the water subphase containing 0.2 mM nickel sulphate was maintained either at 'high pH' (8.5–9.0) or at 'normal pH' (6.0–6.5) using different amount of sodium hydroxide (NaOH, Merck, 98%). The monolayer was compressed at a constant rate of 3 mm/min. All depositions were done at 30 mN/m pressure and at room temperature (22 °C). Depositions were carried out at a speed of 2 mm/min and the drying time allowed after each up stroke was 10 min.

Prior to the deposition, Si (001) substrates were made H-terminated by keeping it in a solution of hydrogen fluoride (HF, Merck, 10%) for 3 min at room temperature after ultrasonic cleaning in trichloroethylene (10 min) and methanol (10 min) solution. Immediately after the HF-treatment, all the substrates were kept inside the Milli-Q water until LB deposition. First two NiA LB films were deposited in the 'high pH' condition (similar to that of 2s-NiA/H-Si sample prepared earlier [12]), one by single (up) stroke and another by three (up–down–up) strokes, referred as 1s-NiA/H-Si and 3s-NiA/H-Si, respectively. Two more samples were prepared in 'normal pH' condition, one by single (up) stroke and another by three (up–down–up) strokes, referred as 1s-NiA/H-Si (NpH) and 3s-NiA/H-Si (NpH), respectively. Then one film was prepared by single up stroke in 'high pH' condition after keeping the substrate in the subphase of water for longer time (about 90 min), referred as 1s-NiA/H-Si (LT). One further sample was prepared by three (up–down–up) strokes in 'high pH' condition, however, arachidic acid molecules were spread



**Figure 2.** XRR data (symbol) and analyzed curve (solid line) of 'high pH' NiA LB films on H-terminated Si substrates deposited by (a) one stroke and (b) three strokes. Insets: corresponding EDPs showing the structures of the LB films.



**Figure 3.** XRR data (symbol) and analyzed curve (solid line) of 'normal pH' NiA LB films on H-terminated Si substrates deposited by (a) one stroke and (b) three strokes. Insets: corresponding EDPs showing the structures of the LB films.

on the trough only before final up stroke, referred as 1s-NiA/H-Si (2sNi). The films prepared before [12] were also used for comparison.

XRR measurements were carried out using a versatile X-ray diffractometer (VXRD) setup to investigate the structure of deposited NiA LB films. VXRD consists of a diffractometer (D8 Discover, Bruker AXS) with Cu source (sealed tube) followed by a Göbel mirror to select and enhance  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The diffractometer has a two-circle goniometer ( $\theta-2\theta$ ) with quarter-circle Eulerian cradle as sample stage. The latter has two circular and three translational motions. Scattered beam was detected using NaI scintillation (point) detector. Data were taken in specular condition, i.e. the incident angle ( $\theta$ ) is equal to the reflected angle ( $\theta$ ) and both are in a scattering plane. Under such condition, a non-vanishing wave vector component,  $q_z$ , is given by  $(4\pi/\lambda) \sin \theta$  with resolution  $0.0014 \text{ \AA}^{-1}$ .

The topography of the LB films on HF-treated Si substrates were mapped through AFM technique (beam-deflection AFM, Omicron NanoTechnology) in different length scales and in different portions of the samples, after completion of XRR measurements. AFM images were collected in noncontact mode and in UHV ( $\sim 10^{-9}$  mbar) conditions to minimize the tip induce modification of the soft films and to get clean images, respectively. WSXM software [41] was used for image processing and analysis.

To verify the hydrophilic or hydrophobic nature of the Si surface treated differently, contact angle measurements using home built setup were carried out.  $4 \mu\text{l}$  of water was placed on the treated Si surface using Hamilton syringe and the shape of the water droplet was captured by a traveling microscope followed by a digital camera. To know the chemical nature of the Si surface after treatment and after LB film deposition, XPS measurements of four different samples were performed in a multiprobe chamber (Omicron NanoTechnology) equipped with an  $\text{AlK}\alpha$  ( $E = 1486.6 \text{ eV}$ ) source and a hemispherical analyzer (EA 125).

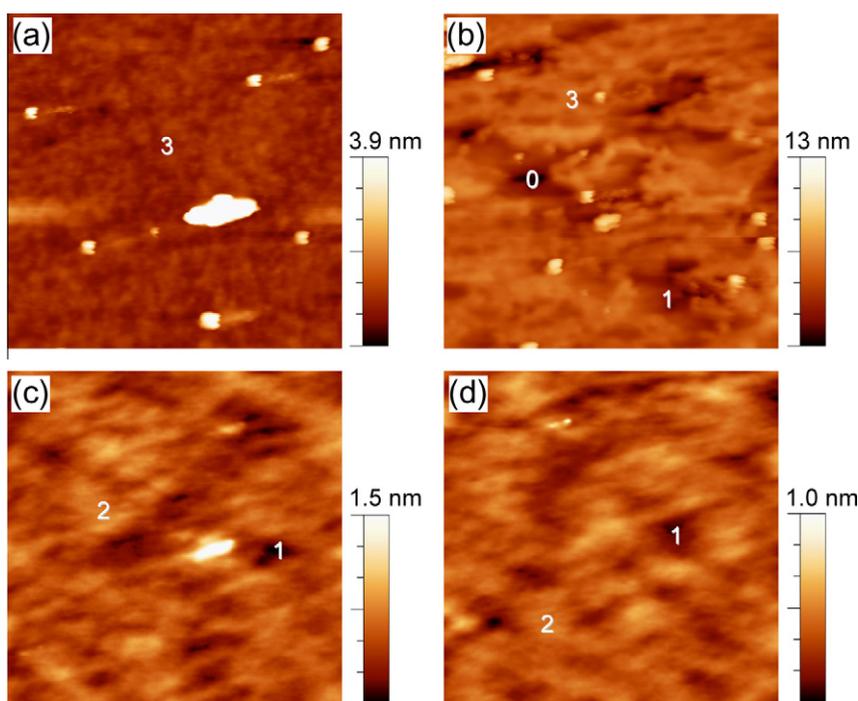
### 3. Results and discussion

#### 3.1. X-ray reflectivity and electron-density profile

XRR technique essentially provides an electron density profile (EDP), i.e. in-plane ( $x-y$ ) average electron density ( $\rho$ ) as a function of depth ( $z$ ) in high resolution [40]. From EDP it is possible to estimate the structure of a film and by knowing the structure (AML or SML) just above the substrate one can predict the nature (hydrophobic or hydrophilic) of the substrate [12]. To obtain the EDP, XRR data has been analyzed using Parratt's formalism [42] and for the analysis, each film has been divided into a number of layers including roughness at each interface.

XRR data and analyzed curves of 1s-NiA/H-Si and 3s-NiA/H-Si samples are shown in Figure 2. It can be noted that XRR profile of 1s-NiA/H-Si sample (Figure 2a) is different from that of 1s-NiA/OH-Si sample (Figure 1), while XRR profile of the 3s-NiA/H-Si sample (Figure 2b) is quite similar to that of 3s-NiA/OH-Si sample (Figure 1). This is also clear from the EDPs shown in the insets of Figures 1 and 2. EDPs suggest that for 1s-NiA/H-Si sample, the structure is AML + SML, i.e. both AML and SML structures are present side-by-side, in nearly equal ratio, on the substrate, while for 3s-NiA/H-Si sample, the structure is AML/SML, i.e. only AML structure is present on the substrate. The AML and SML which are present in 3s-NiA/H-Si sample are quite perfect (straight and compact), while those in 1s-NiA/H-Si sample are imperfect (tilted and jumbled).

XRR data and analyzed curves of 1s-NiA/H-Si (NpH) and 3s-NiA/H-Si (NpH) samples are shown in Figure 3. EDPs obtained from the analysis are shown in the insets of Figure 3. Both XRR curve and EDP (Figure 3a) for 1s-NiA/H-Si (NpH) sample are similar to those of 1s-NiA/H-Si sample (Figure 2a), and so the corresponding structure. However, for the single stroke 'normal pH' sample, the coverage of SML structure is greater than that of AML structure, unlike 'high pH' one. For 3s-NiA/H-Si (NpH) sample, both XRR curve and EDP (Figure 3b) are quite different from those of 3s-NiA/H-Si



**Figure 4.** AFM images (of scan size  $1 \times 1 \mu\text{m}^2$ ) showing topography of different pH NiA LB films on H-terminated Si substrates deposited by different strokes. (a) 'High pH' three strokes, (b) 'normal pH' three strokes, (c) 'high pH' one stroke and (d) 'normal pH' one stroke. Presence of layers of different heights (in unit of AML length) are indicated by the numbers.

sample (Figure 2b). The structure of three strokes 'normal pH' sample is AML + AML/SML. Although, SML structure is not found on the substrate, the coverage of first layer with AML is quite low and the coverage with AML/SML structure is even lower.

Analysis of the XRR curves of 1s-NiA/H-Si (LT) and 1s-NiA/H-Si (2sNi) samples (not shown here) suggest that the structures of both films are AML + SML. Although, the area corresponding to AML structure on the substrate is slightly greater than that of SML one, the surface is never completely covered with AML structure.

### 3.2. Atomic force microscopy and topography

Typical AFM images of four LB films are shown in Figure 4. The topography of 3s-NiA/H-Si sample (Figure 4a) is quite smooth and compact. Considering the XRR result, the height can be assigned to 3 (in unit of AML length), corresponding to the AML/SML structure. Domains of different heights, namely 0, 1 and 3 corresponding to substrate, AML and AML/SML structures are clearly visible in the AFM image of 3s-NiA/H-Si (NpH) sample (Figure 4b), consistent with XRR result. The topography of 1s-NiA/H-Si and 1s-NiA/H-Si (NpH) samples (Figure 4c and d) are quite similar. Both seems to compose of domains of two different heights and considering the XRR results, the heights can be assigned to 1 and 2, corresponding to the AML and SML structures. The fact that the height difference between two such structures is less than 1 nm, is the imperfect nature of the films, as predicted by XRR.

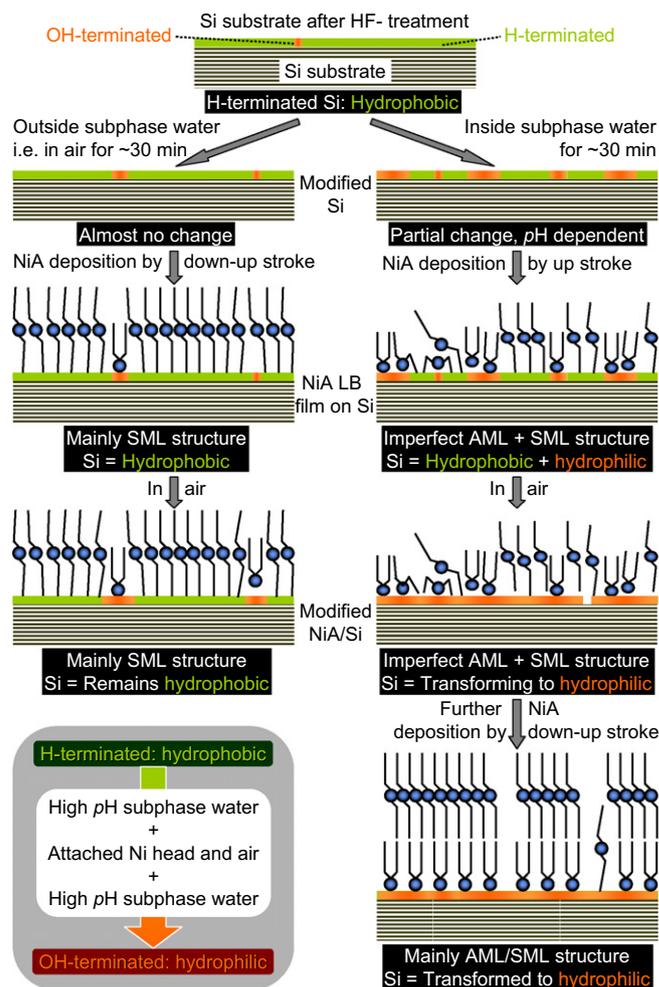
### 3.3. Hydrophobic–hydrophilic transition pathway

Structures of the NiA LB films on HF-treated Si substrates deposited by different number of strokes and their stability obtained from XRR and AFM results, provide the hydrophobic to hydrophilic transition pathway, which is shown schematically in Figure 5. SML structured NiA LB film is formed on H-terminated Si surface by two (down–up) strokes of deposition (i.e. in 2s-NiA/H-Si sample), which almost remains unchanged in air. This is a clear signature of stable hydrophobic nature of the H-terminated Si surface. On the other hand, AML + SML structured NiA LB film is formed on HF-treated Si surface by single (up) stroke of deposition (i.e. in 1s-NiA/H-Si, 1s-NiA/H-Si (NpH) and 1s-NiA/H-Si (LT) samples). This indicates partial conversion of hydrophobic surface to hydrophilic one, inside subphase water. The ratio between the coverage of AML and SML structures increases with the pH of the subphase water and with the duration for which the substrate was inside it, indicating increase in conversion with those two parameters. However, never completed with AML structure in such single stroke of deposition, unlike 1s-NiA/OH-Si sample, implying that the hydrophobic to hydrophilic transition of the HF-treated Si surface inside subphase water is always partial.

AML + AML/SML structured LB film, with partial coverage is formed on HF-treated Si surface by three (up–down–up) strokes of deposition in 'normal pH' condition (i.e. in 3s-NiA/H-Si (NpH) sample). Although, SML structure is not formed on the substrate, the hydrophilic nature of the substrate is only partial. The film formed on HF-treated Si surface by three (up–down–up) strokes of deposition in 'high pH' condition (i.e. 3s-NiA/H-Si sample), however, shows AML/SML structure similar to that of 3s-NiA/OH-Si sample. It can be noted that for the 1s-NiA/H-Si (2sNi) sample, where only last up stroke is through Langmuir monolayer, the structure is neither AML/SML or complete AML. That means complete hydrophilic nature of the HF-treated Si surface is observed for the NiA LB film deposited in 'high pH' condition and in three strokes, all through Langmuir monolayer.

### 3.4. Hydrophobic–hydrophilic transition mechanism

H-terminated Si surface is hydrophobic in nature, while OH-terminated Si surface is hydrophilic in nature. So, in principle, the mechanism behind hydrophobic to hydrophilic transition is very simple, conversion of H-terminated surface to OH-terminated one. However, the questions are – when and how such conversion take place, i.e. what are the parameters responsible for such conversion? It is known that depending upon the sequence of deposition of LB films, substrate needs to place either inside subphase water (for odd number of stroke) or outside subphase water, i.e. in air (for even number of stroke) for about 30 min, until the pressure of Langmuir monolayer reached to a constant value of 30 mN/m to transfer. In air mainly oxygen interacts with the HF-treated surface whereas in solution apart from the dissolved oxygen many ions like  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ni}^{2+}$ , etc. are there which may interact with the passivated surface. Although native oxide grows on the passivated Si surface in ambient condition by desorbing the passivating element, the oxide growth rate depends on the passivating element. For H-passivated Si surface, the oxide growth rate in air is such that very little oxide or hydrophilic area could grow in 30 min. On the



**Figure 5.** Schematics of the structures of NiA LB films on HF treated Si substrates deposited by different number of strokes and the process involved for hydrophobic to hydrophilic transition of corresponding Si surface. SML structure on Si substrate: hydrophobic nature corresponding to H-terminated Si surface, AML or AML/SML structure on Si substrate: hydrophobic nature corresponding to OH-terminated Si surface and in between AML and SML mixed structure corresponding to H- and OH-terminated mixed Si surface.

other hand, partial and complete hydrophilic transition of H-passivated Si surface in subphase water and in 3s-NiA/H-Si film are due to the growth of oxide on the Si surface. Since the amount of dissolved oxygen is much less in the subphase water compared to that in air, chemical reactions must take place under subphase water and there after in air for the growth of oxides on Si surface, which needs understanding.

### 3.4.1. Partial transition

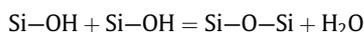
The possible conversion mechanism of the H-terminated Si surface to OH-terminated one, through oxide formation, in subphase of water [8,9,43] is shown pictorially in Figure 6. When H-terminated Si substrate is immersed into subphase water, H atoms are replaced by OH groups to form Si–OH (silanol) groups, according to the following reaction.



Due to the strong electronegativity of OH group, the charge induces to the Si atom bonded directly to it ( $\delta++$ ) is more compared to the next one ( $\delta+$ ). This polarization weakens the Si–SiOH back bond. In the next step, water molecules or dissolved  $\text{H}^+$  and  $\text{OH}^-$  ions attack that back bond to form Si–H and Si–OH as given below.



Si–H bond is further replaced by OH group to form Si–OH. When two such neighboring OH groups face each other then oxide is formed through a bridging reaction.



In this way, OH-terminated oxide layer is formed on the Si substrate under subphase water. It is necessary to mention that such reaction hardly occur for Br-terminated Si surface, which is evident from the similar structure for two LB films (deposited either by up stroke or by down-up strokes) on Br-terminated Si surface [12]. Due to the higher electronegativity of Br atom (2.96) compared to that of H atom (2.20) [44], OH group could not replace the former one easily as they do the latter one. Even for H-terminated Si surface, such reaction rarely takes place in pure water. Presence of different ions, mainly  $\text{OH}^-$  ions in subphase water essentially helps such reaction. The coverage of OH-terminated oxide layer on the Si surface increases with the pH of the subphase water and with the duration for which the substrate was inside it, but never complete or full. Accordingly, hydrophobic to hydrophilic transition is only partial. However, is there exists any limiting value for such partial transition, similar to that observed for Si surface using selective surface-chemistry route [45], is not clear and need further experimental and theoretical studies.

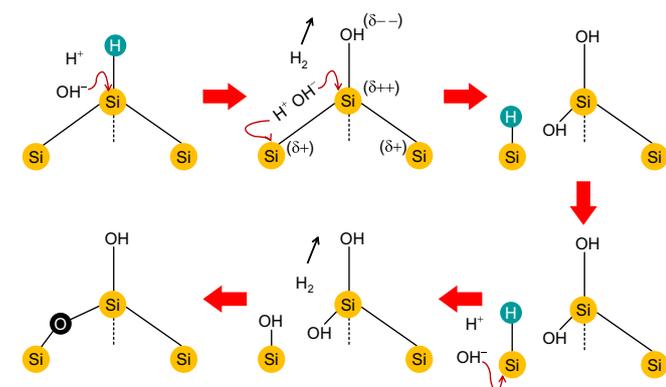


Figure 6. Possible conversion mechanism of Si surface under subphase water: from H-terminated to OH-terminated oxide.

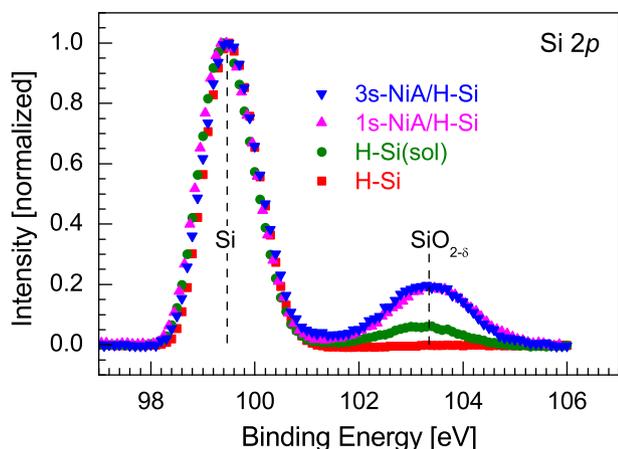
### 3.4.2. Complete transition

Complete hydrophobic to hydrophilic transition occurs in air due to the presence of Ni head groups on partially transformed Si surface. It is known that the presence of some metals on the Si surface can create instability [46,47] and enhance the oxidation rate of Si in air [36–39]. This is because the underlying Si–Si covalent bonds are weakened in presence of those metals (or metal ions) and accordingly associated Si atoms readily react with the ambient oxygen to form native oxide layer. In the partially transformed Si surface, AML structure is formed on hydrophilic portion and SML structure is formed on hydrophobic portion. That means Ni head groups are attached to the oxide (hydrophilic) portion of the surface and those head groups, although connected with the carboxylic ligands through ionic bonding, weaken the nearby Si–Si covalent bonding by crossing the H-passivated layer and thereby increasing the oxide coverage in air. It can be noted that such Si–Si bond weakening may not occur through Br-passivated layer because of its large size (1.14 Å) and/or bond length with Si (2.15 Å) compared to those of H (0.37 and 1.48 Å, respectively) [44]. Since this conversion took place near the attached Ni portion, the final coverage of oxide layer depends on the amount of attached Ni and its distribution on the Si surface. This is in agreement with our results. For the 1s-Ni/H-Si (2sNi) sample, probably very few  $\text{Ni}^{2+}$  ions were physisorbed on Si surface in first up stroke, which limits the formation of OH-terminated oxide layer in air. The formation of OH-terminated oxide layer is not even complete in subsequent subphase water, which is evident from the final structure of the film (i.e. from the partial coverage with AML structure). For the films deposited in single up stroke and in two pH conditions, the number of Ni head groups attached to the Si surface and hence the formation of oxide layer in air are considerable. Among those two films, the number of Ni head groups attached to the Si surface is more for the film prepared in ‘high pH’ condition and correspondingly, the OH-terminated oxide layer in air is nearly complete. Although, complete hydrophilic nature of HF-treated Si surface we observed for 3s-Ni/H-Si sample, the complete transition essentially occur in air after first up stroke of deposition, as discussed. The fact that the structure of the 1s-Ni/H-Si sample do not change completely to SML with time, because in air the change in the configuration of molecules is very difficult. Subphase water in subsequent deposition can however change the structure through reorganization (or configurational change) of NiA molecules, as observed.

### 3.4.3. Direct evidence

The proposed mechanism for hydrophobic to hydrophilic transition of HF-treated surface is well supported by contact angle and XPS measurements. Contact angles for HF-treated Si surface (referred as H-Si) and RCA cleaned Si surface (referred as OH-Si) are found to be  $\sim 79^\circ$  and  $14 - 17^\circ$ , respectively. These correspond to hydrophobic and hydrophilic natures of H-Si and OH-Si, respectively [48]. Contact angle for H-Si substrate after keeping it inside  $\text{NiSO}_4$  solution for about 40 min [referred as H-Si (sol)] is  $\sim 34^\circ$ . This suggests that the surface of H-Si (sol) becomes hydrophilic compared to H-Si substrate but less hydrophilic compared to OH-Si substrate. That means inside  $\text{NiSO}_4$  solution, OH-terminated hydrophilic spots grow on H-terminated hydrophobic matrix, making overall substrate partially hydrophilic.

The Si 2p core-level XPS spectra of H-Si, H-Si (sol), 1s-NiA/H-Si and 3s-NiA/H-Si samples are shown in Figure 7. XPS spectra for first two samples were collected just after preparation, while those for latter two samples were collected after performing all XRR measurements. The peak at  $\sim 99.5$  eV represents  $\text{Si}^0$  chemical state, while that at  $\sim 103.4$  eV represents  $\text{Si}^{4+}$  chemical state, corresponding to silicon (Si) substrate and silicon oxide ( $\text{SiO}_{2-\delta}$ ) layer, respectively [49,50]. It is necessary to mention that the spectra in



**Figure 7.** XPS spectra of four different samples in the Si2p binding energy region. Two peaks appear due to substrate (Si) and surface or interfacial oxide layer ( $\text{SiO}_{2-x}$ ), are indicated.

Figure 7 are presented after normalizing each spectrum with its  $\text{Si}^0$  peak intensity. Presence of silicon oxide in the H-Si sample is not observed, while that in other three samples is clearly evident. This indicates that the surface of H-Si sample is well passivated with H atoms and is stable in air, at least for the time, before it transfer into the UHV chamber. It can be noted that for the 2s-NiA/H-Si sample, this was the substrate condition when deposition of NiA molecules starts and complete hydrophobic nature of such is quite natural. The oxide signal for 1s-NiA/H-Si and 3s-NiA/H-Si samples are quite strong and nearly similar, while that for H-Si (sol) is relatively weak. Latter indicates that the oxide growth on the surface of H-Si (sol) sample is only partial. This was the substrate condition for the 1s-NiA/H-Si sample when deposition starts and partial hydrophilic and hydrophobic natures of such substrate is well expected. XPS spectrum of 1s-NiA/H-Si sample clearly shows that further oxide really grows at the film–substrate interface of such sample with time in air and is nearly complete (comparing with the XPS spectrum of 3s-NiA/H-Si sample) as proposed, although not much structural change is observed.

#### 4. Conclusions

HF-treated Si surface, which is hydrophobic in nature and quite stable in air, transformed partially or completely to hydrophilic surface, inside subphase water or during NiA LB film growth by up–down–up strokes of deposition and in ‘high pH’ condition. This transition essentially takes place by conversion of H-terminated Si surface to OH-terminated one, through oxide formation. Although the amount of oxygen inside subphase water is less compared to that in air, the oxide formation inside subphase water is more, which takes place by chemical reaction in presence of highly electronegative  $\text{OH}^-$  ions. As the pH of the subphase water increases, the amount of  $\text{OH}^-$  ions increases and so the amount of oxide coverage. Also, as the duration for which the substrate was inside subphase water increases, the chances of chemical reaction increases and so the amount of oxide coverage, but never complete or full. The attachment of Ni head groups on the oxide portion of the partially transformed Si substrate by deposition of LB film, essentially weaken the nearby Si–Si bonding, which then readily react with oxygen to form oxides. It is observed that depending upon the amount of attached Ni head groups and its distribution on the Si surface, it is possible to have complete oxide coverage through such reaction in air. The signature of which, from structural point

of view, is only visible after subsequent deposition, i.e. after reorganization of molecules under subphase water.

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#### References

- [1] J.A. Zasadzinski, R. Viswanathan, L. Madsen, J. Garnæs, D.K. Schwartz, *Science* 263 (1994) 1726.
- [2] J.K. Bal, S. Hazra, *Phys. Rev. B* 79 (2009) 155412.
- [3] V. Derycke, P.G. Soukiassian, F. Amy, Y.J. Chabal, M.D. D’Angelo, H.B. Enriquez, M.G. Silly, *Nat. Mater.* 2 (2003) 253.
- [4] H. Ubara, T. Imura, A. Hiraki, *Solid State Commun.* 50 (1984) 673.
- [5] E. Yablonovitch, D.L. Allara, C.C. Chang, T. Gmitter, T.B. Bright, *Phys. Rev. Lett.* 57 (1986) 249.
- [6] V.A. Burrows, Y.J. Chabal, G.S. Higashi, K. Raghavachari, S.B. Christman, *Appl. Phys. Lett.* 53 (1988) 998.
- [7] V.A. Shchukin, D. Bimberg, *Rev. Mod. Phys.* 71 (1999) 1125.
- [8] F. Okorn-Schmidt, *IBM J. Res. Dev.* 43 (1999) 351.
- [9] X.G. Zhang, *Electrochemistry of Silicon and Its Oxide*, Kluwer Academic, New York, 2004.
- [10] C.-Y. Ruan, V.A. Lobastov, F. Vigliotti, S. Chen, A.H. Zewail, *Science* 304 (2004) 80.
- [11] P.L. Silvestrelli, F. Toigo, F. Ancilotto, *J. Phys. Chem. B* 110 (2006) 12022.
- [12] J.K. Bal, S. Kundu, S. Hazra, *Phys. Rev. B* 81 (2010) 045404.
- [13] K.B. Blodgett, *I. Langmuir*, *Phys. Rev.* 51 (1937) 964.
- [14] M.C. Petty, *Langmuir–Blodgett Films, An Introduction*, Cambridge University, New York, 1996.
- [15] D.K. Schwartz, *Surf. Sci. Rep.* 27 (1997) 245.
- [16] J.K. Basu, S. Hazra, M.K. Sanyal, *Phys. Rev. Lett.* 82 (1999) 4675.
- [17] J.K. Basu, M.K. Sanyal, *Phys. Rep.* 363 (2002) 1.
- [18] S. Kundu, A. Datta, S. Hazra, *Chem. Phys. Lett.* 405 (2005) 282.
- [19] I.K. Robinson, D.J. Tweet, *Rep. Prog. Phys.* 55 (1992) 599.
- [20] J. Daillant, A. Gibaud (Eds.), *X-ray and Neutron Reflectivity: Principles and Applications*, Springer, Paris, 1999.
- [21] S. Morita, R. Wiesendanger, E. Meyer (Eds.), *Noncontact Atomic Force Microscopy*, Springer, Heidelberg, 2002.
- [22] K.L. Mittal (Ed.), *Contact Angle, Wettability and Adhesion*, VSP BV, Utrecht, Netherlands, 1993.
- [23] J.F. Watts, J. Wolstenholme, *An Introduction to Surface Analysis by XPS and AES*, Wiley, 2003.
- [24] T. Strother, W. Cai, X. Zhao, R.J. Hamers, L.M. Smith, *J. Am. Chem. Soc.* 122 (2000) 1205.
- [25] K.-Y. Tse, B.M. Nichols, W. Yang, J.E. Butler, J.N. Russell, R.J. Hamers, *J. Phys. Chem. B* 109 (2005) 8523.
- [26] M. Dai, Y. Wang, J. Kwon, M.D. Halls, Y.J. Chabal, *Nat. Mater.* 8 (2009) 825.
- [27] R. Boukherroub, *Curr. Opin. Solid State Mater. Sci.* 9 (2005) 66.
- [28] X. Zhang, E. Garfunkel, Y.J. Chabal, S.B. Christman, E.E. Chaban, *Appl. Phys. Lett.* 79 (2001) 4051.
- [29] S. Rivillon, F. Amy, Y.J. Chabal, M.M. Frank, *Appl. Phys. Lett.* 85 (2004) 2583.
- [30] M. Niwano, J. Kageyama, K. Kurita, K. Kinashi, I. Takahashi, N. Miyamoto, *J. Appl. Phys.* 76 (1994) 2157.
- [31] T. Ohmi, *J. Electrochem. Soc.* 143 (1996) 2957.
- [32] E.S. Snow, G.G. Jernigan, P.M. Cambell, *Appl. Phys. Lett.* 76 (2000) 1782.
- [33] Y.J. Chabal, S.B. Christman, *Phys. Rev. B* 29 (1984) 6974.
- [34] M. Ranke, Y.R. Xing, *Surf. Sci.* 157 (1985) 339.
- [35] E. Kondoh, M.R. Baklanov, F. Jonckx, K. Maex, *Mater. Sci. Semicond. Process.* 1 (1998) 107.
- [36] T. Hanada, M. Kawai, *Vacuum* 41 (1990) 650.
- [37] D. Graf, M. Grundner, D. Muhlhoff, M. Dellith, *J. Appl. Phys.* 69 (1991) 7620.
- [38] S. Xu, P. Xu, M. Ji, X. Liu, M. Ma, J. Zhu, Y. Zhang, *J. Mater. Sci. Technol.* 9 (1993) 437.
- [39] N. Takano, N. Hosoda, T. Yamada, T. Osaka, *Electrochim. Acta* 44 (1999) 3743.
- [40] J.K. Bal, S. Hazra, *Phys. Rev. B* 75 (2007) 205411.
- [41] I. Horcas, R. Fernandez, J.M. Gwez-Rodriguez, J. Colchero, J. Gomez-Herrero, A.M. Baro, *Rev. Sci. Instrum.* 78 (2007) 013705.
- [42] L.G. Parratt, *Phys. Rev.* 95 (1954) 359.
- [43] D. Graf, M. Grundner, R. Chulz, *J. Vac. Sci. Technol. A* 7 (1989) 808.
- [44] J.K. Bal, S. Hazra, *Defect Diffus. Forum* 297–301 (2010) 1133.
- [45] D.J. Michalak, S.R. Amy, D. Aureau, M. Dai, A. Esteve, Y.J. Chabal, *Nat. Mater.* 9 (2010) 266.
- [46] A. Hiraki, *Surf. Sci. Rep.* 3 (1983) 357.
- [47] J.K. Bal, S. Hazra, *Phys. Rev. B* 79 (2009) 155405.
- [48] S. Adachi, T. Arai, K. Kobayashi, *J. Appl. Phys.* 80 (1996) 5422.
- [49] F.J. Himpsel, F.R. McFeely, A. Taleb-Ibrahimi, J.A. Yarmoff, G. Hollinger, *Phys. Rev. B* 38 (1988) 6084.
- [50] A. Pasquarello, M.S. Hybertsen, R. Car, *Phys. Rev. B* 53 (1996) 10542.