Growth and stability of Langmuir-Blodgett films on OH-, H-, or Br-terminated Si(001)

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Growth of Langmuir-Blodgett (LB) films of nickel arachidate (NiA) on differently terminated (OH-, H-, or Br-terminated) Si(001) substrates and their structural evolution with time have been investigated by x-ray reflectivity technique and complemented by atomic force microscopy. Stable and strongly attached asymmetric monolayer (AML) of NiA is found to grow on freshly prepared oxide-covered Si substrate while unstable and weakly attached symmetric monolayer (SML) of NiA grows on H-terminated Si substrate, corresponding to stable hydrophilic and unstable hydrophobic natures of the substrates, respectively. The structure of LB film on Br-terminated Si substrate, however, shows intermediate behavior, namely, both AML and SML are present on the substrate, indicative of coexisting (hydrophilic and hydrophobic) nature of this terminated surface. Such coexisting nature of the substrate shows unusual growth behavior of LB films: (i) hydrophilic and hydrophobic attachments of NiA molecules in single up stroke of deposition and (ii) growth of few ring-shaped large-heights islands in subsequent deposition. These probably occur due to the presence of substrate-induced perturbation in the Langmuir monolayer and release of initially accumulated strain in the film structures near hydrophilic/hydrophobic interface, respectively, and provide the possibility to grow desired structures (AML or SML) of LB films by passivation-selective surface engineering.

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I. INTRODUCTION

Metal-organic films[1,2] of well-ordered structure and controlled thickness[3,4] can be grown easily using Langmuir-Blodgett (LB) technique.[5,6] Such LB films are ideal for testing basic physics of low-dimensional systems, viz., electrical transport, magnetism, and melting in two-dimensional (2D) systems,[6–8] specific growth mechanism arising from different types of observed in-plane correlations,[9–12] etc. These films also show unique properties and have promising applications in the field of biosensors, catalysis, nonlinear optics, microelectronics, and nanotechnology.[13–20] However, physical properties of LB films strongly depend on their structure. Defects,[2] imperfection,[21] and instabilities[22] in the structure are the main obstacles behind their proper applications. Defects, which are mainly observed in the LB films, are the "pinhole"-type defects[10,23] and can partially be removed by increasing pH (Refs. 24 and 25) of or by dissolving different metal ions[2] in the water subphase. Different substrates have also been used to understand the substrate effects in controlling LB structure.[2–4,22,26]

It is well known that substrate surface condition plays important role in the growth and stability of any nanolayer on it.[22,27] Substrate surface condition can be modified through different ways; by passivating with foreign atomic layer (such as hydrogen, bromine, etc.) or by growing self-assembled monolayer (of say silane). This essentially modifies the surface free energy or polarity of the surface and accordingly, wetting-dewetting or hydrophilic-hydrophobic nature of the surface can be tuned.[27–32] Studies of LB films on some such modified substrates have already been carried out, which show that the different layered structure can indeed be grown.[2,21,33,34] However, in-plane control or overall stability of such structure has not been studied well. On the other hand, strong influence has already been observed in the growth and stability (time-evolution in-plane and out-of-plane structures) of metal nanolayer on differently passivated silicon substrates,[27] namely, the interfacial instability at ambient conditions induces the wetting to dewetting transition in the Ag nanolayers, which then provides interesting nanostructures having different size, number density, and even crystallinity and/or epitaxy, depending on initial Si surface passivation. Such passivated Si surfaces also have different hydrophilic-hydrophobic nature, which can control the growth and stability of the LB films or can control the formation of interesting metal-organic nanostructures. However, not much study has been made in this direction.

In this paper, our aim precisely is to look into this matter and for that nickel arachidate (NiA) LB films have been deposited on differently terminated Si(001) substrates. The structure of the LB films and its evolution with time have been monitored using complementary x-ray reflectivity (XRR) (Refs. 35 and 36) and atomic force microscopy (AFM) (Refs. 2 and 37) techniques. It is clear from the study that hydrophilic-hydrophobic nature of the substrate and its relative strength and stability decide the growth of interesting structure and give rise to a possibility to tune them through proper passivation-selective surface engineering.

II. EXPERIMENT

Arachidic acid [$CH_3(CH_2)_{18}COOH$, Sigma, 99%] molecules were spread from a 0.5 mg/ml chloroform (Aldrich, 99%) solution on Milli-Q water (resistivity 18.2 MΩ cm) containing nickel sulfate ($NiSO_4.2H_2O$, Merck, 99%) in a Langmuir trough (Apex Instruments). The pH of the water subphase containing 0.2 mM nickel sulfate was maintained at 8.5–9.0 using sodium hydroxide (NaOH, Merck, 98%). No buffers were used to maintain the pH of the subphase. Nearly 8 h were spent for pH stabilization including initial magnetic stirring. Prior to deposition, surface pressure-specific molecular area ($\pi-A$) isotherm of NiA Langmuir monolayer on water surface was recorded. π was measured with a Wilhelmy plate and the monolayer was compressed at a constant rate of 3 mm/min. All depositions were done at $\pi = 30$ mN/m 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 treated differently. Different treatments provide differently terminated surfaces.[29,30] Such surfaces can be hydrophilic, hydrophobic, or mixed in nature. Si substrates were made OH terminated after keeping it in a mixed solution of ammonium hydroxide (NH_4OH, Merck, 30%), hydrogen peroxide (H_2O_2, Merck, 30%), and Milli-Q water ($H_2O:NH_4OH:H_2O_2=2:1:1$, by volume) for 5–10 min at 100 °C. OH-terminated Si substrates are expected to show hydrophilic nature.[29,30] Si substrates were made H terminated by keeping it in a solution of hydrogen fluoride (HF, Merck, 10%) for 3 min at room temperature (22 °C). H-terminated Si substrates are expected to show hydrophobic nature.[29,30] Br-terminated Si substrates were made after the removal of the oxide layer by HF etching and keeping it inside the Br-methanol solution (thoroughly rinsed by 0.05% Br-methanol solution). The nature of Br-terminated Si surface is not known. Immediately after the chemical treatment, all the substrates were kept inside the Milli-Q water until LB deposition. LB films on differently terminated Si(001) substrates were deposited using different numbers of down and/or up strokes of substrates through Langmuir monolayers. On OH-terminated Si surfaces, two NiA LB films were deposited, one by one (up) stroke and another by three (up-down-up) strokes, referred as 1*s*-NiA/OH-Si and 3*s*-NiA/OH-Si, respectively. On H-terminated Si surface, one NiA LB film was deposited by two (down-up) strokes and referred as 2*s*-NiA/H-Si. On Br-terminated Si surfaces, three NiA LB films were deposited, first by one (up) stroke, second by two (down-up) strokes, and third by three (up-down-up) strokes, referred as 1*s*-NiA/Br-Si, 2*s*-NiA/Br-Si, and 3*s*-NiA/Br-Si, respectively. Films have been checked for reproducibility.

XRR measurements were carried out using a versatile x-ray diffractometer (VXRD) setup as a function of time to see the evolution of LB films on differently pretreated Si(001) substrates. VXRD consists of a diffractometer (D8 Discover, Bruker AXS) with Cu source (sealed tube) followed by a Göbel mirror to select and enhance Cu $K\alpha$ radiation ($\lambda = 1.54$ Å). The diffractometer has a two-circle goniometer (θ-2θ) with quarter-circle Eulerian cradle as sample stage. The latter has two circular (χ and ϕ) and three translational (X, Y, and Z) motions. Scattered beam was detected using NaI scintillation (point) detector. Data were taken in specular condition, i.e., the incident angle (θ) is equal to the reflected angle (θ) and both are in a scattering plane. Under such condition, a nonvanishing wave-vector component, q_z, is given by $(4\pi/\lambda)\sin\theta$ with resolution 0.0014 Å^{-1}. XRR technique essentially provides an electron-density profile (EDP), i.e., in-plane (x-y) average electron density (ρ) as a function of depth (z) in high resolution.[38] From EDP it is possible to estimate film thickness, electron density, and interfacial roughness. Analysis of XRR data has been carried out using Parratt's formalism.[39] For the analysis, each film has been divided into a number of layers including roughness at each interface.[40]

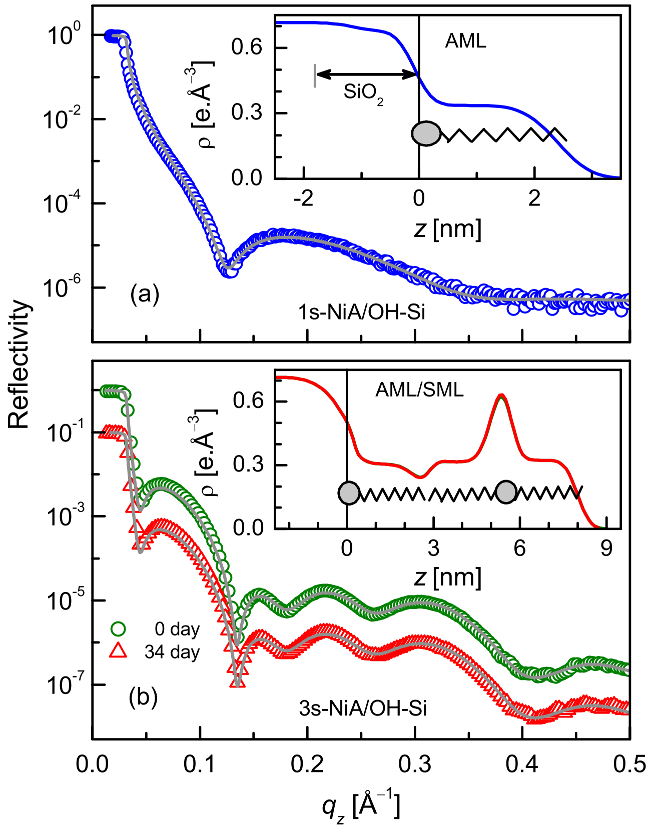

FIG. 1. (Color online) XRR data (different symbols) and analyzed curves (solid line) of NiA LB films deposited on OH-terminated Si(001) substrates, (a) after deposition by one stroke and (b) as a function of time after deposition by three strokes (curves are shifted vertically for clarity). Insets: corresponding EDPs showing possible structures and stability of LB films on OH-terminated surfaces.

The topography of the NiA LB films on differently passivated Si(001) substrates were mapped through AFM technique, few days after deposition. Topographic images were collected either in tapping or noncontact mode to minimize the silicon-tip-induced damage of the soft film. Scans of different sizes and in different portions of the sample were carried out to get statistically meaningful information about the topography. WSXM software[41] has been used for AFM image processing and analysis.

III. RESULTS AND DISCUSSION

A. X-ray reflectivity and electron-density profile

1. NiA LB films on OH-terminated Si substrates

XRR data and analyzed curves of NiA LB films deposited by one stroke and three strokes on freshly oxide grown Si(001) substrates are shown in Fig. 1. EDPs obtained from the analysis are shown in the inset of Fig. 1. EDPs confirm that the NiA molecules are attached to the substrates through heads and formed single asymmetric monolayer (AML, i.e.,

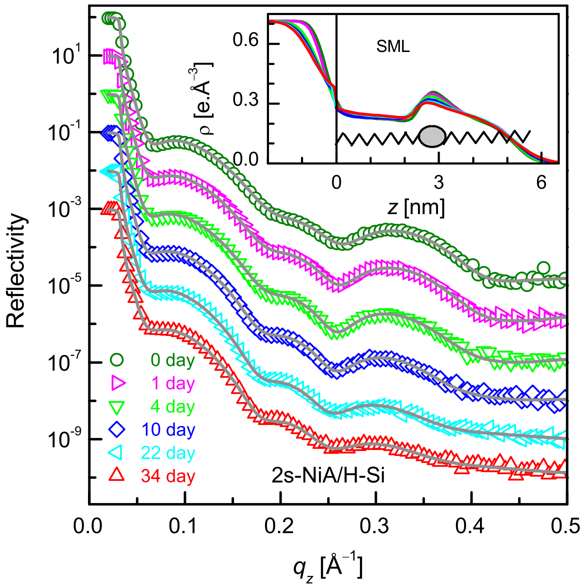

FIG. 2. (Color online) Time-evolution XRR data (different symbols) and analyzed curves (solid line) of NiA LB film on H-terminated Si(001) substrate, deposited by two strokes (curves are shifted vertically for clarity). Insets: corresponding EDPs showing possible structures and stability of LB films on H-terminated surfaces.

molecules in asymmetric configuration[42] with hydrophilic head in one side and hydrophobic tails in other side) structure in 1*s*-NiA/OH-Si LB film, while formed one AML followed by one symmetric monolayer (SML, i.e., molecules in symmetric configuration[42] with Ni containing head in the middle and hydrocarbon tails in both sides) structures in 3*s*-NiA/OH-Si LB film. EDP of 3*s*-NiA/OH-Si LB film also suggests that the coverage of the top SML structure is similar to that of bottom AML structure. It can be noted that the thickness of one SML is double that of one AML. No changes have been observed in the XRR curves and its analyzed EDPs with time, suggesting clearly that such LB films are very stable.

2. NiA LB films on H-terminated Si substrates

Time-evolution XRR data and analyzed curves of NiA LB film on HF-treated Si(001) substrate, deposited by two strokes, are shown in Fig. 2. EDPs obtained from the analysis are shown in the inset of Fig. 2. EDPs suggest that the NiA molecules are attached to the substrate through tails and form one SML. However, the height and width of the peak (corresponding to the heads) in the EDPs clearly indicate that the coverage as well as the organization of molecules in the SML are less compared to that of three strokes NiA LB films deposited on OH-terminated Si(001) substrates. Also, the NiA LB film on the H-terminated Si(001) substrate is not very stable. Changes with time, although small, are evident from the EDPs. The electron densities of the top portion of the substrate and the head region of the film decrease with time. The first one can be associated with the growth of native oxide on silicon, which takes place even in presence of covered layer[27,38] while the latter one might be due to the reorganization (or configurational change) of the NiA molecules. To understand such changes or instability of the film quantitatively, the oxide coverage (C_{ox}) at substrate surface and the head amount (M_H) in SML configuration have been plotted in Fig. 3. The growth of C_{ox} or the decay of M_H can be analyzed using following relations:

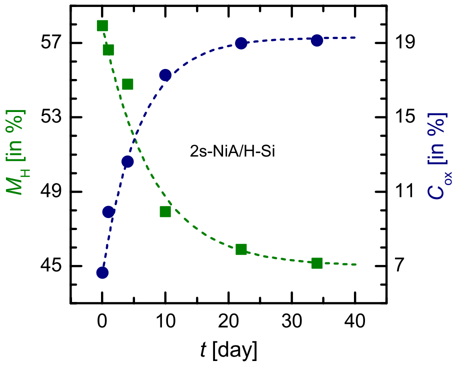

FIG. 3. (Color online) Head amount (M_H) in SML configuration and oxide coverage (C_{ox}) at substrate surface as a function of time (t) for NiA LB film on H-terminated Si(001) substrate, deposited by two strokes.

$$C_{\mathrm{ox}}(t) = C_{\mathrm{min}} + \Delta C(1 - e^{-t/\tau_{\mathrm{ox}}}), \tag{1}$$

$$M_H(t) = M_{\mathrm{min}} + \Delta M e^{-t/\tau_H}, \tag{2}$$

where C_{min} is the minimum oxide coverage present initially, $C_{\mathrm{min}}+\Delta C$ is the maximum oxide coverage reached finally, ΔC is the change in coverage, and τ_{ox} is its growth time while $M_{\mathrm{min}}+\Delta M$ is the maximum head amount present initially, M_{min} is the minimum head amount reached finally, ΔM is the change in head amount, and τ_H is its decay time. The analyzed curves obtained using Eqs. (1) and (2) are shown in Fig. 3. The analysis shows that the change in both the parameters with time is about 13% while the value of τ_{ox} is about 6 days and that of τ_H is about 8 days.

3. NiA LB films on Br-terminated Si substrates

XRR data and the analyzed curves of NiA LB films on Br-terminated Si(001) substrates, deposited by different numbers of strokes, are shown in Fig. 4. Corresponding EDPs are shown in the inset of Fig. 4, which indicate that in all the cases the attachments of NiA molecules with Br-terminated Si surfaces are partially through heads and partially through tails. EDPs of the films deposited by one and two strokes are almost similar. In both cases the Br-terminated Si surface is covered with two different structures, namely, AML and SML. EDP of the film deposited by three strokes is quite interesting. Deconvolution of EDP suggests that, in such film, Br-terminated Si surface is covered with four different structures, such as AML, SML, AML/SML, and SML/SML. Also no appreciable change in the EDP has been observed as a function of time, suggesting such structures of NiA LB films on the Br-terminated Si surface are quite stable.

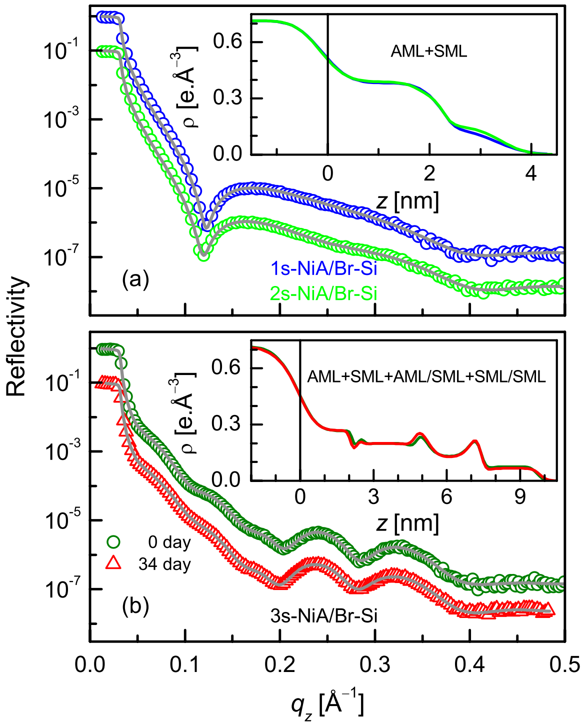

FIG. 4. (Color online) XRR data (different symbols) and analyzed curves (solid line) of NiA LB films on Br-terminated Si(001) substrates (a) after deposited by one and two strokes and (b) at two time intervals after deposited by three strokes. Curves are shifted vertically for clarity. Insets: corresponding EDPs showing possible structures and stability of LB films on Br-terminated surfaces.

B. Atomic force microscopy and topography

AFM images of NiA LB films deposited on differently terminated Si(001) substrates after prolonged evolution are shown in Fig. 5. Topography is composed of different heights or layers, which are indicated by the number (in unit of AML length) in the images. It is again necessary to mention that the height of SML (~5.5 nm) is double of that of AML (~2.7 nm). So, the numbers 0, 1, 2, 3, and 4 correspond to the heights of Si surface (reference plane), AML (~2.7 nm), SML (~5.5 nm), AML/SML (~8.2 nm), and SML/SML (~11.0 nm) structures, respectively. Topography of NiA LB film on OH-terminated Si surface, deposited by three strokes [Fig. 5(a)], shows that the top surface is quite smooth (compact) with some pinhole defects, characteristics of LB films.[2,10,25] The observed heights of the pinhole-type defects, i.e., the depths of the black regions from top surface are mostly about 5 nm with maximum about 8 nm. Considering maximum depth arising from the bare Si substrate, the thickness and the corresponding structure of the film are about 8 nm and AML/SML, respectively, consistent with the XRR analysis. On the other hand, though the heights of the majority of the defects, according to the AFM image, are about 5 nm (which corresponds to the absence of top SML structure), the actual heights of the majority of the defects are about 8 nm (corresponding to the absence of total AML/SML structure) as evident from the EDP (no significant decrease in the electron density of the top SML region compared to that of the bottom AML one). This difference can be understood by considering the convolution effect of the AFM tip with the small in-plane size pinhole defects, which restrict the estimation of actual depth. Defect free or at least small size defects are expected for the LB films deposited at high pH compared to that for the normal pH one.[25] Topography of NiA LB film on H-terminated Si surface, deposited by two strokes [Fig. 5(b)], shows that the top surface is relatively rough (less compact) although defect free. The relative height of the film compared to the scratched portion [Fig. 5(c)], corresponds to the SML thickness, consistent with the XRR analysis. It can be noted that the LB film on H-terminated Si surface can be easily scratched with AFM tip by applying force, just above 1.5 nN, unlike LB films on other terminated Si surfaces. Topography of NiA LB film on Br-terminated Si surface, deposited by two strokes [Fig. 5(d)], shows areas having two distinct heights. The height difference is about 2 nm. Considering the XRR results, low and high height areas can be identified as AML and SML, respectively. Topography of NiA LB film on Br-terminated Si surface, deposited by three strokes [Fig. 5(e)], verifies the presence of four different structures, as obtained from the XRR results. It is necessary to mention that apart from such four structures, ring-shaped islands of large heights [Fig. 5(f)] are also present. However, number or fractional cover-

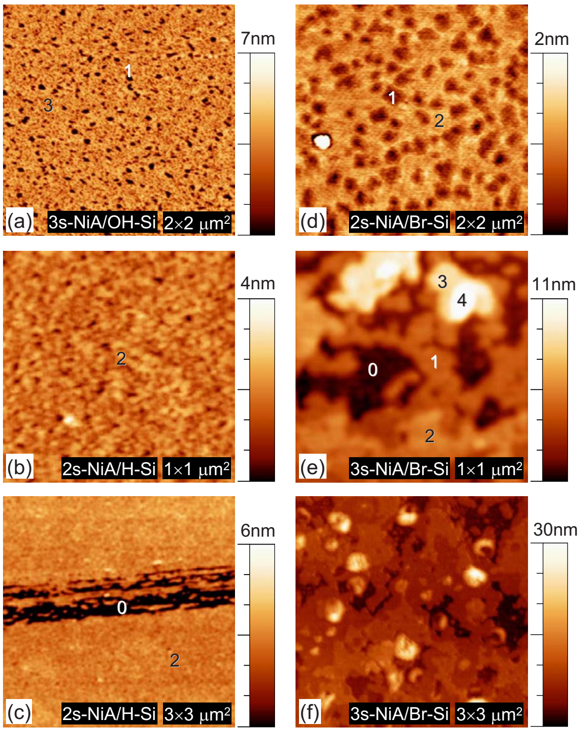

FIG. 5. (Color online) AFM images showing topography of NiA LB films (a) on OH-terminated Si(001) substrates, deposited by three strokes, of scan size 2×2 μm^2, (b) and (c) on H-terminated Si(001) substrate, deposited by two strokes, of scan sizes 1×1 and 3×3 μm^2, respectively, (d) on Br-terminated Si(001) substrates, deposited by two strokes, of scan size 2×2 μm^2, and (e) and (f) on Br-terminated Si(001) substrate, deposited by three strokes, of scan sizes 1×1 and 3×3 μm^2, respectively. Presence of layers of different heights (in unit of AML length) are indicted by the numbers.

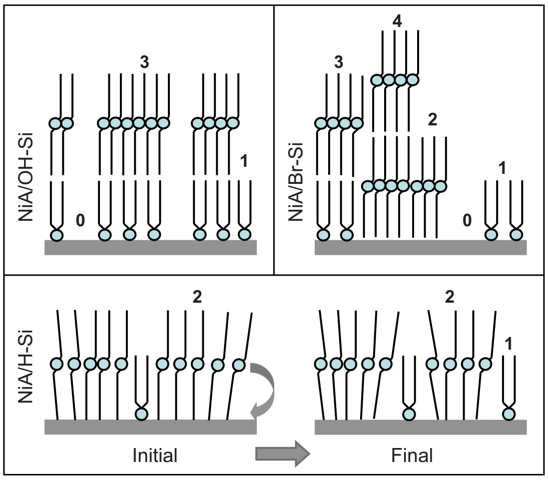

FIG. 6. (Color online) Schematic illustration of structures of NiA LB films on differently terminated Si(001) substrates and their time evolution. Different numbers indicate the heights (in unit of AML length) of a film on those areas with corresponding structures.

age of those islands are very small and do not appear in the XRR results as they are insensitive to the analysis.

C. Structure and growth mechanism

The structures of the NiA LB films on differently terminated Si substrates, as obtained from the EDP and topographic results, are shown schematically in Fig. 6. In order to understand the structure or growth mechanism of the LB films on differently terminated Si surfaces, let us first discuss little bit about Si surface passivation mechanism. Treatment of Si substrates with mixed solution of H_2O, NH_4OH, and H_2O_2, dissolves native oxide layer in one hand and reoxidizes the Si on the other hand, as a result hydroxyl (OH) ion attacks the Si surface and forms silanol group (Si-OH). This wet chemically grown oxide layer, terminated with OH, passivates the surface and also makes the surface hydrophilic.[29,30] Treatment of Si substrate with HF, removes the native oxide layer and makes the Si surface H passivated, which is hydrophobic in nature. It is well accepted that such native oxide etching and passivation of silicon surface occur in two steps: in first step, the oxide layer is rapidly dissolved and forms SiF_6^{2-} ions in HF solution, making the surface temporarily F terminated. In second step, large electronegativity of F polarizes the Si-Si back bonds[43] and anodic dissolution of the last monolayer of oxidized Si (Si^{n+} with $n=1,2,3$) takes place, resulting H-passivated Si surface with dihydride species on the (001) surface and monohydride species on the (111) surface.[29,30] When the H-terminated substrate is further subject to the treatment with Br-methanol solution, then relatively strong electronegativity of Br atom helps to replace the H atom, leaving the surface Br passivated.

It can be noted that the hydrophilic or hydrophobic nature of the surface can be easily verified with naked eyes. As it is known that if the surface is hydrophilic, the water layer tries to wet the surface and if the surface is hydrophobic, it dewets. So, by observing the wetting or dewetting properties of the water with the surface, one can infer the nature of the surface, at least qualitatively. Regarding stability, it is well known that oxide-passivated (here OH-terminated) Si surface is stable but H- or Br-passivated Si surface is not so stable in ambient condition, even in the presence of overlayer.[27,38] With time, H- or Br-passivated layer desorbs and native oxide layer grows. The growth time of oxide layer is, however, different for differently passivated surface.

1. AML/$(\mathrm{SML})_n$ *on OH-terminated Si surfaces*

As the OH-terminated Si surface is hydrophilic in nature, the attachment of NiA molecules to the substrate is through hydrophilic heads, which takes place during first up stroke of deposition. Consequently, the first layer is AML and subsequent layers are SMLs. Single SML forms after one complete down-up stroke. Accordingly, AML/$(\mathrm{SML})_n$ structure can be grown on OH-terminated Si substrate by n number of down-up strokes after first up stroke. The in-plane structure of the film is quite smooth, apart from pinhole defects. Presence of pinhole defects is the signature of less number of molecules in a layer, which is probably related to the transfer ratio less than 1 and/or further dissolution. Observed structure (shown schematically in Fig. 6) can be understood considering strong in-plane (head-head) interaction of NiA molecules compared to out-of-plane (substrate-head) interaction and uniform nature of the passivated Si surface. Combination of both probably allow NiA molecules to diffuse in plane to form compact smooth structure separated by defects. Since the OH-terminated Si surface is stable, the LB structure form on it is also stable.

2. SML/$(\mathrm{SML})_n$ *on H-terminated Si surfaces*

The H-passivated Si surface behaves hydrophobic in nature and correspondingly hydrophobic tails of NiA molecules attached to the substrate during first down stroke of deposition. After complete down-up stroke, the layer that form on the substrate is SML, which will be same for subsequent down-up strokes. Accordingly, SML/$(\mathrm{SML})_n$ structure can be grown on the H-terminated Si surface by n number of down-up strokes after first down-up stroke. It can be noted that no pinhole defects have been observed (from AFM), although there are less number of molecules in a layer (as evident from EDP), which can be understood considering inhomogeneous and unstable natures of the H-passivated Si surface.[27] Inhomogeneous nature probably imposes restriction in the in-plane diffusion of NiA molecules through tails within hydrophobic domains while the growth of hydrophilic region through open space destabilizes the nearby molecules, making the in-plane structure comparatively rough and less compact. Additionally, the in-plane and out-of-plane interactions of NiA molecules on H-terminated surface are through tail-tail and substrate-tail, respectively, unlike NiA molecules on OH-terminated surface. Such different interactions can also play some role in making different structure.

With time, depending upon the compactness of the film, native oxide layer grows in some fraction of the Si surface [indicated by C_{ox} (Fig. 3)], transforming hydrophobic nature of that fraction to hydrophilic. Hydrophilic part then tries to

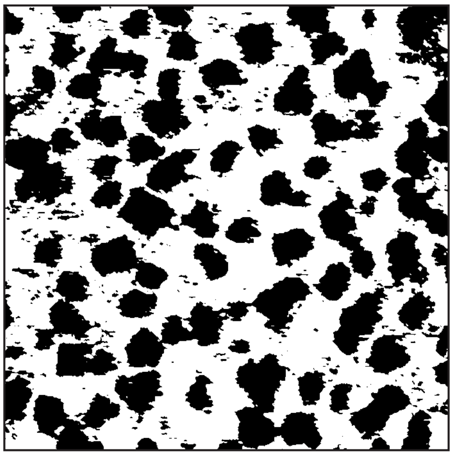

FIG. 7. Schematic presentation of Br-passivated Si(001) surface showing presence of both hydrophobic (white) and hydrophilic (black) areas, arising from inhomogeneous nature of passivation. The surface areas, where native oxide layer already grown are considered hydrophilic while the area, which till remains Br-passivated is considered hydrophobic.

repel tails and attract heads, which creates further instabilities in the film and modifies the structure (shown schematically in Fig. 6) at the later stages of growth. But again depending upon the compactness of the film, not all heads are able to reach the substrate. Nonetheless, those heads are dislodged from the initial z position [as evident from time-evolution EDP (Fig. 2) and indicated by M_H (Fig. 3)]. The oxide growth time (τ_{ox}) that obtained from the analysis is about 6 days, which is a measure of the stability of the H-passivated Si(001) surface in presence of NiA LB covered film. On the other hand, the decay time of head amount (τ_H) is about 8 days, which is a measure of the stability of NiA LB film on H-passivated Si(001) surface. $\tau_H > \tau_{\text{ox}}$ clearly indicates that the instability in the film occurs once (after) instability in the interface takes place.

3. $\mathbf{AML/(SML)_{0,1,\ldots,n}+SML/(SML)_{0,1,\ldots,n}}$ *on Br-terminated Si surfaces*

The Br-passivated Si surface is whether hydrophilic or not, is not known. However, it is known that the Br-passivated Si surface is more unstable than H-passivated Si surface[27,38] and inhomogeneous in nature. So, it is expected that prior to deposition, oxide layer might have grown on some portion of the Br-treated Si surface by replacing the Br atom. This has been shown schematically in Fig. 7. The areas, which are weakly passivated (shown by black color) can change easily to oxide-covered one, thus becoming hydrophilic while other areas, which are strongly passivated (shown by white color) still remain Br passivated and probably behave like hydrophobic.

Deposition of NiA LB film on Br-passivated Si substrate, by one stroke or two strokes, show nearly similar structure. By deposition through single up stroke, heads of NiA molecules are expected to attach with the hydrophilic portion of the substrate and accordingly, AML structure with partial coverage, is only expected. However, in practice SML structure is also observed. The coverage of the film, combining AML and SML, is quite good as evident from the EDP [Fig. 4(a)]. This can occur either by direct attachments of heads and tails to the hydrophilic and hydrophobic portions, respectively, or through continuous diffusion and configurational change in some of the NiA molecules from initially attached hydrophilic to nearly hydrophobic portions thereby enabling further attachment to the hydrophilic portion during single up stroke. Any such unusual process can take place if the inhomogeneous nature of the substrate creates perturbation in the Langmuir monolayer or if the flipping speed is much higher than deposition speed. In case of deposition through a complete down-up stroke, tails of NiA molecules are attached to the hydrophobic portion of the substrate during down stroke while heads are attached to the hydrophilic portion during up stroke. Accordingly, both AML and SML structures grow on Si surface, as observed experimentally.

In subsequent down-up stroke of deposition, SML structure is expected to grow above the previous one and accordingly, $\text{AML}/(\text{SML})_n+\text{SML}/(\text{SML})_n$ structure is expected to form by n such down-up strokes. In practice, we observed $\text{AML}/(\text{SML})_{0,1,\ldots,n}+\text{SML}/(\text{SML})_{0,1,\ldots,n}$ structure with some ring-shaped islands of large heights. Due to the presence of both hydrophobic and hydrophilic regions, strain is probably developed in the structure across the hydrophobic/hydrophilic interface. Such strain, which is developed in the film by one or two strokes of deposition, will try to release. We propose that in subsequent deposition this release takes place by flipping of some molecules from the substrate and dumping it near that interface. Large-heights ring-shaped islands are formed due to this dumping while AML or SML structure again formed by deposition in the region from where the materials have been flipped off. If this is the process, then size and shape of the ring should be related to those of the hydrophobic areas in the Br-terminated surface [i.e., AML areas in Fig. 5(d) or black areas in Fig. 7]. Although there are some similarities, we find deviation as well. So further studies are require for proper understanding.

D. Inference on possible physical properties

Knowing the structures and stabilities of different LB films one can infer about their possible physical properties, which however need actual measurements for verification. The electrical transport and magnetic properties of 2*s*-NiA/H-Si LB film are expected to behave closer to perfect 2D system,[44] as single and nearly continuous sheet of Ni is formed in such film unlike others. On the other hand, the interaction of LB film with OH-terminated substrate is strong, which must appear in its mechanical properties. Indeed this has been observed while imaging the topography with AFM in contact mode, namely, easy movement of LB film on H-terminated surface compared to that on OH-terminated one by means of AFM tip. Also, large number of well-stacked layers of LB film can be prepared on OH-terminated Si surface, which is expected to provide electrical transport and magnetic properties similar to that for parallel 2D sheets (separated by ~5.5 nm) with or without defects.[45] The size and number density of such defects can be controlled, to some extent, through pH.[42] Although the stability of the Br-terminated Si surface is less compared to that of the H-terminated one, it seems that the interaction, hence the mechanical stability of LB film is otherwise. Due to the initial instability of the Br-terminated surface, hydrophilic and hydrophobic domains are formed before deposition. Accordingly, parallel disks on one type of domain are vertically shifted by half of the parallel sheet separation compared to that on other type of domain. Electrical transport properties of this interesting structure is likely to be that of weakly connected (through hydrocarbon tails of length ~2.7 nm) sets of parallel (separated by ~5.5 nm) 2D disks (made of Ni heads).

IV. CONCLUSIONS

Structural changes in NiA LB film with different passivations of Si(001) surface have been studied by XRR and AFM techniques. By introducing the foreign atomic layer of H and Br in place of native oxide layer on Si(001), the nature of the substrate can be changed and accordingly different structured LB films, such as AML, SML, or AML plus SML having different stability can be prepared. AML structure, which grows on freshly covered oxide surface is quite stable and strongly attached while SML structure, which grows on H-passivated surface is weakly attached and not so stable. Oxide layer, at the NiA-Si interface of the latter one, grows by desorbing the H atoms, modifies the nature of the interface from hydrophobic to hydrophilic and creates instability in the film. Whereas, hydrophilic (weakly Br-passivated) and hydrophobic (strongly Br-passivated) regions coexist on Br-passivated Si surface and both AML and SML structures form on substrate even in single up stroke of deposition, which is either through direct deposition or through quick diffusion and configurational change. In such structures, strain seems to develop at the hydrophilic/hydrophobic interface. On further down-up stroke, AML and AML/SML structures grow on hydrophilic regions while SML and SML/SML structures grow on hydrophobic regions. Additionally, few ring-shaped islands of large heights are also observed, which are probably occur due to the release of so-called strain in the LB structures by subsequent deposition. Thus by controlling the shape, size, and strain (relative strength) of hydrophobic/hydrophilic interface, interesting metal-organic nanostructures can be grown.

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