

Modification of Octadecylphosphonic acid Langmuir-Blodgett film on Aluminium oxide surface by hydrogen ion bombardment and its characterization

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Abstract

We report surface modification with kinematics-driven reaction on uniform and well-ordered Octadecylphosphonic acid Langmuir-Blodgett on aluminium oxide surface and characterized few of its mechanical properties using different surface analysis techniques. The hyperthermal hydrogen induced collision (HHIC) approach with low proton energy can induce the hydrocarbon long chain chemical bonding and the actual ordered LB lattice into an array of clusters of the OPA virgin film. By enhancing the kinematics-driven reaction fluence at constant bombardment energy, the nanocluster growth of OPA coated surface can be controlled on aluminum oxide substrate. Following this, in a specified reaction condition with a controllable degree of cross-linking, this hyper thermal hydrogen-driven reaction can modify the cluster shape and consequently enhance the mechanical strength as well. The OPA Langmuir-Blodgett film on oxidized Al was the only system stable enough to retain a cohesive and smooth molecular layer after the cross-linking process in compared with Muscovite mica and silicon oxide substrates.

Keywords: Langmuir-Blodgett film, Atomic force microscopy, Self-assembled monolayers, Octadecylphosphonic acid, Silicon wafer, X-ray photoelectron spectroscopy, Contact angle, Surface energy, Hydrogen bombardment, Cross-linking.

1 INTRODUCTION

For many-polymer system, it has been observed that the polymeric long hydrocarbon chain is a crucial factor in forming the monolayer using self-assembly monolayer technique; rather it has been examined and proved in this research that this is not a factor in using Langmuir-Blodgett technique. The main difficulty is to deposit well-ordered Octadecylphosphonic acid film on roughed aluminium oxide surface to form the Aluminium

oxide-functional group system. Nowadays, the experiment of Langmuir-Blodgett film on variety of surfaces gives rise to nanomaterial scientists with a significant importance. Langmuir-Blodgett monolayers are well-ordered and homogeneous molecular assemblies which are continuously formed by the transformation of molecules lied on the DI water with functional head groups that enables well-ordering on the different substrates¹. Langmuir-Blodgett films are now of great interest in vast amount of scientific literature due to its potential application, such as, microelectronics, biosensors, biomedical devices and so on².

Polymeric amphiphilic molecules immersed in a solution can be adsorbed on a metal substrate results an ordered assembly of molecules^{3,4}.

According to Woodward et al., the interaction occurred between the OPA functional headgroup and variety of surfaces serves as a model system to understand molecule-substrate interaction. In addition, organic phosphonic acid dissolved in a polar or non-polar solvent is expected to have strong adsorption with Al oxide surface in self-assembly-monolayer technique. For short-length organic phosphonic acids, the functional phosphonic headgroup adsorbed with chemical bonding onto oxidized Aluminium surface extracting the water molecules where the bonding between organic phosphonic acid and Al oxide surface is formed via P-O-Al through condensation reaction of overlayer group with surface hydroxyl groups. In this work, the aluminium-oxide functional acid system has been examined. Aluminium holds a potential in expanded demand of technological applications. And phosphonic acid functional group plays a significant role on Al substrate with a condensation reaction where hydroxyl groups on the surface interact with those from the headgroup of the phosphonic acid. The chemical bonding of the functional acid group, PO(OH)₂, with the oxide is much more stronger than carboxylic acid group which is one of the reasons to imply this in this work. I describe in this work modification of OPA on interacting the functional phosphonic headgroup with hydrophilic surface of oxidized Al.

2 MATERIALS AND METHODS

2.1 OPA LB preparation

The solution of OPA (n-Octadecylphosphonic Acid, $\text{CH}_3(\text{CH}_2)_{17}\text{P}(\text{O})(\text{OH})_2$; purchased from Alfa Aesar, Ward Hill, MA) with concentration 1mM (3.34 mg/10ml, Molecular weight of OPA: 334.47 g/mole) dissolved in chloroform (99.9%; Alfa Aesar, Ward Hill, MA) was made in room temperature. Later on, the solution was heated with hotplate to 65°C for 20 min prior to use. Following this, the amphiphilic organic molecules layer was compressed at a speed of $2.3\text{-}2.5\text{ cm min}^{-1}$ by the double barrier of LB system. The Aluminium substrate was then dipped through the water subphase maintaining the Y-type method to transfer the OPA phosphor-organic molecules onto the hydrophilic substrate. During the LB experiment real time surface pressure was continuing to measure with a paper Wilhelmy plate which was suspended from a KSV microbalance at around $23.4\pm 0.2^\circ\text{C}$.

2.2. Preparing substrate

A layer of 50-nm-thick Al film was deposited with the HOSER E-beam metal evaporator onto cleaned n-type Si (100) wafer. 99.9995% pure Al target was used at $\sim 10\text{ kV}$ in this evaporation process. Later the Al sample was blown with N_2 gas and was pre-treated with UV/ozone experiment with a discharge ozone generator from dry air flow for around 60 min. UV/ozone experiment was served to remove organic contamination from the Al surface and render it more hydrophilic. And it exposed in air in lesser period of time.

3 RESULTS AND DISCUSSIONS

Physical appearance of OPA on Al oxide

Fully extended OPA with long zigzag tail is a linear-shaped amphiphilic molecule with a length of 2.5 nm whereas the length of tail is around 2.2 nm. The phosphonic acid group contains three oxygen groups which might interact with substrates differently depending on its constituents.

The orientation of the molecules on variety of substrates is coverage-dependent, that is, “lying down” phase is related with low coverage whereas “standing up” phase is observed in high coverage. On rough surfaces ($>1\text{ nm}$) such as Al, it is difficult to measure the real height of film molecules with an optical method due to its undulation/corrugation difficulties of aluminium oxide surface. In the following table, we show our results of OPA thickness onto Al oxide where corresponding angle of those surfaces determined by general geometry as well.

However, we performed XPS EAL (Effective Attenuation length) method to determine the approximate thickness of OPA molecules on Al oxide surface. This

model used for quantitative XPS analysis requires specific assumptions and empirical parameters.

In this formalism, the observed intensity of the aluminium substrate signal, I_{Al} , is given by the intensity from a clean aluminium substrate, $I_{\text{Al}0}$, attenuated by the OPA film of thickness t as, $t = -L_{\text{Al}} \ln[I_{\text{Al}}/I_{\text{Al}0}]$

Where, I_{Al} -> **intensity of the OPA on Al substrate signal (Al)**

$I_{\text{Al}0}$ -> **intensity of the clean Al substrate signal (Al)**

t -> **thickness of overlayer**

L_{Al} -> **EAL of Al (measured using NIST program)**

Table 1. OPA layer thickness for Al (2s), Al (2p) and corresponding angle determined by XPS EAL methods and normal geometry respectively.

Thickness (nm) measured by XPS EAL method	2.0 (for both 2s and 2p spectra)
Corresponding angle away from normal (in degree)	53°

Table 1 shows OPA layer thickness for Al (2s), Al (2p) and corresponding angle determined by XPS EAL methods and normal geometry respectively.

After oxidizing and cleaning the Al film using UVO treatment and with nitrogen gas blowing, on which OPA LB film was formed immediately. The average corrugation height of Al surface was greater than 1 nm (Figure 1a), where it seems that the thickness of OPA LB film is $1.9 \pm 0.2\text{ nm}$ (Figure 1b), is greater than that of bare Al oxide surface. Figures 1b and 1d shows the phase shift image of those corresponding topography images. Comparing with the extended OPA molecular length and the estimated height of OPA coated thin film on Al oxide suggests that OPA molecules are tilted on the Al surface. We observed that due to greater rms roughness features, OPA monolayer surface can not be observed with AFM morphology for thicker surface (around 180 nm) showing a rather rough surface. Surface corrugation thickness should be less than 2.5 nm to detect the OPA monolayer using AFM method and therefore surface is to be pre-treated to control the corrugation height before transferring the OPA molecules on it. I believe first full-coverage OPA LB film evidence on bare non-crystalline Aluminium oxide surface has been shown in this work. One can control the coverage of OPA with controlling the barrier of LB trough, concentration of OPA solution and amount of solution to be poured onto the subphase (water). Monolayers containing OPA molecules formed on the subphase surface were transferred to Al

oxide at a surface pressure of ~ 60 mN/m. These monolayers do not show mixture of small and large islands, rather they show full coverage LB film. Note that the irregularity of OPA coated Al surface results the incapability to determine the lower coverage OPA molecules using AFM technique. It has been observed the height of the highest phases are 1.9 ± 0.2 nm higher than surrounding bare surface, whereas some lower phase has higher depth, 2.3 ± 0.2 nm, suggests higher rms roughness of bare Al surface. Phase shift (Fig. 1b) image of a bare aluminium is planer than that of OPA coated surface (Fig. 1d) which indicates that the similar mechanical properties are found in uncoated surface and distinguished properties found in coated surface due to irregularity of OPA surface that confirms OPA molecules on substrate. The variable of Al thickness after a certain level (100 nm) changes the morphology of OPA layer dramatically. Note that the chemical analysis of X-Ray photoemission spectrum allows us to visualize the existence of OPA molecules that might not be confirmed by scanning microscopy technique.

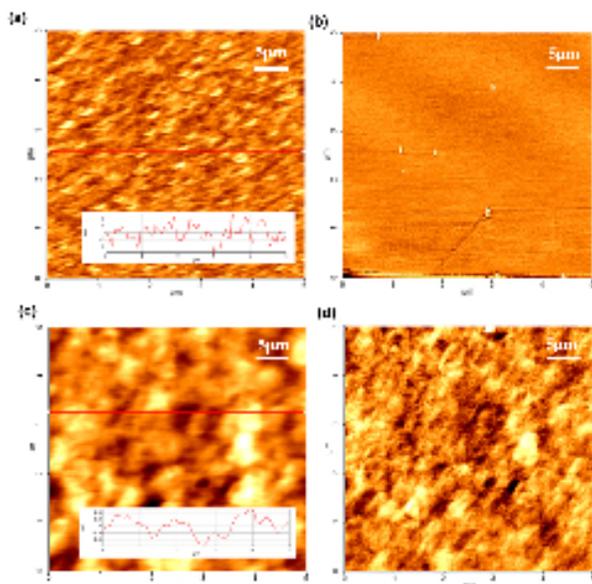


Fig 1. Schematic illustrations of non-contact dynamic force mode AFM images (scan area: $5 \mu\text{m} \times 5 \mu\text{m}$) of (a) UV/Ozone treated bare Al oxide surface: (a) topography image and (b) phase shift image; OPA LB film morphology at $23.4 \pm 0.2^\circ\text{C}$: (c) topography image and (d) phase shift image. Inset shows the root mean square roughness of those corresponding film.

Surface Modification: OPA coated aluminium oxide as a function of bombardment time

The kinematics driven reaction in order to cross-link molecular OPA LB films on aluminium oxide with specific mechanical and chemical properties had been implemented in this work by adopting hyperthermal hydrogen-hydrocarbon collision. In order to develop applications of

the HHIC technique, we demonstrate breaking C-H bonds without any breaking phosphonic acid headgroups ($-\text{P}(\text{O})(\text{OH})_2$), which results in cross-linking of C-C between the alkyl chains of OPA on an Al oxide.

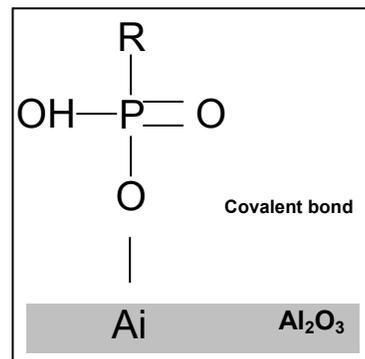


Fig 2. Condensation reaction of hydroxyl of phosphonic acid group with aluminium surface.

Fig. 2. illustrated the OPA bonding with aluminium with condensation reaction where water molecule is extracted from this chemical reaction. Indeed, here we would show the modified morphology of cross-linking OPA coated films on Al surface in comparison with varying bombardment time. In this experiment, hydrogen projectile having kinetic energy of ~ 5 eV with 8.0×10^{-4} Torr was employed with a function of two bombardment times 10 s and 40 s. The cross-linked OPA LB film shows an increase in mechanical strength with intact chemical functionalities as determined from analyses of AFM and XPS.

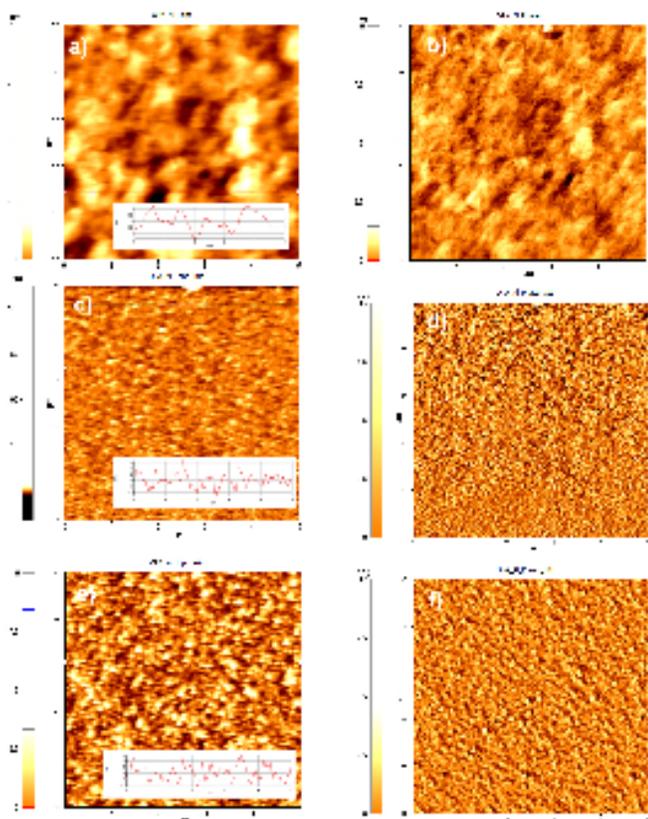


Fig 3. Schematic illustrations of non-contact dynamic force mode AFM images (scan area: 5 μm X 5 μm) of OPA LB film morphology: (a) topography image and (b) phase shift image; modified surface with hyperthermal hydrogen induced collision which was bombarded for (c) 10 s (topography) (d) 10 s (phase shift) (e) 40 s (topography) (f) 40 s (phase shift) onto 50 nm thick evaporated Al film. Inset shows the rms roughness of those corresponding film.

According to Fig. 3 c, the AFM images show that the domain structure of the OPA monolayer has been broken into smaller shapes after 10 s bombardment and the size of domain is greater with higher bombardment time, 40 s (Figure 3 e). Figs. 3 a and b show coated OPA topography and phase shift image with 0s bombardment. The root-mean square deviation of the 10 s bombarded sample was 2.4 nm and that of the 40 s 4 nm. Figs. 3d and 3f show phase shift images where the a bit changes has been observed with the function of bombarded time in this kinematics-driven reaction effect indicating that the molecules were becoming a little bit aggregated and mosaic-shaped.

To sum up, it is clearly seen that the degree of residual defects was enhanced with increasing the degree of cross-linking. Root mean square roughness was increased significantly after bombardment and cluster size became larger with increasing bombardment time. It seems that for 40 s.

Hyperthermal hydrogen collision leads to C-H cleavage preferentially with no cleavage of phosphonic acid group of adsorbed hydrocarbon When adjacent molecules

form cross-linked C-C bond to replace van der Waals interaction forces, this change may overcome the substrate-molecule adsorption. Therefore, increasing the degree of cross-linking as a function of time (40 s) at constant hydrogen energy (around 5 eV) leads to higher root mean square roughness. Also, it turns uniform and ordered OPA coated surface to the larger island clusters. Thus, Fig. 3e shows larger clusters growth of hydrocarbon molecules in increased degree of reaction via fluence.

4 CONCLUSIONS

The uniform and well-ordered Octadecylphosphonic acid Langmuir-Blodgett film on evaporated aluminum oxide surface was formed and characterized few properties. In this work, it demonstrated that long hydrocarbon chain chemical bonding was modified with hyperthermal hydrogen induced collision effect which induced cross-linking keeping its functional group of Octadecylphosphonic acid intact. Inherently, OPA functional group bonds chemically with aluminum oxide following the condensation reaction which makes the bonding stronger by default. Nevertheless, taking advantage of the fact that phosphonic functional headgroup (-P(O)(OH)₂) bonds are stronger than C(1s)-H bonds, we enhanced the mechanical strength of the OPA film on aluminum without modifying the chemical functionalities of the molecules which were analyzed by few surface analysis.

In this work, kinematics-driven approach with hyperthermal proton energy can induce cross-linking of the adsorbed OPA onto surface and can modify the actual ordered LB lattice into an array of clusters of the OPA film on aluminum oxide. The nanocluster growth is to be narrowed by increasing the dry-reaction time at fixed bombardment energy and at a modified fluence which indicates the degree of cross-linking can be controlled with a function of bombardment time. Thus with a controllable bombardment condition with function of fluence can modify the cluster shape and enhance the mechanical strength.

5. REFERENCES

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