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GROWTH AND PROPERTIES OF COMPLETE MONOLAYER FILMS OF OCTADECYLPHOSPHONIC ACID (OPA) ON OXIDIZED ALUMINUM SURFACES

H.-Y. Nie, M.J. Walzak, N.S. McIntyre
Surface Science Western, Room G-1, WSC, University of Western Ontario, London, Ontario N6A 5B7, Canada

Abstract

We use a new experimental approach for the formation of octadecylphosphonic acid (OPA) self-assembled monolayers on hydrophilic oxide surfaces using a hydrophobic medium and a spin-coating process. In contrast to previously developed processes where the substrate is immersed in the bulk of the solution, the new method makes use of the ordering of the amphiphillic OPA molecules on the surface of the hydrophobic medium. This approach results in the easy formation of complete monolayers on a wide variety of surfaces, including oxidized silicon and aluminum. The OPA SAMs formed on oxidized Al surface appear to be of chemical bonding, which promises applications in surface protection and self-cleaning.

Keywords

Aluminum surface modification, octadecylphosphonic acid, self-assembled monolayers, hydrophobic solvent, complete coverage, organic monolayer lubricant, self-cleaning agent

1 Introduction

Self-assembled monolayers (SAMs) have aroused enormous interest in interdisciplinary research areas because they have many possible applications in the engineering of surfaces, including protection from corrosion and modification of tribological properties [1-4]. Recently, octadecylphosphonic acid (OPA) on mica has been shown to serve as a general model system for investigating the fundamentals of SAM formation [5] and a method for growing SAMs on aluminum surfaces from hydrophilic and hydrophobic solutions has been described [6-7].

Previous researchers have concentrated on developing methods that would deposit SAMs on surfaces by immersion of the substrate from the bulk phase of a liquid solvent. Thus, the polarity of the solvent was chosen so as to dissolve those molecules that would comprise the SAM. We have described elsewhere a different experimental approach that achieves complete coverage of an OPA SAM on oxide surfaces from a moderately hydrophobic medium (dielectric constant of ~4) and a spin-coating process; these oxide surfaces include oxidized Si wafers, quartz, glasses, oxidized metals, sapphire and minerals such as muscovite and biotite [8]. Our approach produces full coverage OPA SAMs on oxide surfaces in seconds, compared to hours or days as suggested by conventional immersion methods. Further, we have shown that use of a hydrophobic medium, within a limited dielectric constant range is an effective way for delivering controllable OPA SAMs on many hydrophilic oxide surfaces. In this present communication we will concentrate on applications involving aluminum surfaces [8].

Shown in Figure 1 is a schematic illustration for the method of forming OPA monolayers on a hydrophilic substrate. When the hydrophobic OPA medium is spread on this hydrophilic surface by the spin process, the hydrophilic OPA headgroups aggregated and oriented at the surface of the liquid, are well positioned to interact with the surface. While the hydrophobic medium is repelled from the hydrophilic surface, the hydrophilic headgroups continue to adhere. This process allows formation of full coverage OPA SAM on a hydrophilic surface [8].

2 Experimental

Crystalline powder of OPA [$CH_3(CH_2)_{17}P(=O)(OH)_2$] was purchased from Alfa Aesar (93% purity, Ward Hill, MA). A nominally 2 mM OPA solution in trichloroethylene (TCE) was used to prepare the

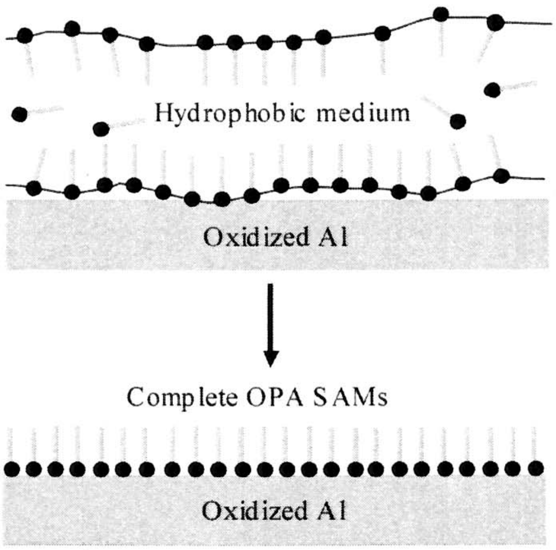

Fig. 1 – Schematic illustration of the concept of using a hydrophobic OPA solution to deliver OPA monolayers with a coverage up to 100% by applying the OPA solution onto a rotated hydrophilic substrate.

OPA/Al

Name	Pos.	FWHM	Area	At%
O 1s	530.07	2.84	5.2	27.5
C 1s	282.52	1.99	3.2	50.4
P 2p	131.47	2.08	0.2	2.0
Al 2p	72.73	2.58	0.7	19.7

UV/ozone treated Al

Name	Pos.	FWHM	Area	At%
O 1s	532.87	3.00	6.7	40.9
N 1s	401.40	3.14	0.2	1.9
C 1s	286.01	2.35	1.5	26.7
Al 2p	76.22	2.50	0.9	30.5

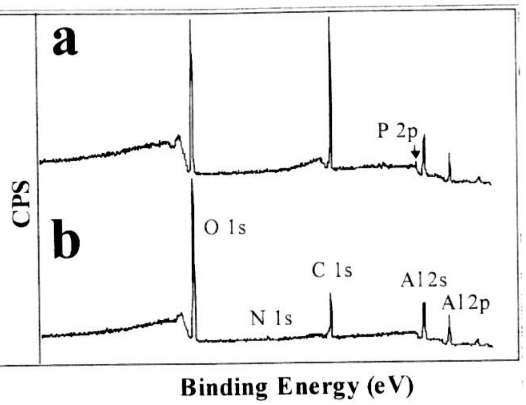

Fig. 2 – XPS broad scans for a UV/ozone-treated Al film after OPA SAM deposition (a). The substrate before OPA deposition is shown in (b) for reference. As shown in (a), increase in C 1s peak and appearance of P 2p peak are observed after OPA deposition. Tables on the left hand side show the elements detected on the different surfaces and their positions in binding energies in eV and atomic percentages.

OPA monolayers on various aluminum oxide surfaces. Raising the temperature of the solution helps to dissolve more OPA molecules in the hydrophobic solvent. The aluminum oxide substrates used were mostly either wafers of sapphire or air oxidized metallic aluminum thin films coated on a Si wafer by RF magnetron-sputtering. However, in some cases, used were aluminum plates polished to 0.25 microns or the shiny side of commercial aluminum foil. Substrates were cleaned with methanol followed by UV/ozone treatment for a period of 45-60 min. The UV/ozone cleaning/oxidation served to remove organic contamination from the surface and to render it hydrophilic [9]. A home-made spin-coater was used to cast OPA SAMs on the aluminum surfaces at a spin rate of 5,000 rpm in air under a relative humidity of 70%.

An SSX-100 (Surface Science Laboratories) X-ray photoelectron spectroscopy (XPS) was used to detect the existence of phosphorus and carbon from the OPA SAMs on an oxidized Al surface using a monochromatic Al K_γ X-ray source.

Dynamic force mode atomic force microscopy (AFM, TopoMetrix's Explorer) was used to image the OPA layers prepared on the oxide substrate. This mode of AFM measures the surface morphology through a feedback mechanism of maintaining constant damped oscillation amplitude while the vibrating tip scans the contour of the surface. Rectangular-shaped silicon cantilevers with a spring constant of ~40 N/m were used. The cantilever was 125 μm long, 3 μm wide and 4.0 μm thick. The tip integrated on the cantilever had a nominal apex radius of 10 nm.

Grazing-angle Infrared (IR) absorption spectra were obtained using an Fourier transform IR (FTIR) spectrometer (Bruker IFS 55) equipped with a grazing-angle reflectance accessory and a polarizer for the incident IR radiation. The experiment was conducted by measuring reflectance of the p-polarized IR beam with an 85° angle of incidence. FTIR spectra were recorded at a 2 cm^{-1} resolution with 20,000 averaged scans.

A contact angle goniometer (Ramé-Hart Model 100-00) was used to collect the data of contact angles for hexadecane and de-ionized water on the OPA samples having a complete coverage. A sessile liquid drop of interest was used to measure the contact angles.

3 Results and Discussion

OPA SAMs were formed on an air oxidized Al film (10 nm thick) deposited on a Si substrate that had been oxidized and cleaned using a UV/ozone treatment for ~1 hr. XPS results for an Al film magnetron-sputtered on a Si substrate before and after OPA deposition are shown in Figure 2, in which the detected elements are also shown. The broad scan shows a large increase in C 1s peak after OPA deposition, reflecting the presence of hydrocarbon chains presented on the coated surface. The presence of ~ 2% of P 2p confirms the presence of the phosphonate group on the OPA coated surface. High resolution XPS scan (not shown here) for C 1s peak shows that the increase in this peaks is due to C-C and C-H bonds, which originate from the hydrocarbons chains of the OPA molecule. It has been shown that the C 1s peak from the OPA SAMs provides a standard for charge compensation superior to that from adventitious carbon, due to the well-defined monolayer formation [10].

AFM images for the surface morphology before and after OPA deposition are shown in Figures 3(a) and 3 (b), respectively. As shown in Figure 3(b), the bare Al film is characterized by nanometer particles. We confirmed that a complete OPA monolayer on such a surface is invisible to AFM as the molecules are anchored with the contour of the Al particles. The AFM image shown Figure 3(b) is obtained on a surface where the OPA monolayer covers the Al film partially, resulting in a morphological contrast (i.e., height difference between the OPA layer and the exposed substrate) allowing AFM observation of the layered structure of the OPA SAMs. The apparent thickness of the OPA layer estimated by AFM is ~2.2

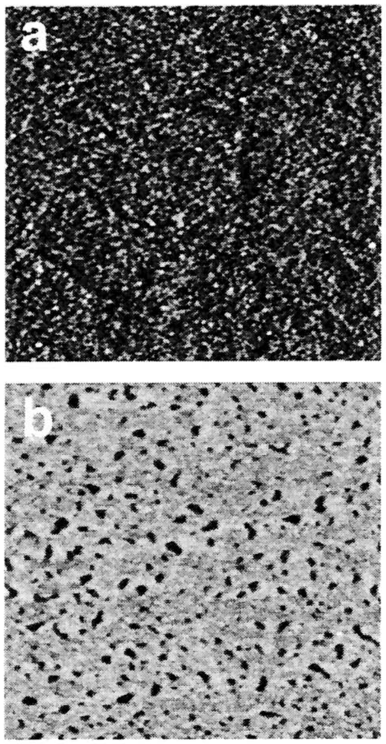

Fig. 3 – AFM images (scan area: 1.5 μm × 1.5 μm) show (a) the particle structure for a 10-nm-thick Al film sputter-coated on a Si substrate and (b) OPA SAMs delivered onto the Al film surface by spin-coating a trichloroethylene solution of OPA. The height range of the gray scale is 1.7 and 4.5 nm for image (a) and image (b), respectively.

nm, which is close to the length of the OPA molecule when it is fully extended (2.5 nm) [5]. For thicker Al films (e.g., ~200 nm) on Si substrates as well as Al sheets and foils, the OPA monolayers were not able to be detected using AFM images because of rough surface features. However, other methods, such as contact angle with hexadecane and IR absorption were able to determine that the OPA-coated surface was terminated by methyl groups and the methylene chains were closely-packed and had a crystalline-like structure. Water contact angle on the OPA coated Al surface also showed that the surface was hydrophobic and strongly repelled water. All these experimental observations point to the formation of OPA SAMs on the oxidized Al surface. Other researchers observed lubrication due to OPA SAMs formed on an oxidized Al surface through measuring the friction efficient of the coated Al surface [7].

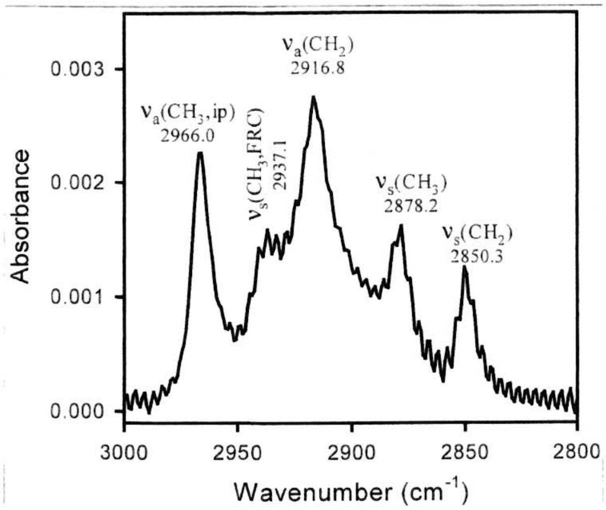

Fig. 4 – Grazing-angle FTIR absorption spectrum for OPA SAMs spin-coated on a UV/ozone-treated Al foil surface.

In order to verify the orderliness of the OPA SAMs produced with our method, we conducted FTIR spectroscopic study on OPA SAMs formed on an Al foil. It has been established that the orderliness of methylene chains can be determined by the positions of the frequencies of the peak frequencies in IR spectra for their symmetric and asymmetric methylene stretch modes, denoted as $\nu_s(CH_2)$ and $\nu_a(CH_2)$, respectively [11,12,13-15]. A crystalline-like methylene chain structure has its $\nu_s(CH_2)$ and $\nu_a(CH_2)$ at 2851 and 2918 cm^{-1}, respectively, while disordered hydrocarbon chains are characterized with the two absorption bands shifting to higher frequencies [12,15]. The grazing-angle FTIR spectrum for the OPA SAMs on an Al foil is shown in Figure 4. The peak frequencies for the $\nu_s(CH_2)$ and $\nu_a(CH_2)$ were found at 2850.3 and 2916.8 cm^{-1}, respectively, suggesting the methylene chains are closely-packed and have a crystalline-like structure. Also assigned in the spectrum are the symmetric methyl stretch [$\nu_s(CH_3)$] at 2878.2 cm^{-1}, its Fermi resonance splitting component [$\nu_s(CH_3)$,FRC)] at 2936.1 cm^{-1} and the in-plane asymmetric methyl stretch [$\nu_a(CH_3,ip)$] at 2965.0 cm^{-1}. We concentrated on clarifying the crystallinity of the OPA SAMs formed on oxidized aluminum surfaces through detecting the position of the methyl and methylene stretching modes [8]. However, other groups have shown that phosphonic acid is attached on an oxidized aluminum surface through chemical bonding inferred from the lack of P=O peak at 1176 cm^{-1} and P(OH) peak at 1026 cm^{-1} [16].

Table1

Contact angles for Hexadecane (HD) and de-ionized water on OPA SAMs prepared on an Al surface.

	Advancing (HD)	Advancing (water)	Receding (water)	Static (water)
OPA/Al	45°-47°	110°-115°	90°-94°	100°-105°

Hexadecane (HD) can be used to probe the orderliness of terminating methyl groups for the OPA SAMs, as a surface terminated by well-ordered methyl groups has an advancing contact angle of ~45° with HD [12,17,18]. As shown in Table 1, the HD advancing contact angle on OPA SAMs is 45-47°, indicating that the surface is terminated by well-ordered methyl groups. It is clear from the results of FTIR and HD contact angle measurements, that the OPA SAMs have similar orderliness to that of other well-studied SAMs, such as alkanethiol on gold [17] and alkylsilane on silicon [19].

Water contact angle is a simple, yet powerful method to monitor the hydrophobicity of OPA SAMs on Al film, as most Al surfaces do not allow the presence of OPA monolayer to be monitored by AFM due to the fact that their surfaces are too rough compared with the height of the OPA monolayer. For the OPA SAM deposited on a UV/ozone treated Al film (an Al foil or a magnetron-sputtered Al film on a Si substrate), the advancing/receding water contact angle is 110-115°/90-93° and the static contact angle is 100-105°. Surface terminated by methyl group having water contact angles like these should have a surface energy ~20 mJ/m^2 [17]. Thus, formation of an OPA SAM on a UV/ozone-treated Al surface renders this hydrophilic surface hydrophobic. For water to bead up on a surface, the surface energy of the substrate surface should be significantly smaller than the surface tension of water (72 mJ/m^2). For a water drop to freely roll over on an inclined surface, the receding contact angle should be over 90°. The large receding contact angle ensures that the surface is truly hydrophobic, that is, water does not wet the surface. Thus OPA-coated Al surface has an effect of self-cleaning as the water receding contact angle is more than 90°; this means when water is present on an inclined surface, water beads up and rolls over the surface taking away dusts along the way. We confirmed that water on OPA-coated Al surface rolls over freely once on such surface once it is provided a inclination. Such OPA-coated Al surface emerged dry from water. The OPA-coated Al surface thus can be kept dusts free when rain washes the surface. We also observed that methanol does not spread on an OPA-coated Al surface, instead, it forms a certain contact angle (~40°) on the surface.

OPA SAMs deposited on Al surface are chemically strong, as methanol washing did not change the wetting property. It has been believed that OPA is attached to an Al film through chemical bonding between an oxygen atom from the phosphonate group and the Al atom from the substrate surface [7]. This suggests that OPA SAMs can serve as a organic monolayer lubricant through the compliance of the hydrocarbon chains when a pressure is applied and their relaxation upon removal of the pressure [7,20].

We have demonstrated our ability to deposit a complete OPA SAM on an oxidized Al film via use of an appropriate hydrophobic medium and a spin-coating process. The driving force for SAM formation is concentration and orientation of the hydrophilic phosphonate headgroup at the medium surface. The basic requirement for this to happen is the contact between the hydrophilic headgroup and the hydrophilic substrate. Therefore, dip-coating as well as immersion method are also effective in depositing OPA on a Al surface using a hydrophobic medium, as inserting a hydrophilic substrate into the hydrophobic medium creates an interface where the exposed hydrophilic OPA headgroups on the hydrophobic medium surface will be transferred onto the hydrophilic substrate in the hydrophobic medium. This is clearly advantageous for objects that are not suitable for spinning process. However, selection of an appropriate hydrophobic solvent is essential to ensure full coverage by OPA SAMs. The solvent should be such that it allows as much as concentration and orientation of the headgroup at the medium surface.

4 Conclusions

We have demonstrated coating full coverage OPA SAM on an oxidized Al surface using hydrophobic medium and a spin-coating process. The SAMs are chemically bonded to the Al surface and the hydrocarbon chains are closely-packed and have a crystalline-like structure, and the SAM surface is terminated by well-ordered methyl groups. The crystalline-like and hydrophobic SAMs are only ~2 nm thick, yet, it provides surface protection and a self-cleaning capability for the underneath Al film.

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