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Durability of self-assembled monolayers on aluminum oxide surface for determining surface wettability

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ABSTRACT

The durable non-wettability of functionalized aluminum oxide (Al_2O_3) thin films coated with two different self-assembled monolayers (SAMs), phosphonic acid (HDF-PA) and trichlorosilane (HDF-S), was investigated by a water flow test method. After exposing the surface to 5 L of water droplets, the contact angle of HDF-S coated Al_2O_3 thin films remained at the initial value of ~102.7°, while the contact angle of HDF-PA coated Al_2O_3 thin films decreased from an initial value of ~99.9° to a value of ~69.3°. Thermal annealing effect at various temperature post formation of the self-assembled HDF-PA on the Al_2O_3 were investigated and shown to enhance the durability of SAMs with a constant contact angle (~100°) annealed at 100–150 °C.

1. Introduction

Lotus leaves show superhydrophobic properties because of their unique patterns and hierarchically micro/nanostructures that minimize adhesion of water droplets. Thus, these leaves exhibit a natural self-cleaning property, where dust and pollutants on their surface are easily removed by raindrops. The inner surface of the pitcher-shaped leaf of the pitcher plant exhibits slippery properties that prevent insects that fall into the leaf pocket from crawling out. To mimic the slippery nature of these leaves for use in industrial and scientific applications, many studies focusing on controlling surface properties such as non-wettability and water repellence by imparting certain functionalities to the surfaces have been conducted [1,2].

The hydrophobicity of a solid surface can be improved by either increasing the roughness of the surface or by chemically assembling low surface energy materials on the surface [3–7]. Generally, increase in roughness of a hydrophobic surface leads to decrease in surface energy and results in enhancement of the hydrophobic properties of the surface [8]. For instance, an air cushion structure resembling a springtail skin with a contact angle of 150° was fabricated using hydrophilic polymeric materials [9]. There has also been an attempt to impart characteristics to porous Teflon membranes and epoxy-based nanostructured surfaces that would make them repellent to any viscous fluid including water. This was achieved by coating the surfaces with lubricants so that they resembled a lotus leaf [10].

Self-assembled functional materials on the substrate can be formed strongly by chemical bonding to the surface. Appropriate selection of molecules for self-assembly can aid the control of permanent surface characteristics. Recently, a variety of self-assembly approaches for engineering surface wetting properties have been reported mostly based on trichlorosilane or metal–ligand coordination chemistry [11–13]. While trichlorosilane-based reagents are highly moisture sensitive due to hydrolysis and self-condensation of silanes, phosphonic acid-functionalized molecules are quite stable in water with a tendency for stable metal–ligand coordination and heterocondensation between phosphonate and metal oxide surfaces. Therefore, formation of phosphonic acid based self-assembled monolayers (SAMs) is an important method to modify surface properties in ambient air. As a result, phosphonic acid-based SAMs offer a cost-effective approach to high-throughput process compared to SAMs formed by trichlorosilane chemistry. For practical applications, molecular stability of the SAM on the substrate under ambient conditions as well as the economic feasibility of the process is important. For this reason, an in depth study focusing on the durability of non-wetting properties of substrates coated with phosphonic acid based SAMs is required.

In this study, we prepared two types of SAMs, namely (1*H*,1*H*,2*H*,2*H*-heptadecafluorodec-1-yl) phosphonic acid (HDF-PA) and

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(heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (HDF-S) on substrates coated with Al_2O_3 thin films. To examine the reliability of HDF-PA and HDF-S self-assembled substrates, especially the stability of the chemical bond, the contact angle characteristics of the prepared substrates were studied using a water flow method. An additional thermal annealing process after self-assembly was also performed to obtain a strong chemical bond between HDF-PA and the oxide substrate, which helped maintain stability of the water repellent properties.

2. Experimental

HDF-PA and HDF-S based SAMs were formed on Al_2O_3 thin film coated substrates. The Al_2O_3 coated substrates were prepared by deposition of a 30 nm thick Al_2O_3 film on a silicon wafer using atomic layer deposition (ALD) at the temperature of 300 °C and a reaction cycle of 300. The substrates were cleaned by sonication in semiconductor grade isopropyl alcohol (IPA) and then dried under flowing nitrogen, followed ultraviolet ozone (UVO) cleaning for 5 min to remove organic contamination and to improve the wettability. SAMs of phosphonic acid containing fluorocarbon (HDF-PA, Apollo Scientific) were then formed on the Al_2O_3 coated substrates by immersing in a 2 mM IPA solution for 1 h. After rinsing with fresh IPA and deionized water (DI) twice, the samples were dried under a nitrogen stream. To facilitate self-assembly of trichlorosilane based molecules (HDF-S, JSI Silicone Co. Ltd.), the Al_2O_3 coated substrates were immersed in a 3 mM solution of anhydrous toluene under a nitrogen atmosphere for 1 h. Following this, the substrates were rinsed with fresh toluene and IPA, and subsequently dried under a nitrogen stream. The formation of HDF-PA and HDF-S based SAMs was confirmed using X-ray photoemission spectroscopy (XPS). Contact angles made by water on the SAM coated substrates were measured using a contact angle analyzer (Phoenix 300, SEO), by placing 5 μl water droplets on the surface of the samples at room temperature and atmospheric pressure.

3. Results and discussion

Fig. 1 illustrates the self-assembly process of phosphonic acid and trichlorosilane-based molecules (HDF-PA and HDF-S) on Al_2O_3 coated substrates. HDF-PA has a phosphonic acid anchor group, whereas HDF-S has a trichlorosilane anchor group for self-assembly. The Al_2O_3 film has specific surface characteristics that facilitate both HDF-S and HDF-PA self-assembly. As shown in Fig. 1(a), HDF-PA molecules were deposited via heterocondensation and metal–ligand coordination (M—O—P) between the metal oxide surface and phosphonates, thereby forming a strong chemical bond [14]. In contrast, HDF-S molecules were bound by hydroxyl groups (—OH) on the oxide surface, forming strong siloxane networks, which resulted in strong covalent bonds (Fig. 1(b)).

To verify successful self-assembly of HDF-PA and HDF-S on the surface of Al_2O_3, XPS analysis was performed using a binding energy range of 0–1200 eV. Fig. 2(a) shows the surface chemical states of bare, HDF-PA coated, and HDF-S coated Al_2O_3 thin films. On pristine Al_2O_3, Al 2p and O 1s peaks were observed at 75.7 eV and 532.3 eV, respectively, along with a Si 2p peak (102.8 eV) from the Si substrate. On HDF-PA coated Al_2O_3, strong F 1s and C 1s peaks were observed at 688.0 eV and 291.0 eV, respectively. The distribution of the C 1s peak indicated the presence of 44.3% CF_2 and 11.1% CF_3. In addition, C—C=O (16.8%), C—C (12.27%), C—O (12.27%), and C = O (3.19%) were also observed. On HDF-S coated Al_2O_3, strong F 1s and C 1s peaks were observed at 687.9 eV and 290.6 eV, respectively. The intensities of Al 2p and O 1s peaks were reduced compared to that for pristine Al_2O_3. The distribution of the C 1s peak indicated the presence of 52.2% CF_2, and 12.3% CF_3. In addition, C—C=O (16.8%), C—C (7.9%), C—O (8.3%), and C=O (2.5%) were also observed. This result indicates that the self-assembly of HDF-PA and HDF-S on Al_2O_3 substrate results in the deposition of the fluorocarbon chain.

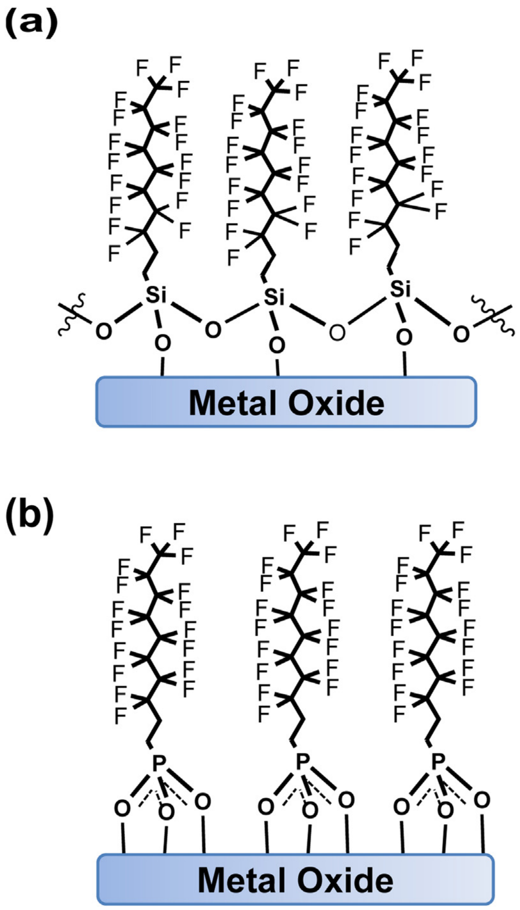

Fig. 1. Schematic illustration of the formation of self-assembled monolayers of HDF-PA and HDF-S on Al_2O_3 thin films.

The wetting characteristics of Al_2O_3 before and after coating with HDF-PA and HDF-S SAMs were analyzed using aqueous contact angle measurements (Fig. 3). The contact angle was measured at five different locations on each sample, and the average and standard deviation of the measurements were calculated. As shown in the figure, while bare Al_2O_3 films showed contact angle values of 70.0° ± 1.5°, the contact angles of HDF-PA and HDF-S coated Al_2O_3 films increased to 99.9° ± 1.0° and 102.7° ± 2.4°, respectively. Intriguingly, HDF-S coated Al_2O_3 showed a higher contact angle compared to HDF-PA coated Al_2O_3. Despite similarity in fluorocarbon chain lengths and the presence of identical functional groups, HDF-PA and HDF-S showed different wetting properties due to different self-assembly mechanisms for the two types of molecules [15]. Generally, trichlorosilane based fluorocarbon chain molecules can only be deposited on hydroxylated surfaces via self-limiting assembly, resulting in highly ordered monolayers with cross-linked siloxane networks. Therefore, the density of SAMs is not limited by the type of surface due to strong siloxane linkage and is similar for different oxide surfaces. On the other hand, phosphonic acid functionalized fluorocarbon molecules can self-assemble strongly on metal oxide surfaces through heterocondensation and coordination (P—O—M) [16]. Therefore, in this case, the density of SAMs will be determined by the type and concentration of metal on the oxide surface.

To prove the durability of HDF-PA and HDF-S coatings on oxide thin films, water flow test was performed on HDF-PA and HDF-S