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Characterization of self-assembled monolayer on anodized aluminum by XPS, AFM and low-voltage SEM

H. Habazaki, H. Sato, E. Tsuji, Y. Aoki, K. Shimizu
Division of Materials Chemistry & Frontier Chemistry Center, Faculty of Engineering, Hokkaido University
Sapporo, Hokkaido 060-8628, Japan

Self-assembled monolayers (SAMs) on metal and metal oxide substrates are of interest for a wide range of applications, including lubrication, corrosion protection, wettability control, biosensors, electron-optics and catalysis. The most studied SAM systems are alkanethiols on gold and alkylsilanes on silica, and there are numerous reports in the literature. Alkyl phosphonic acids are also useful self-assembling molecules, since they form SAMs on a range of metals and metal oxides, including aluminum, iron and stainless steels.

On aluminum, SAMs of alkyl phosphonic acids, alkylsilanes and alkyl carbonates are often used. Such SAMs have been often used to develop superhydrophobic surfaces and it has been reported that an anodized aluminum surface coated with fluorinated alkyl phosphonic acids showed higher contact angles for water and organic liquids in comparison with the alkylsilanes with the same alkyl groups, although the reason was not clarified. Thus, in this study, SAMs of alkyl phosphonic acid and alkylsilane have been formed on a flat anodized aluminum surface. The resultant coated surfaces have been characterized by XPS, AFM and low-voltage SEM in order to understand the coating process.

High purity aluminum sheet was electropolished in perchloric acid-ethanol mixed electrolyte below 10ºC and then anodized to 200 V at 100 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte. The anodized specimens with and without plasma cleaning were immersed in 2 wt% $CH_3(CH_2)_{13}PO_3H_2$, (TDP) in ethanol or 2 vol% $CH_3(CH_2)_{17}Si(OC_2H_5)_3$, (OES) in hexane for 1 to 96 hours to form SAMs. The coated specimens were characterized by the contact angle measurements, AFM, XPS, and low-voltage SEM.

The contact angle measurements revealed that the TDP coated specimens without plasma cleaning needed the immersion time of more than 80 hours to show the steady high contact angle for water. In contrast, the steady contact angle was obtained within 15 hours for the plasma-cleaned aluminum specimens. The plasma-cleaned surface, which shows the contact angle for water of ~0 degree, is suitable for the formation of SAMs more rapidly.

The AFM observations revealed that the surface roughness decreased slightly with the immersion time for the TDP-SAM coating without plasma cleaning. However, locally, multi-layered SAMs were formed after immersion for 72 hours. The multilayer structure was also clearly observed by the low-voltage SEM. The thickness of each layer was ~3.4 nm, corresponding to the thickness of two-layer of TDP.

When aluminum was coated with OES, the contact angle for water was less than that with TDP. AFM observations revealed that many small islands of OES appeared to develop on the anodized aluminum surface. The formation of the islands, composed of small agglomerates of OES molecules, became less significant by plasma cleaning.

The coated surfaces were also characterized by XPS. At high take-off angle of photo electrons with respect to the surface normal, the high concentration ratio of carbon to phosphors was obtained for TDP at the conditions of the steady contact angle for water. In contrast, the carbon to silicon ratio was not largely different from the atomic ratio of OES. The results suggested that highly aligned SAMs were formed for TDP, but not for OES on anodized aluminum.