Communication

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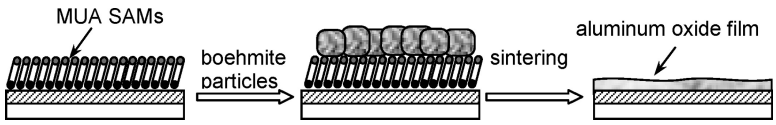

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A Self-Assembled Monolayers Assisted Solid-State Conversion of Boehmite Particles to Aluminum Oxide Film

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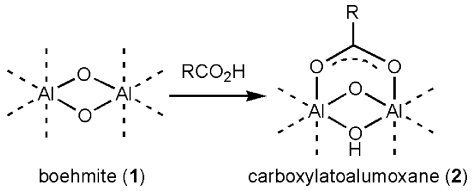
Aluminum oxide (Al_2O_3) film is used in various applications including anticorrosion coatings, insulating layers, catalyst supports, and dielectric films owing to its unique mechanical, thermal, and electronic properties.[1] In the past several years, the topic of high-*k* dielectric gate layers[2] and transparent super-water-repellent coating films[3] have attracted a great deal of attention. Depending on the application, a number of the aluminum oxide film preparation techniques are available including chemical vapor deposition (CVD),[4] magnetron reactive sputtering,[5] atomic layer deposition (ALD),[6] spray-pyrolysis,[7] and sol−gel methods.[8] All of these methods require either high vacuum conditions, except the sol−gel method, or flat objects, except ALD, to prepare evenly coated surfaces.

In this Communication, we demonstrate a newly developed solid-state conversion method for the preparation of aluminum oxide film from boehmite ($AlOOH{\cdot}nH_2O$) particles that can be applicable to surfaces with complicated shapes. A boehmite particle, also known as pseudoboehmite or aluminum oxyhydroxide, is a poor crystalline form of mineral boehmite, which has an infinite arrangement of the Al−O−Al core structure with the aluminum atom octahedrally coordinated by five oxide and one hydroxide anions. Boehmite is used as a precursor for aluminum oxide synthesis by thermal dehydration.[9] As regards to reactivity, an oxo ligand of boehmite (**1**) is readily protonated in the reaction with carboxylic acid to give a carboxylatoalumoxane (Scheme 1), in which a carboxy group occupies the bridging position across the two adjacent Al atoms (**2**).[10]

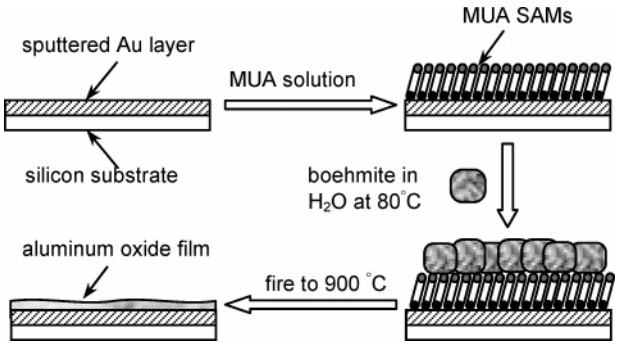
In our approach, 11-mercaptoundecanoic acid (MUA) self-assembled monolayers (SAMs) are used as sacrificial binders that keep boehmite particles on a substrate surface. The typical SAM technology utilizes the action of the chemisorption of alkanethiolates on gold substrates and their spontaneous assembly into ordered monolayers.[11] Tailoring the terminal methyl groups in alkanethiolates enables integration of heterostructures on the SAM-modified substrates. For example, the terminal carboxy groups of MUA SAMs can covalently attach boehmite particles on the monolayer surface. Subsequent sintering and dehydration will prepare aluminum oxide film.[12] Furthermore the adhesion of aluminum oxide to gold[13] may be enhanced by the presence of carbon residuals yielded by decomposition of MUA SAMs.[14]

A schematic representation of the aluminum oxide film fabrication processes is shown in Scheme 2. The Au layer with thickness of 50−100 Å was ion-sputtered onto the clean silicon substrate. The densely packed MUA SAMs were formed by soaking in a 0.50 mmol ethanolic solution of MUA with 1.0% (*v*/*v*) CF_3COOH at ambient temperatures for 2 h.[15,16] After it was rinsed with ethanol containing 10% (*v*/*v*) NH_4OH, the MUA SAMs covered silicon substrate was immersed in a suspension of boehmite particles in water[17] and maintained at 80 °C for 1 h to foster the bond formation. After it was dried under a stream of pure nitrogen gas, the boehmite

Scheme 1



Scheme 2



particle-decorated substrate was sintered at 900 °C in an electric heating furnace.

Figure 1 shows progressive images of tapping mode atomic force microscopy (AFM) observed in the process of film fabrication. Topographic (left) and phase (right) images of MUA SAMs in Figure 1a reveal that the monolayers (the bright area in the topographic image) are forming mosaic patterns of a few tens of nanometers in diameter, imitating the results reported by Onuma et al.[15] Boehmite particles adhered on the MUA SAMs are shown in Figure 1b, where aggregates of boehmite particles appear as irregularly shaped blocks. Sizes of the blocks in the image do not conflict with average diameter of water dispersed boehmite particles (90.6 nm) estimated by an electroacoustic spectrometer. The sparsely observed dark areas in the topographic image correspond to bare MUA SAMs. After sintering at 900 °C for 24 h in air, the uneven block structure is converted into a flat surface, suggesting the creation of a smooth filmlike structure (Figure 1c). Incomplete fusion of relatively large particles is attributed to the presence of humplike residuals that are 20 nm or smaller across the surface. Indeed, prolonged heat treatment for an additional 24 h achieved a featureless, monolithic structure (Figure 1d). Cross-sectional surface profiles of Figures 1b and 1d along the lines are shown in Figure 1e and 1f, respectively. The maximum height difference is reduced from 48 nm to less than 4 nm before and after sintering. The X-ray photoelectron spectroscopy (XPS) analysis of the substrates shown in Figure 1b and 1d ascertained the Al 2p binding energy of 74.2 and 73.9 eV, respectively, corresponding to values for the hexa-coordinate Al atoms.[18]

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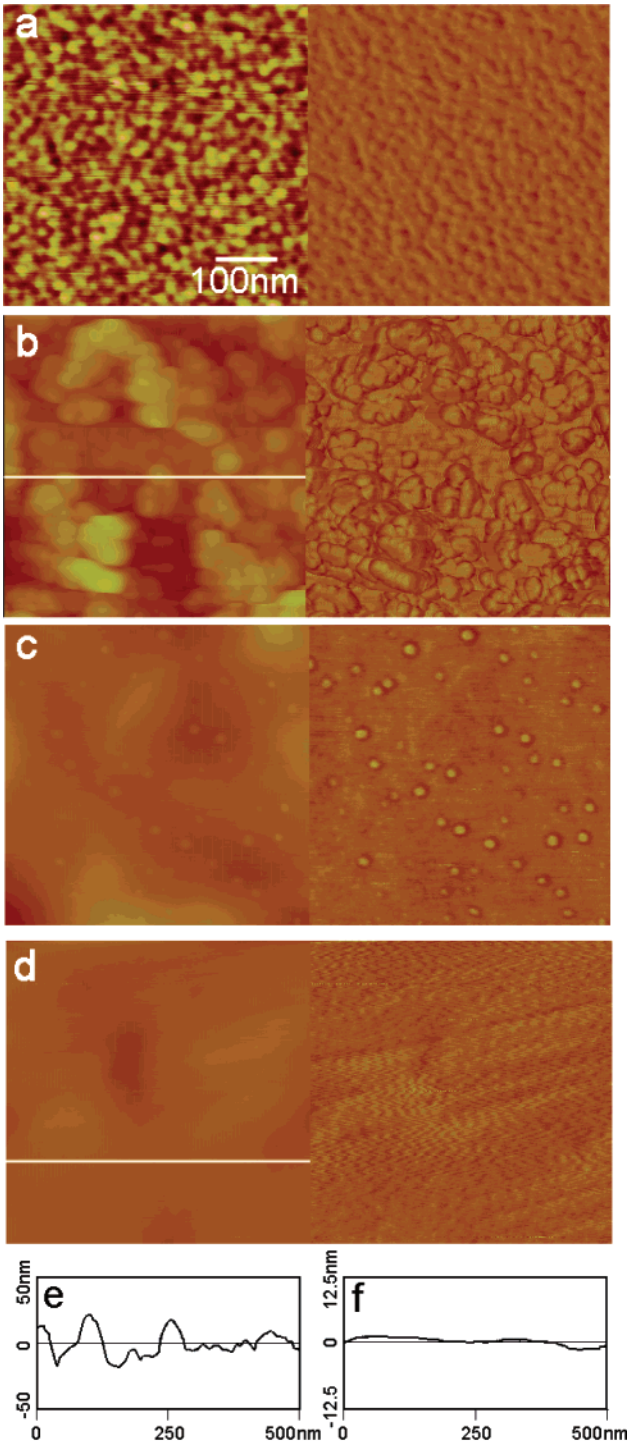

Figure 1. AFM topographic (left) and the corresponding phase (right) images of (a) the MUA SAMs covered surface, (b) the boehmite particle-decorated surface, (c, d) surfaces sintered at 900 °C for 24 and 48 h, respectively. (e, f) The surface cross-sections of panel b (left) and panel d (right) observed at horizontal lines in the figures.

Thermal dehydration of boehmite ultimately prepares thermodynamically stable α-alumina via sequential transitions of crystalline phases ($\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$) with subtle variation in the hexacoordinate Al environment.[19] In this sequence, γ-alumina is obtained from a boehmite precursor at temperatures below 1000 °C, and that is the most plausible product presented here as well.[20]

In summary, we demonstrated solid-state conversion of boehmite particles to fabricate aluminum oxide film. Because the SAM technique is applicable to curved materials as well as flat ones, the process in this experiment has potential to fabricate conformal aluminum oxide films on surfaces of complicated shape. Although we built the film on a Au layer for demonstration purposes, this methodology is applicable to any metal and metal oxide surfaces that are capable of carboxy-terminated SAMs formation and can be a low-cost alternative to the current mainstream methods.

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Supporting Information Available: TEM image of boehmite particles and the size distribution measured by an electroacoustic spectrometer. XPS spectra of the samples in Figure 1b and 1c. This material is available free of charge via the Internet at http://pubs.acs.org.

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