Abstract

Titanium dioxide (TiO_2)-based substrates and added silicon oxide (SiO_2) layers are the subjects of an extensive research aiming at applications to photocatalysts for environmental purification, photoinduced superhydrophilic coatings, and electrodes of dye-sensitized photochemical solar cells. The SiO_2-TiO_2 composite system is promising to extend the lifetime of the hydrophilicity in dark, which is activated with UV light irradiation. Control of the crystalline structures and thickness of SiO_2 layers deposited on TiO_2 surfaces can enhance their unique physical and chemical properties. To date various kinds of SiO_2–TiO_2 systems have been studied using a range of different techniques, including sol-gel dip coating, evaporation-induced self-assembly using dip-coating, electrochemical deposition, and ion milling. Nevertheless, most of the techniques cannot control side reactions nor film homogeneity on a nanoscale. Thus, it is keenly expected to reveal the mechanism of their fascinating phenomena fully using surface analytical methods by combining with sample preparation methods to prepare well-defined surfaces of SiO_2-TiO_2 systems.

In this study, silicon oxide growth on a single crystal rutile TiO_2(110) surface by annealing in a quartz case (SiO_2) in air at 1000°C is characterized by X-ray photoemission spectroscopy (XPS), low energy electron diffraction (LEED), frequency modulation-atomic force microscopy (FM-AFM) operated in pure water. Furthermore, to confirm the growth of silicon oxide by SiO vapor from the quartz case, we anneal the TiO_2 substrate stored in a single crystal sapphire case (Al_2O_3), from which no SiO vapor comes out, as a control experiment. We evaluate the hydrophilicity of the silicon oxide overlayers on the TiO_2 surface by water contact angle (WCA)

measurement. This leads us to fundamental understanding of the relationship between nano-scale surface features and its wettability, which is useful to improve the characteristics of industrial and ecological products using TiO_2.

XPS analysis for the silicon oxide deposited on TiO_2(110) were as follows: contamination were found for as-received TiO_2(110), and disappeared after chemical cleaning and annealing processes in both quartz case and sapphire case. On one hand, Si 2s and 2p XPS peaks found for samples annealed in the quartz case were not observed for annealed in the sapphire case. The shoulders on the higher binding energy side of each O peak were assigned to either hydroxyl group or O atoms bonded to Si and Ti. The hydroxyl group can be associated with water hydrophilicity. The existence and increasing of the Si XPS peak with annealing time as well as the change of LEED patterns of TiO_2(110) periodicity from (1x1) to (1x2) indicated the formation of epitaxial growth of silicon oxide ultra-thin layers on TiO_2(110) substrate. The patches were found in FM-AFM images of annealed TiO_2 in quartz case, which are attributed to the SiO_2 growth: rectangular shaped patches were grown with extending annealing time.

Water wettability measurements showed that the surface annealed in sapphire, corresponding to a fully oxidized stoichiometric surface, was less hydrophilic at a WCA of 32°. Due to photo-catalytic nature, TiO_2(110) surfaces were strongly affected by UV irradiation, showing super-hydrophilicity. As in a large amount of literature, the hydrophilicity quickly disappears when those are stored in dark. On the other hand, SiO_2/TiO_2 surfaces formed by vapor phase epitaxial deposition in air displayed more hydrophilic. In particular for 72 hours annealing, the SiO_2/TiO_2 surface showed super-hydrophilic without UV illumination. The super-hydrophilicity corresponds to the saturated Si peak height in XPS analysis, the transition of atomic periodicity

from (1×1) to (1×2) in the LEED pattern, and the rectangular patch formation of silicon oxide. Moreover, the ability of the sample annealed for 72 hours to maintain hydrophilicity was greater than that of TiO_2(110) surfaces annealed for shorter time. This is probably attributed to the hardness and durability of top most silicon oxide layer as well as the photo-catalytic power of sub-surface TiO_2(110) surface. An atomic model of SiO_2/TiO_2 surface was proposed to elucidate the relationship between the change in atomistic characteristics at the surfaces and the conversion of hydrophobic/hydrophilic properties of SiO_2/TiO_2 systems.

In this study, we demonstrated to distinctly fabricate a fully oxidized TiO_2(110)-(1x1) surface and ultra-thin layers of SiO_2 hetero-epitaxially grown on a rutile TiO_2(110) surface by annealing in air in different cases of sapphire and quartz, in which the substrate was stored. Their structures and characteristics were analyzed on a nano-scale, and the surface wettability was examined; the correlations between them were discussed to disclose the fascinating properties of titanium dioxide and silicon dioxide systems. The findings in this study suggest the potential of conventional hetero-epitaxial growth of oxides by vapor phase transport in air, and shed light on the mechanism of super-hydrophilicity utilized in commercial products such as anti-fog mirrors of SiO_2-TiO_2 hybrid materials.

Key words: titanium dioxide, silicon dioxide, hetero-epitaxy, stishovite, super-hydrophilicity.