Photo-induced super-hydrophilicity of SiO_2 overlayers epitaxially grown on a rutile TiO_2(110) surface

Le Tran Uyen Tu, Akira Sasahara, Masahiko Tomitori
School of Materials Science, Japan Advanced Institute of Science and Technology
E-mail: letutran@jaist.ac.jp

Coating of SiO_2 on TiO_2 has been used to enhance the water wettability of TiO_2-related materials in industrial applications. However, the mechanism of wettability is not clear from a viewpoint of surface science, because it is not easy to prepare model surfaces, to which nanoscale analytical techniques can be applied. Recently we have developed a method of vapor-phase epitaxial growth of SiO_2 overlayers on single crystalline TiO_2 surfaces in air and examined the hydrophilicity of the overlayers [1]. The SiO_2 overlayers epitaxially grew as rectangular patches with a monolayer thickness on a rutile TiO_2(110) surface, and the hydrophilicity in dark was enhanced with the SiO_2 coverage. This was possibly attributed to the high density of OH groups on the overlayers by our structural and compositional analysis. In this work, we focus on the photo-induced super-hydrophilicity of the SiO_2-covered rutile TiO_2(110) surface.

In the epitaxial growth process rutile TiO_2(110) wafers were placed in a quartz case and annealed at 1273 K in an electric furnace in air to fabricate the SiO_2 monolayer. The vapor of SiO was generated from the quartz case and deposited on the wafer surfaces. The SiO_2 monolayer coverage was controlled by changing the annealing time. The samples were analyzed by non-contact atomic force microscopy (NC-AFM) and X-ray photoemission spectroscopy (XPS). Water contact angle (WCA) was measured for samples exposed to air after ultraviolet (UV) light (400 mW/cm^2) irradiation.

The WCA of a sample annealed for 6 h at 1273 K without the UV light was 16°, which was covered with a 15% area ratio of SiO_2 monolayer patches around steps of the TiO_2. The WCAs after annealed for 24 and 48 h for 44% and 74% area ratios were 11° and 5°, respectively. The WCA approached to 0° (super-hydrophilic) after annealed for 72 h or more, almost fully covered with the SiO_2. The wettability of the surface increased with the coverage of the SiO_2 layer probably with the high density of OH groups on the surface owing to the hydration of water molecules over the OH groups and the charge transfer at the interface between the TiO_2 surface and the SiO_2 layer. Meanwhile, all samples showed super-hydrophilic under the UV light (Fig. 1). Afterward, the surfaces turned from super-hydrophilic to less hydrophilic with exposing to lab air. While an oxidized TiO_2 surface showed a WCA of 60° in 2 h after the UV irradiation, the SiO_2-covered TiO_2 expanded the lifetime of super-hydrophilicity. The almost fully-covered SiO_2/TiO_2 surface showed the change from 0° to 16° after 24 h in dark. Note that the irradiation changed the wettability of not only oxidized TiO_2 but also SiO_2/TiO_2. The photo-induced hole-electron pairs in TiO_2 and their tunneling can contribute to the super-hydrophilicity. We will discuss them in detail.

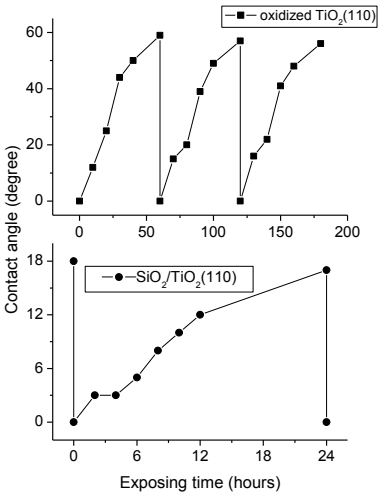

Fig. 1: Water contact angle as a function of time for oxidized TiO_2 (upper) and SiO_2/ TiO_2 (below) under UV irradiation.

Reference

[1] Tu Tran Uyen Le, et al.: J. Phys. Chem. C **117** (2013) 23621.