Extension of endurance of superhydrophilicity in Cassie-Baxter law by epitaxial growth of SiO$_2$ overlayers on a rutile TiO$_2$(110) surface

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Deposition of SiO$_2$ on TiO$_2$ has been widely known as one of the most effective methods to enhance the water wettability of TiO$_2$-related materials. We examined the hydrophilicity of the TiO$_2$(110) surfaces covered by SiO$_2$ monolayers [1]. The SiO$_2$ monolayers epitaxially grew as rectangular patches, and the hydrophilicity of the surface was enhanced with the coverage of the SiO$_2$ monolayers. The hydrophilicity of the SiO$_2$ monolayer was attributed to the high density of surface OH groups on the basis of structural and compositional analysis. In this work, we focused on the durability of the hydrophilicity of the SiO$_2$-covered TiO$_2$(110) surface in laboratory air.

TiO$_2$(110) wafers were placed in a quartz case and annealed at 1273 K in an electric furnace to fabricate the SiO$_2$ monolayer. The coverage of the SiO$_2$ monolayer was controlled by changing the annealing time. The TiO$_2$ wafers were analyzed by non-contact atomic force microscopy (NC-AFM), and X-ray photoemission spectroscopy (XPS). Water contact angle (WCA) measurement was conducted to examine the conversion from superhydrophilic to less hydrophilic for samples exposed to air after UV light (400 mW/cm$^2$) irradiation.

The WCA for a surface annealed for 6 h at 1000 °C without the UV was 16°, covered with SiO$_2$ patches of 15 % area ratio around step lines of the TiO$_2$. The WCAs after annealed for 24 and 48 h for 44% and 74% area ratio were 11° and 5°, respectively. The WCA approached to 0° (superhydrophilic) after annealed for 72 or more, almost fully covered with the SiO$_2$. Figure 1 shows a summary of the changes of WCA of SiO$_2$/TiO$_2$ surface with different area ratios of SiO$_2$ during air exposure for 0, 2, 4, 6, 8, 10, 12 and 24 h after UV light irradiation for 2 min. All samples showed superhydrophilic just after the irradiation. The WCA, however, increased with time possibly owing to contamination covering except the area ratio of 0%. By covering with the SiO$_2$, the endurance of hydrophilicity can be extended. The change of cosine WCA is always linearly proportional to the decrease in TiO$_2$ area ratio. This was satisfied with Cassie-Baxter law for a surface consisting of two components with different WCAs, expressed as the following equation:

$$\cos \theta_k = f_1 \cos \theta_1 + f_2 \cos \theta_2$$

where $\theta_k$, $\theta_1$, $\theta_2$ are contact angles of the composite surface, one component surface, and the other component surface, respectively, $f_1$ and $f_2$ are the area ratio of one and the other component on the surface. For our data, $\theta_2$ for the SiO$_2$ can be regarded as 0°. To our knowledge our result shows the new finding for the validity of Cassie-Baxter law down to nanoscale with two component patches.

Reference


Fig. 1: Change of $\cos \theta_k$ (WCA) for SiO$_2$ deposited on rutile TiO$_2$(110) versus the area ratio of bare TiO$_2$ region (not covered with the SiO$_2$ overlayer) to the total surface area at 0, 2, 4, 6, 8, 10, 12 and 24 hours after UV light irradiation in air.