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# Ultra-thin $SiO_2$ epitaxial heterogeneous growth on rutile $TiO_2(110)$ surfaces with improving hydrophilicity

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Recently, heterogeneous oxide interface is one of the most attractive material systems, opened novels environmentally friendly applications. Among of them, Ti-Si binary oxide is one of prominent candidates to improve the catalyst performance, hydrophilicity and durability of photocatalytic $TiO_2$ materials. Here, the ultra-thin $SiO_2$ films on rutile $TiO_2(110)$ were prepared using a conventional vapor-deposition method in environment. Their surface morphologies, compositions and crystallographic were charaterized by using frequency modulation atomic force microscopy (FM-AFM) operated in water, photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). In addition, water contact angle measurement (WCA) was operated to estimate the change in hydrophilicity with increasing $SiO_2$ areas.

Rutile $TiO_2$ (110) wafers (Shinko-sha) were used as a substrate after ultrasonically washed in acetone, etched in an aqueous HF solution and rinsed in Milli-Q water. The $TiO_2$ substrates were annealed at 1000 °C in an electric furnace in air; the substrates were encapsulated in a sapphire case with a sapphire lid, or in a quartz case with a quartz lid which acts as a SiO vapor source. A contact angle of water droplet on their surface was measured with a water droplet of 2 μl in air immediately after annealing.

Figure 1 shows the AFM images of samples annealed in the sapphire case for 6 hours, and in the quartz case for 6 to 48 hours. We found the growth of patches after annealing in the quartz case, the area of which increased with annealing time; they look lengthwise growing from the steps to the [001] direction. But no patch was observed for the samples annealed in the sapphire case. Figure 2 shows the changes in the contact angle of water droplet, the area ratio of patches, and the XPS intensity ratio of Si 2p to O 1s, plotted versus annealing time for the samples annealed in the quartz case; neither patches nor Si peaks were found in the sapphire case. From XPS and FM-AFM analyses, the patches consist of $SiO_2$ in a few-layer thickness owing to the vapor transport of $SiO_2$ from the quartz case to the substrate. The $SiO_2$ patches probably epitaxially grew, because the LEED pattern of the annealed samples showed 1×2 to the 1×1 of rutile $TiO_2$ (110). Since the contact angle decreased inversely with increasing patch area and peak ratio, the patches play a crucial role in improving hydorphilicity. We will discuss the mechanism of the change in the hydrophilicity of the oxides.

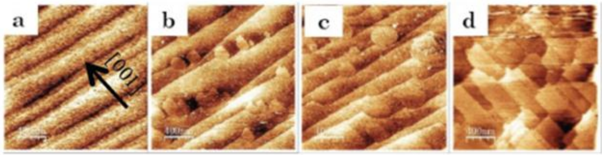


Figure 1: FM-AFM images of $SiO_2/TiO_2(110)$ surfaces (2000×2000 $nm^2$) annealed at 1000 °C. Arrow shows the [001] direction. (a) for 6 h in a sapphire case. Constant frequency shift ($\Delta f$) = +193 Hz; (b) annealed for 6 h in a quartz case, $\Delta f$ = +170 Hz; (c) for 24 h in the quartz case, $\Delta f$ = +356 Hz; (d) for 48 h in the quartz case, $\Delta f$ = +248 Hz.

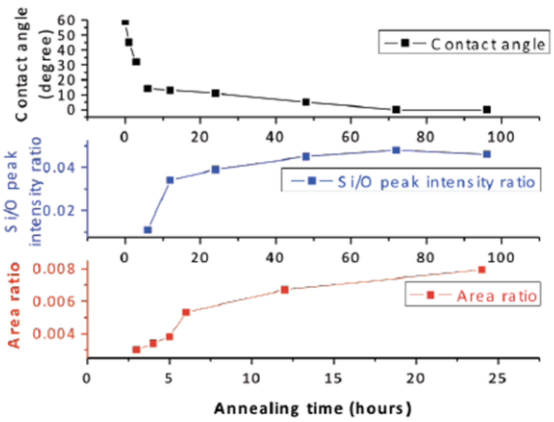


Figure 2: Dependence of contact angle of water droplet, XPS peak intensity ratio of $Si/O_{TiO2}$ and the patch area versus annealing time for the samples annealed in the quartz case.