Hetero-epitaxial growth of vertically-aligned TiO$_2$ nanorods on m-cut sapphire substrate with (001) SnO$_2$ buffer layer

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1. Experimental Details

Preparation of SnO$_2$ buffer layer. M-cut (100) sapphire was used as a substrate. Before deposition, the substrate was ultrasonically cleaned in acetone, ethanol, and de-ionized water for 10 min. Highly (001) oriented epitaxial SnO$_2$ film was deposited by plasma enhanced atomic layer deposition (PE-ALD). The Sn precursor was dibutyl tin diacetate (DBTDA, \(((\text{CH}_3\text{CO}_2)\text{Sn}(\text{CH}_3)_2\text{CH}_3)\)). The time sequence for source pulse, first purge, plasma pulse, and second purge was 2, 8, 10, and 8 s, respectively. The deposition was conducted with an rf power of 100W at 240 mTorr for 500 cycles. The SnO$_2$ buffered m-cut sapphire substrate was annealed at 600 °C to enhance their crystallinity before the TiO$_2$ nanorod growth.

Synthesis of TiO$_2$ nanorods. For TiO$_2$ nanorod growth, 25 mL of de-ionized water was mixed with 25 mL of concentrated hydrochloric acid (36.5% ~ 38% by weight) and stirred at ambient conditions for 5 min. and then 0.8 mL of titanium butoxide (Ti(OBu)$_4$, 97% Aldrich) was added to the solution and stirred until the solution became transparent. As-prepared solution was transferred to the Teflon-lined stainless steel autoclave with 120 mL capacity. A piece of SnO$_2$ buffered M-cut sapphire was placed against the wall of the Teflon-liner just below the solution surface. The hydrothermal synthesis was conducted at 150 °C for 0.5~3.0 h in an electric oven. After synthesis, the autoclave was naturally cooled to room temperature. The as-synthesised TiO$_2$ nanorods were taken out, rinsed with de-ionized water, and dried in ambient air.

Materials Characterization. The morphology of as-synthesized product was observed by field-emission scanning electron microscopy (FE-SEM, JSM-7401F, JEOL). The phase and in- and out of-plane orientation relationships between nanorods and substrate were examined by X-ray diffraction (XRD) and X-ray pole figure. The out-of plane orientation was examined by 0-20 X-ray diffraction (Model D8-Advance, BRUKER MILLER Co.) using Cu Kα radiation ($\lambda=1.5406\text{Å}$), and the in-plane orientation was investigated by X-ray pole figure (Model X’Pert Pro, PANalytical, the Netherlands), which was performed in Schulz reflection geometry by
scanning the tilt angle of goniometer, $\chi$ (Chi), in the range of 0–85° and the azimuthal angle, $\phi$ (phi), in the range of 0–360° with a step size of 5°. High-resolution transmission electron microscopy (HR-TEM, JEM-3000F, JEOL) analysis was further performed to investigate the crystal structure of nanorods and interfaces between nanorod, buffer layer, and substrate.

2. Results and Discussion

![SEM images](image)

**Figure S1.** SEM images of TiO$_2$ rods grown on (a) bare m-cut sapphire and (b-d) SnO$_2$ buffered m-cut sapphire.
**Figure S2.** SEM images of TiO$_2$ rods grown for (a) 0.5 h, (b) 1.0 h, and (c) 2.0 h.

**Figure S3.** (a) Atomic configurations of m-cut sapphire, SnO$_2$ buffer layer, and TiO$_2$ nanorod based on the determined in-plane orientation relationships and (b) estimated lattice mismatches.
Figure S4. The preparation of cross-sectional TEM sample by FIB.

Figure S5. The energy dispersive X-ray spectroscopy (EDS) analysis of TiO$_2$ nanorods/SnO$_2$ buffer layer/m-cut sapphire substrate.
Figure S6. Atomic configurations and simulated diffraction patterns; (a) m-cut sapphire with a view direction of [0\overline{1}0], (b) SnO$_2$ buffer layer with a view direction of [010], and (c) TiO$_2$ nanorod with a view direction of [010].

Figure S7. (a) HRTEM image of TiO$_2$ nanorod and (b) filtered FFT image of (a) (arrows indicate the line defects in the TiO$_2$ nanorods).
Figure S8. HRTEM images of TiO$_2$ nanorod tips.