Supporting Information

Enabling Higher Photoelectrochemical Efficiency of TiO₂ via Controlled

Formation of Disordered Shell: Alternative to hydrogenation process

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1. Experimental Methods

ITO glass was used as a substrate for deposition of TiO_2 thin films. The substrate was immersed in a solution of acetone and ethanol, ultrasonicated for 20 min and rinsed with DI water to remove the contaminants. TiO_2 thin film was deposited on the surface of ITO glass by atomic layer deposition (ALD). The temperature of substrate was set at 100 °C, and TiCl₄ and H₂O were used as precursors for TiO₂. The lengths of pulse time were 0.08 s for TiCl₄ and 0.1 s for H₂O. The vacuum inside the chamber was controlled at 10⁻² torr. The total cycle number of ALD deposition was set at 200, but two additional samples were deposited with 100 and 400 cycles to study the thickness effect. The ALD system and operation procedure have been presented previously.^{1,2}

After the deposition was finished, the samples were immediately transferred to a furnace for thermal treatment in air at 450 °C for 3 h. Later, an ultrathin layer of amorphous TiO_2 was deposited on the crystallized film by ALD with the cycle number of 30, 50, or 100.

The phases and crystal structures were analyzed by grazing incidence X-Ray diffricaton (TTRAXIII, Rigaku) using Cu K_{α} radiation and incident angle of 0.5°. Raman spectra were obtained by microzone confocal Raman spectroscopy (Horiba Jobin Yvon, Labram HR 800). The excitation wavelength was 325 nm (Kimon IK3301R-G) with a laser power of 30 mW (He-Cd laser). The instrument was equipped with an LMU-NUV 40x objective lens resulting in a spot size of 0.79 µm². The optical property of the TiO₂ thin films was evaluated by PL spectroscopy using He-Cd laser with a wavelength of 325 nm as the light source. The X-ray photoelectron spectroscopic (XPS) analysis was conducted on PHI Quantera AES 650. Argon sputtering for 10 s with an average etching rate of 8 nm/min was made prior to analysis to remove contaminants from the surface. In order to eliminate any contribution of substrate to the signal from TiO_2 , the samples for this analysis were prepared with 400 cycles, which is equal to a thickness of ~20 nm. The band gaps of the samples were estimated by UV-vis spectrophotometry (Hitachi UV-3010) with an integrating sphere attachment. An atomic force microscopy (AFM) system equipped with KPFM module (Bruker, Dimension ICON, scan rate 1 Hz, resonant frequency 1.3 MHz) was employed to map height profile and surface potential. For the AFM cross-sectional analysis, a part of ITO glass was covered with a mask. For the KPFM measurement, conductive Si tips with Co-Cr coating and a radius of 35 nm (Bruker, MESP) was applied. The average force constant and resonance frequency of the tip were ~ 2.8 N/m and 75 kHz, respectively.

The electrochemical measurement was performed using a Solartron 1286 potentiostat digitally controlled by a PC. The samples were immersed in 0.5 M KOH solution and illuminated by a 200 W Hg lamp.

2. Figures



Fig. S1 (a) Cross-sectional analysis of TiO_2 film deposited by ALD with 200 cycles on ITO glass. (b) Corresponding thickness profile.



Fig. S2 XRD patterns of TiO₂-(200 cyc./450 °C, 3 h) covered by 30, 50, and 100

cycles of amorphous TiO₂.



Fig. S3 Two-dimensional AFM images of TiO_2 films. (a) As-deposited thin film prepared by ALD with 200 cycles, (b) annealed in air at 450 °C for 3 h, and then covered with amorphous TiO_2 by (c) 30, (d) 50, and (e) 100 cycles of ALD.



Fig. S4 XPS survey scans of as-deposited TiO₂ prepared by 400 cycles of ALD. The right and left insets represeny enlargment in the ranges of 430 eV to 455 eV and 470 eV to 510 eV, respectively. As can be seen from the insets, there is an absence of any traces of Sn (Sn $3d_{3/2}$ at 498 eV and Sn $3d_{5/2}$ at 489 eV) or In (In $3d_{3/2}$ at 453 eV and In $3d_{5/2}$ at 445 eV)³ which evidences that TiO₂ deposited by low-temperature ALD process using TiCl₄ and H₂O as precursors has almost negligible impact on the etching of ITO substrate.



Fig. S5 UV-vis spectra of TiO₂-(200 cyc./450 °C, 3 h) covered by 30, 50, and 100

cycles of amorphous TiO₂.



Fig. S6 Current-voltage curves of amorphous and anatase TiO_2 prepared by ALD with

(a) 200, (b) 400, and (c) 100 cycles, and further annealed in air at 450 °C for 3 h.

3. References

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