# Supporting Information

## Investigation of Ultra-Thin Titania Films as Hole-Blocking Contacts for Organic Photovoltaics

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### Film growth rate

The ALD $TiO_x$ film thickness on a silicon substrate was measured using various-angle spectroscopic ellipsometry (M-2000, J. A. Woollam Co., Inc.). The thickness of the ALD layers versus the number of deposition cycles is plotted in Fig. S1. The ellipsometry spectra were fitted with the Cauchy dispersion model.[1] The measured $TiO_x$ thickness increases linearly with deposition cycles as expected, and the growth rate was observed to be 0.51 Å $cycle^{-1}$, which is very similar to other ALD studies. [2, 3] The growth rate data suggest that the films were deposited by well understood ALD processes, without excessive condensation or desorption of precursors on substrates. [4, 5]

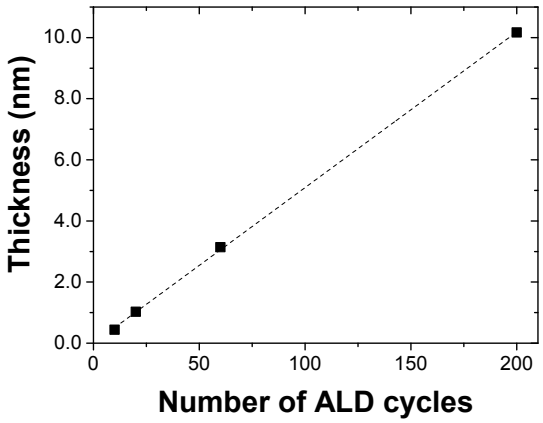


Fig. S1 $TiO_x$ film thickness depending on the number of ALD cycles.

**Chemical composition**

The chemical composition of ALD $TiO_x$ film was analyzed using XPS (Thermo K-alpha, Thermo Scientific) and angle-resolved XPS (Kratos Axis Ultra). Al-Kα X-ray source (1486.6 eV) was used as an excitation source. Fig. S2 shows high resolution XPS spectra of (a) Ti 2p level and (b) O 1s level for the $TiO_x$ film at a normal collection angle. The Ti 2p and O 1s spectra were fitted using 2 Gaussian-Lorentzian peaks. The shape and peak positions of the Ti $2p_{3/2,1/2}$ peaks was consistent with the formation of $TiO_2$ with no observable lower oxidation state mid-gap defects.[6] In the O 1s spectra, however, a distinguishable hydroxide, $OH^-$, peak was found at 532.4 eV, consistent with the presence of a small titanium hydroxide component incorporated into the otherwise stoichiometric $TiO_x$ layer. For the details of thin $TiO_x$ layers, Fig. S3 shows O 1s XPS spectra with various thick $TiO_x$ layers on ITO at two collection angle, (a) 0° and (b) 60°.

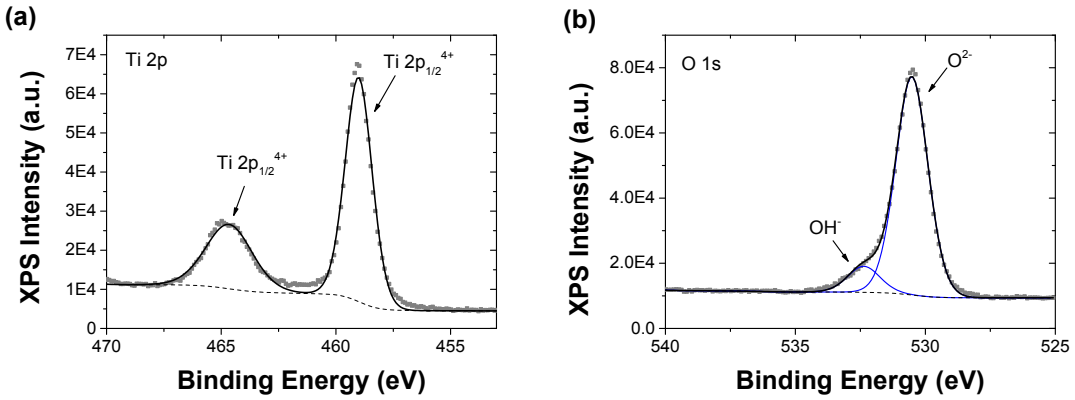


Fig. S2 XPS spectrum of 3 nm $TiO_x$ layer on a silicon wafer. Lorentz-Gaussian fitting line (solid line) and Shirley background (dashed line) are also plotted. (a) Ti 2p spectra, and (b) O 1s spectra.

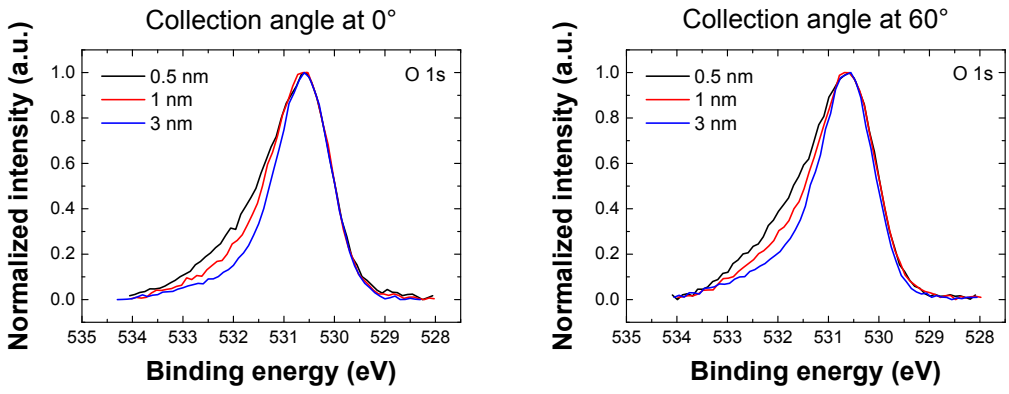


Fig. S3 Angle-resolved XPS of $TiO_x$ on ITO/glass substrates at a collection angle of (a) 0° and (b) 60°.

## OPV characterization – Ideality factor

The local ideality factor is a measure of the slope of the J–V characteristics on a semi-logarithmic plot (Fig. 10 (a)). The ideality factor of the device is determined from the plateau in the Ideality factor – Voltage characteristics.[7] The increase of ideality factor in the low voltage region is an indication of small shunt resistance. Devices with 3 nm $TiO_x$ films provide the lowest reverse saturation current, the best ideality factor and the largest shunt resistance.

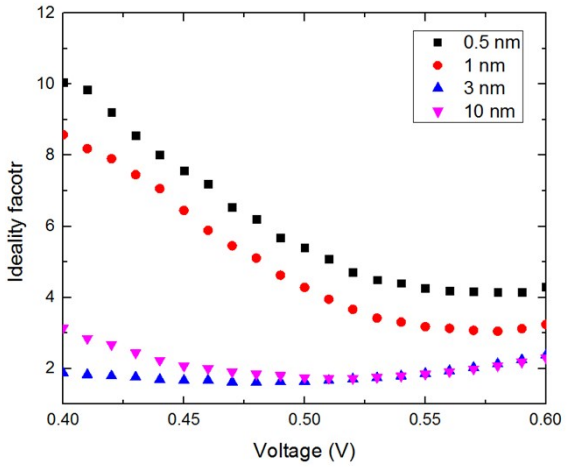


Fig. S4 Ideality factor – Voltage characteristics calculated for the photovoltaic devices with ALD $TiO_x$ films of different thicknesses.

## References


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