Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Picture of Electrode

Figure S1A shows a picture of the front side of a typical electrode. The entire rectangular piece is p-type silicon while the 8 mm circle contains the n^+ doping with the 5nm of Ti/100nm TiO_2. Figure S1B shows a picture of the back side of the same electrode.

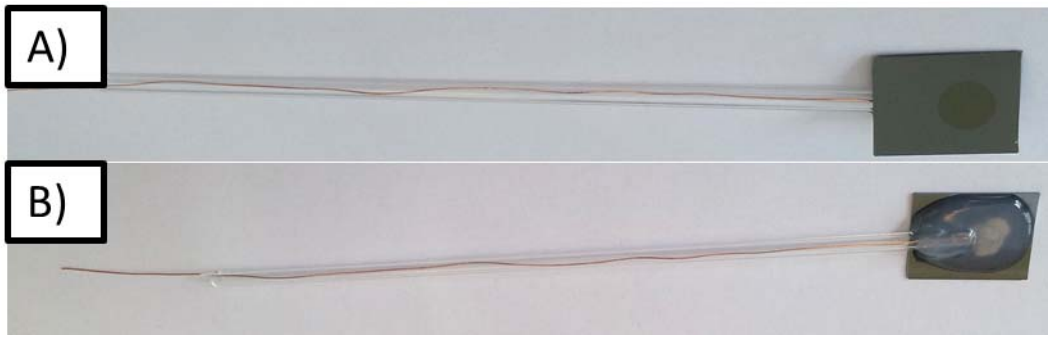

Figure S1: Picture of a typical photo-electrode used in this work.

SEM After 24 Hour Testing of Pt nanoparticles/Unannealed 100nm ALD TiO_2/5nm Ti/n^+p Si

Figure S2 shows 100 nm ALD TiO_2 (unannealed)/5 nm Ti/n^+p Si electrodes. Figure S2A is unannealed, unmeasured and does not contain any Pt. Figure S2B are SEMs from a platinized electrode that was tested for H_2 evolution for 24 hours at 0.300V vs. RHE (e.g. the electrode used in Figure 2a and 2c). This electrode had Pt photodeposited on it and was photoirradiated with the red part of the AM1.5 spectrum while being held at a potential of +0.300 V vs. RHE for 24 hours. It appears that the 24 hour test produces no significant differences in the surface morphology. This indicates that the degradation in

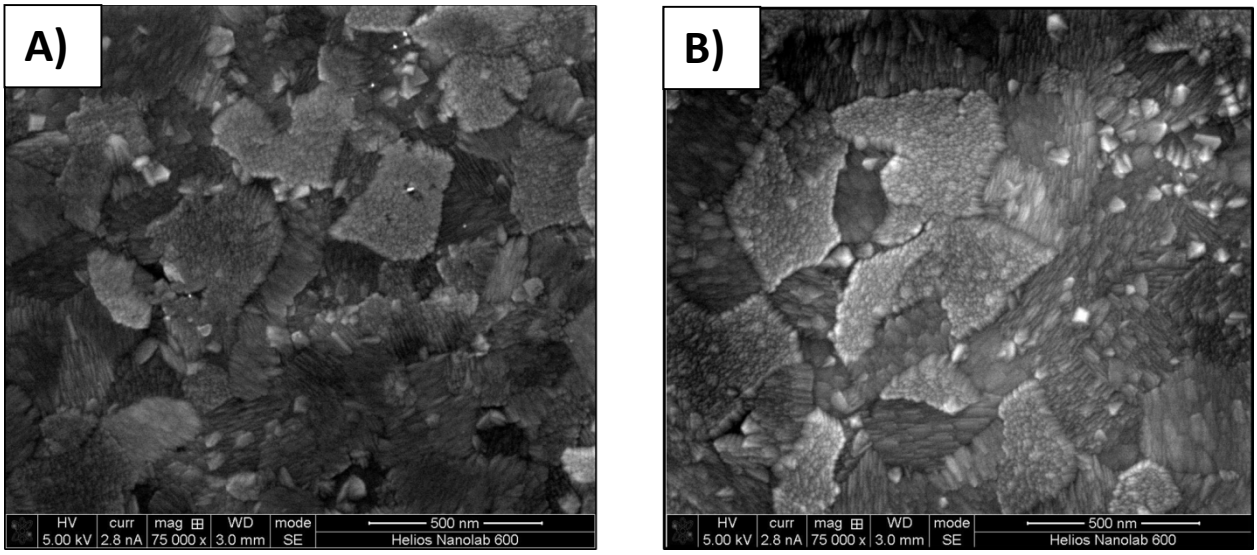

Figure S2: SEM images of a **A)** 100nm ALD TiO_2 (unannealed)/5nm Ti/n^+p Si before testing and **B)** after Pt deposition and for H_2 evolution for 24 hours at +0.300V vs. RHE.

performance of the unannealed sample is probably not caused by the corrosion of TiO_2, but rather another mechanism, such as loss of the catalyst particles from the surface.

Cyclic Voltammograms of Durability Tests

Figure S3 shows cyclic voltammograms of the long term durability tests of the vacuum annealed samples. While initially there is a little fluctuation, the electrodes seem to normalize out after a couple of days and remain constant until 10 days of testing. After 10 days the saturation current seems to fluctuate which may be due to the lamp. After approximately 15 days the electrode starts to slowly degrade. Initially the 1 M $HClO_4$ electrolyte was bubbled with hydrogen, but bubbling was not continued throughout the entire run due to safety issues. The Bio-logic potentiostats allows for simultaneous monitoring of the counter electrode's potential. This potential was typically around 2.0 V vs. RHE for this run indicating that water oxidation was occurring on this electrode. The continuous production of bubbles on the cathode side ensured that H_2 was being produced rather than any other reaction. After the 30 day run, a Pt electrode was tested for H_2 evolution to verify that the reference electrode did not shift. This result showed that it did not shift. The reference used was a Schott Instruments Hg/HgSO4 electrode. It should be noted that the system got bumped after the 28^{th} day, which may have slightly misaligned the system. This may be a potential cause for the steep decrease in saturation current between the 28^{th} and 29^{th} day.

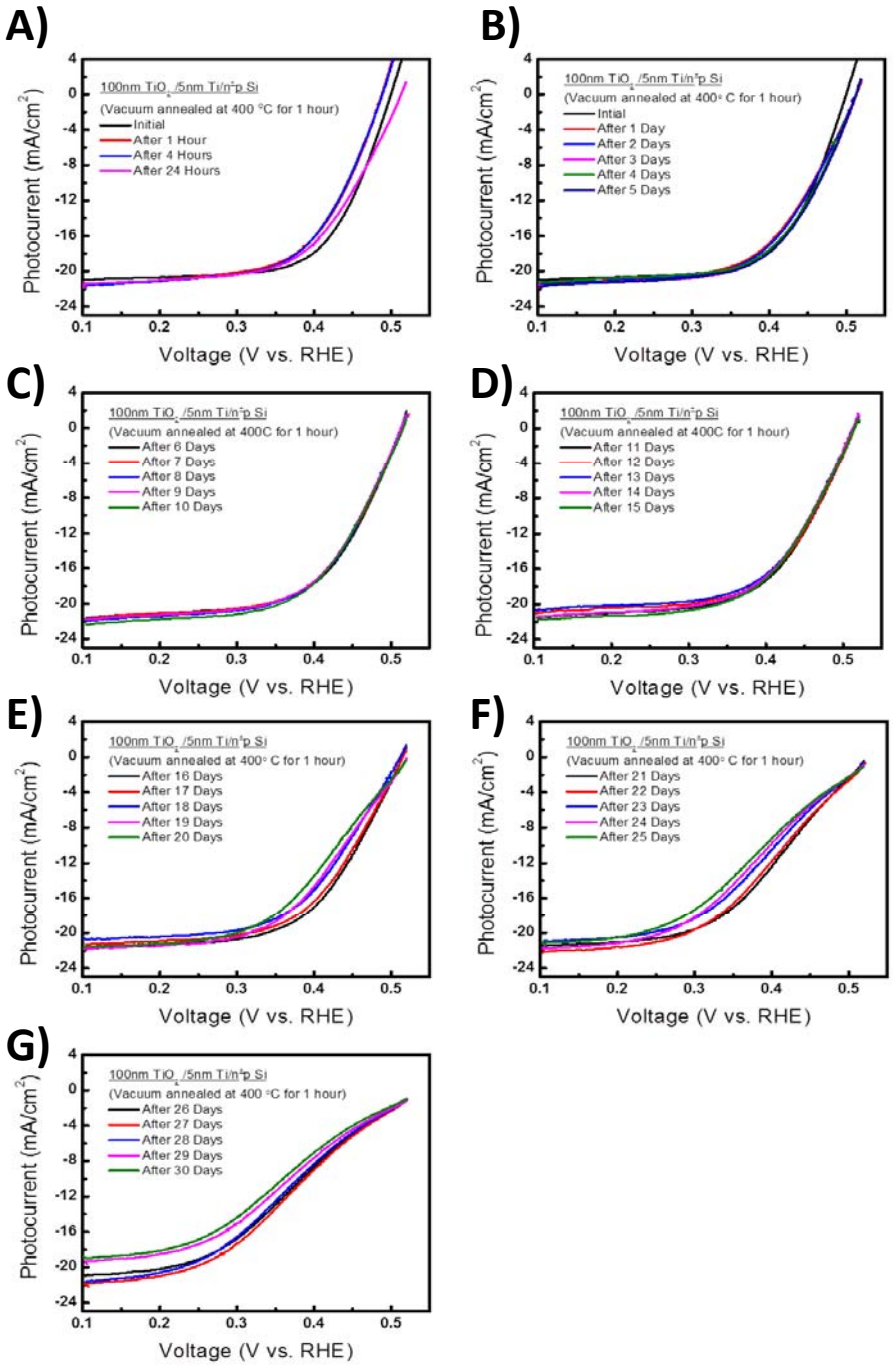

Figure S3: Cyclic voltammograms of a Pt/100 nm TiO_2 (ALD, vacuum annealed)/5 nm Ti/n^+p Si electrodes at time intervals of **A)** Initial- 1 day **B)** Initial-5 days **C)** 6-10 days **D)** 10-15 days **E)**16-20 days **F)** 21-25 days **G)** 25-30 days. The samples were irradiated with a halogen lamp with a 635 nm cut-off with the approximate intensity that would be seen in the red part (λ > 635 nm) of the AM1.5 spectrum (38.8 mW/cm^2)

X-ray Diffraction

Figure S5 shows grazing angle XRD of both unannealed and vacuum annealed 100 nm ALD TiO_2. All the peaks for anatase Ti are pointed out in this figure. While it is clear that both these materials are crystalline anatase, it is also clear that annealing has little if any effect on the crystal structure or grain size. The 2 unmarked peaks near 52° are not related to TiO_2 (possibly related to the underlying single crystalline Si). Thus the fact that they differ between samples should have no impact on the physical state of the TiO_2.

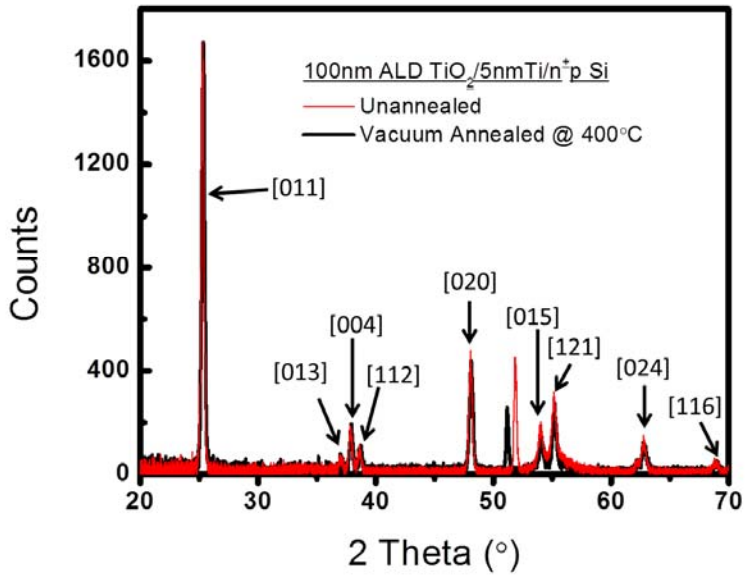

Figure S4: X-ray diffraction data of 100nm ALD TiO_2 that was either unannealed or vacuum annealed.

Cross-Sectional SEM

Cross-sectional SEM was done to check to see if there was any major difference between the unannealed and the vacuum annealed sample. Figure S5 show both the unannealed and vacuum annealed sample. From these images it is apparent there is no major morphological difference between the two samples.

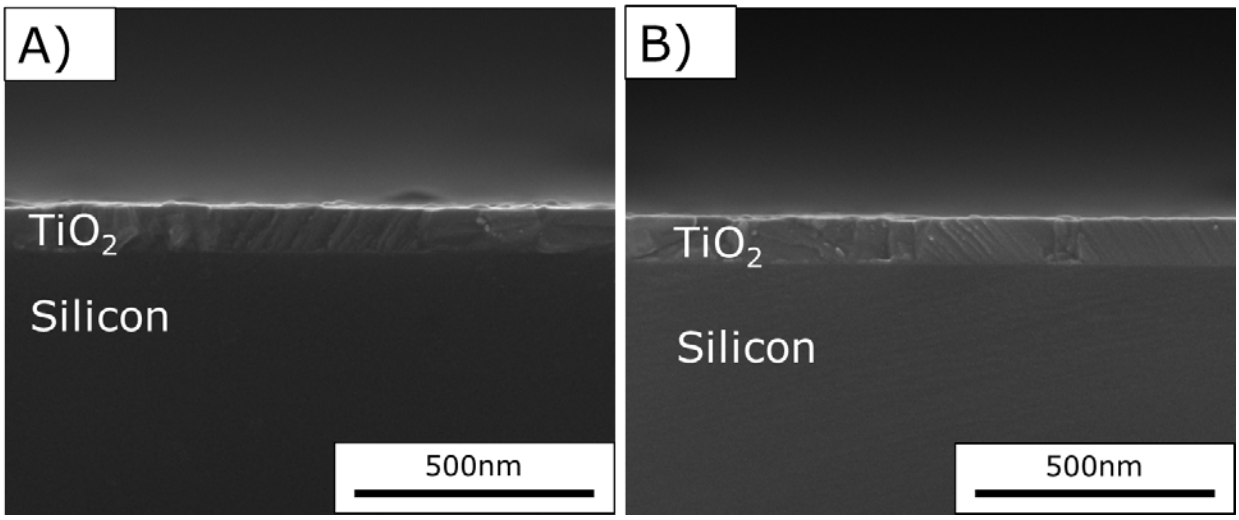

Figure S5: SEM images of A) unannealed 100 nm ALD TiO_2 on 5 nm Ti/n^+p Si and B) 400°C vacuum annealed 100nm ALD TiO_2 on 5nm Ti/n^+p Si