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# Protection of Si photocathode using TiO<sub>2</sub> deposited by high power impulse magnetron sputtering for H<sub>2</sub> evolution in alkaline media

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## ABSTRACT

Si is an excellent absorber material for use in photoelectrochemical (PEC) hydrogen production. Only a few studies have been done using Si in alkaline electrolyte for hydrogen evolution due to its poor chemical stability in high pH electrolyte, indicating that a chemically stable protection layer is essential. Here we investigate thin TiO<sub>2</sub> films deposited by high power impulse magnetron sputtering (HiPIMS) as a protection layer for a p-type silicon photocathode for photoelectrochemical H<sub>2</sub> evolution in a high pH electrolyte. The X-ray reflectometry analysis reveals that the HiPIMS process provides improved film density for TiO<sub>2</sub> films (4.15 g/cm<sup>3</sup>), and consequently results in a significantly less corroded Si surface. The Si photocathode protected by the HiPIMS grown TiO<sub>2</sub> film along with Pt as co-catalyst produced a photocurrent onset potential of ~0.5 V vs. RHE in 1 M KOH and showed a 4% decay over 24 h in KOH. In contrast, the sample with the TiO<sub>2</sub> deposited using conventional DC sputtering technique of similar thickness shows 20% loss in photocurrent for the same time interval. Considering the fact that the experiments were carried out not in the cleanroom, much less corrosion loss can be obtained if done in dust-free condition. Hence, these results suggest the HiPIMS technique as an improved approach for the protection of photoelectrodes, which are unstable in alkaline solution.

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## 1. Introduction

Photoelectrochemical (PEC) solar fuel conversion is a promising approach to solar fuel generation because of the direct conversion of solar energy into hydrogen. To date, considerable efforts have been invested to identify durable photoactive semiconductor materials [1–6]. Si is one of the most studied materials since it is able to show effective photocatalytic properties in an acidic electrolyte [2,3,7,8]. While Si easily passivates to SiO<sub>2</sub> in an acidic environment (which covers the surface and hinders current flow), previous researches [3,8,9], have shown that TiO<sub>2</sub> can be used as an intermediate layer between the photoabsorber and the catalyst with good chemical stability under the hydrogen evolution reaction (HER) at pH 0. This approach prevents Si from passivating, thus allowing efficient PEC activity. Even if there are pinholes,

which allow the electrolyte to contact the Si, the Si will only be locally passivated because the passivation is self-limiting in acid. Thus there will be no noticeable effect on overall performance.

Since the eventual role of Si in this work is for use as a photocathode in a 2-photon overall water splitting system [8,9], Si will need to perform in the same electrolyte as the photoanode side. While there are no good non-noble metal oxygen evolution reaction (OER) catalysts that are stable in acidic electrolyte, in alkaline electrolytes there are many efficient non-noble metal OER catalysts which will allow for substantial cost savings and better scalability [10–12]. Beyond the stability of the catalyst there is also the issue of stability of the light absorber. For instance, most potential absorber materials quite easily dissolve or photocorrode in acidic solution while many show stable photocatalytic performance in neutral and alkaline electrolytes [10–15]. For Si, however, it is the other way around. When Si interacts with alkaline solution it corrodes via dissolution since SiO<sub>2</sub> is not stable under alkaline conditions and therefore the self-limiting passivation mechanism does not work at high pH media. The lack of a self-limiting passivation entails that the underlying Si under any pinholes in a

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protection layer will continuously corrode. Thus, preventing pin-holes in protection layers is essential in alkaline environments.

Fortunately  $\text{TiO}_2$  has a wide stability window (even at  $\text{pH} > 15$ ) implying that Si protected by a dense layer of  $\text{TiO}_2$  can also be employed in alkaline electrolyte as demonstrated in recent research which used Si protected by atomic layer deposited (ALD)  $\text{TiO}_2$  for the oxygen evolution reaction (OER) [16]. However, to the best of our knowledge, only a few stability studies under HER condition have been carried out using the Si-based electrode in high pH alkaline electrolyte. Kast et al. [17] demonstrated a  $\sim 24$  h stable HER photocurrent using Si protected by solution processed Ti/F:SnO<sub>2</sub>/TiO<sub>2</sub> multilayer (TiO<sub>2</sub> on top). Meanwhile, Feng et al. [18] demonstrated the Si photocathode protected by Ni/Ti metallic bilayer showing slow degradation after the 12 h of HER due to the gradual loss of Ni in KOH. A protective oxide layer deposited by atomic layer deposition [19–21] can provide precisely controlled surface coverage, but it may not be very practical for high throughput production [22]. This study aims to evaluate the advantage of high power impulse magnetron sputtering (HiPIMS) grown  $\text{TiO}_2$  as a conducting protective material for HER in an alkaline solution.

We evaluate the chemical stability and photo-electrochemical stability of  $\text{TiO}_2$  deposited on  $\text{pn}^+$ -Si photocathodes using HiPIMS and conventional DC magnetron sputtering (DCMS) as a reference sample. HiPIMS is a novel ionized physical vapor deposition technique in which its major advantages include a denser coating and smoother surface morphology [23,24] due to a high degree of ionization of plasma (up to  $10^{13}$  ions  $\text{cm}^{-3}$  [25]), which is almost two orders of magnitude higher than that of the DCMS technique [26], and contains high fractions of target metal and reactive gas ions. Consequently, the grown film has an enhanced corrosion resistance without large-scale defects [27]. The main focus of this work is on investigating the effect of  $\text{TiO}_2$  packing density and tighter grain boundaries on its protection performance in 1 M KOH electrolyte ( $\text{pH} = 14$ ). Here, we compare the  $\text{TiO}_2$  films grown by the aforementioned deposition methods (DCMS and HiPIMS) at various growth temperatures. Hence, the effect of the improved film density on the stability and durability of the films is investigated in high pH electrolyte (1 M KOH) under dark conditions. Furthermore, we evaluate the long-term photocatalytic  $\text{H}_2$  production performance using  $\text{TiO}_2$ -protected photovoltaic (PV) assisted Si photocathode ( $\text{pn}^+$ -Si/Ti/TiO<sub>2</sub>) under illumination in the same electrolyte condition as mentioned above. Finally, we examine the correlation of the stability of  $\text{TiO}_2$ -protected electrodes with the  $\text{TiO}_2$  packing density measured by means of X-ray reflectometry.

## 2. Experimental details

### 2.1. Si-based photocathode fabrication process

Czochralski crystalline silicon (CZ c-Si) based photocathodes were fabricated as previously described [8,9]. The shallow  $\text{pn}^+$ -junction was formed on p-type Si (100) wafers (Topsil, 1–20  $\Omega\text{-cm}$ , boron-doped) with  $\text{POCl}_3$  as the phosphorus dopant source for n<sup>+</sup> doping using a vapor phase surface doping process in an atmospheric pressure tube furnace. The doping process was carried out at 900 °C for 10 min. Subsequently a shallow  $\text{pn}^+$ -junction was formed on the surface of the p-type wafer, which was expected to form a depletion width of approximately 500 nm [8]. As previously shown [8,9], the  $\text{pn}$ -junction screens the band-bending in Si from the electrolyte (buried junction), which allows for increased photovoltage. A 3  $\mu\text{m}$  deep part of the  $\text{pn}^+$ -Si was patterned by photolithography technique and etched away by reactive ion etching ( $\text{SF}_6$ ,  $\text{O}_2$  and  $\text{C}_4\text{F}_8$  gases were used in a Pegasus DRIE

system from SPTS Technologies) to fabricate a 10 mm diameter isolated circular  $\text{pn}^+$ -junction area (mesa structure).

Ti and  $\text{TiO}_2$  protecting layers were grown by the DCMS and HiPIMS processes. In case of DCMS process, the Si samples were sputter-cleaned by Ar to remove any adventitious carbon-based contaminations and oxide layers at 35 W for 120 s. Then, approximately 10 nm of Ti was deposited followed by 100 nm of  $\text{TiO}_2$  under oxygen and argon gas flow using conventional DC power mode. The base pressure of the vacuum chamber (AJA inc.) was below  $8 \cdot 10^{-8}$  mbar. The detailed procedure can be found elsewhere [8,9]. The Ti interlayer was introduced for both DCMS and HiPIMS cases to prevent the oxidation of the Si surface during the metal oxide deposition at various temperatures, and to provide efficient pathway for the carrier injection by forming an Ohmic contact at the interface. This approach has been applied and verified many times in previous studies [2,8,9,19] using a 5 nm thick Ti interlayer. Since in this work applied a thicker ( $\sim 10$  nm) metallic interlayer, we assume that barrier issue at the interface can be avoided. Investigating the interface properties is useful, but is beyond the scope of this work.

For the case of HiPIMS process, the samples were cleaned ultrasonically using isopropanol, acetone, and methanol each for 5 min. In order to remove the native oxide, the samples were dipped in HF acid (4%) for 5 min then taken out of HF and put into DI water and carried over to the chamber to be loaded. Before loading, the samples were taken out of the DI water and dried by blowing  $\text{N}_2$  on them. A custom-built sputtering chamber was employed to perform the following depositions. The base pressure of the chamber was below  $5 \times 10^{-9}$  mbar. A 3-inch (75 mm) Ti target with the purity of 99.995% was used in a planar magnetron system for growth of both Ti and  $\text{TiO}_2$  layers. The sputtering gas was Ar (99.999%) for the case of Ti growth and Ar mixed with  $\text{O}_2$  (99.999%) in the case of  $\text{TiO}_2$  growth. Total growth pressures of  $4 \times 10^{-3}$  mbar for the growth of Ti and  $7 \times 10^{-3}$  mbar for the growth of  $\text{TiO}_2$  were achieved using an adjustable throttle valve. To prevent any deposition gradient due to the chamber geometry, the samples were rotated during growth.

In the case of the HiPIMS grown Ti interlayers, the power was supplied by a SPIK1000A pulse unit (Melec GmbH) operating in the unipolar negative mode at constant voltage, which in turn was charged by a dc power supply (ADL GS30). The discharge current and voltage were monitored using a combined current transformer and voltage divider unit (Melec GmbH). LabVIEW software acquired the data and calculated the average power using the measured discharge current and voltage for each applied pulse and then set pulse repetition frequency. The pulse repetition frequency was 50 Hz. The pulse length was 110  $\mu\text{s}$  and the cathode voltage was set to 485 V. The resulting average power was then 120–125 W and the achieved target peak power density was  $\sim 850$ – $900$   $\text{W cm}^{-2}$ . The Ti interlayer growth temperature was room temperature (hereafter RT). Using such parameters resulted in 5  $\text{\AA}/\text{min}$  of growth rate and approximately 10 nm Ti with native oxide.

The  $\text{TiO}_2$  films were grown using the same setup for HiPIMS grown Ti layers. The pulse voltage was 423 V with 200  $\mu\text{s}$  long duration at frequency of 270 Hz. The average power and peak power density during growth were 340 W and  $240$   $\text{W cm}^{-2}$ , respectively. The  $\text{TiO}_2$  layers were grown at various growth temperatures of RT, 300, 400, and 500 °C. The mentioned growth parameters resulted in a growth rate of 5 nm/min and the growth time of 20 min produced 100 nm  $\text{TiO}_2$  layers. The growth temperature was kept steady during the deposition.

Ohmic contacts were made using an eutectic gallium–indium alloy and Cu-wire on the backside of the Si substrates as described elsewhere [8,9]. The inactive parts of the electrodes were covered with epoxy, and the Pt was deposited as a co-catalyst by having

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