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# Double-Heterojunction Crystalline Silicon Solar Cell with Electron-Selective TiO<sub>2</sub> Cathode Contact Fabricated at 100°C with Open-Circuit Voltage of 640 mV

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Abstract — A double-heterojunction c-Si solar cell was fabricated at maximum process temperature of 100°C. We demonstrate an electron-selective passivated contact to Si using TiO<sub>2</sub>, which increased the open-circuit voltage by 45 mV compared to a device with a direct metal to n-type substrate contact. In the fabricated structure, PEDOT/Si replaced the front-side p-n junction of conventional Si-based solar cells while the Si/TiO<sub>2</sub> interface is formed on the back-side. Compared to previous work [1], the V<sub>OC</sub> has increased from 620 to 640 mV while maintaining a maximum process temperature of 100°C. Critical to the improved performance is better passivation of the Si/TiO<sub>2</sub> interface. The increase in V<sub>OC</sub> can be attributed to an interface recombination velocity of ~75 cm/s, which is consistent with photoconductance decay measurements.

*Index Terms* — carrier selective contact, heterojunction, passivation, metal-oxide, silicon, titanium oxide

### I. INTRODUCTION

Recently there has been much interest in carrier selective contacts for crystalline silicon solar cells. Carrier selective contacts (CSCs) are a novel approach to realizing high-efficiency silicon solar cells without p-n junctions fabricated at high temperatures (> 800°). TiO<sub>2</sub> on Si(100) has been shown to blocks holes ( $\Delta E_V \ge 2.3 \text{ eV}$ ) while being transparent to electrons ( $\Delta E_C < 0.3 \text{ eV}$ ) [2]. Furthermore, Si/TiO<sub>2</sub> interfaces have demonstrated effective minority carrier recombination velocities below 10 cm/s [3]. The combination of these properties makes TiO<sub>2</sub> an excellent choice for an electron-selective contact for high efficiency and low-cost Sibased photovoltaics.

Previously, we demonstrated a double-heterojunction crystalline silicon solar [1]. The front-side p+/n junction of a conventional Si solar cell was replaced by a heterojunction formed between n-Si and the organic polymer Poly(3,4-ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT) that blocks electrons but passes holes [4]. The back-side n+/n junction was replaced by the electron-selective Si/TiO<sub>2</sub> heterojunction The band-alignment and structure is shown in Figure 1. We showed that the electron-selective TiO<sub>2</sub> contact increased V<sub>OC</sub> by 30 mV without degrading short circuit current or fill factor compared to a direct metal contact to the substrate. In this work, we show an increase of the effect of the TiO<sub>2</sub> contact on V<sub>OC</sub> from 30 mV to 45mV. We accomplished this through reducing interface recombination.



Fig. 1. (a) Band-alignment at PEDOT/Si and Si/TiO2 interface as measured by photoelectron spectroscopy. (b) Device structure [2]

#### II. DEVICE PRINCIPLE

The effect of the  $TiO_2$  is shown in Figure 2. A single-sided PEDOT/Si device (with no  $TiO_2$ ) is displayed in Figure 2(a). The PEDOT/Si interface acts as a hole-selective contact, blocking electrons while being transparent to holes. Furthermore, due to the high work-function of the PEDOT, there is a depletion region in the silicon which collects photogenerated carriers. Because the electron dark current (majority carriers) is blocked by the PEDOT/Si interface, the dark current is now dominated by the hole dark current (minority carriers).

With the electron-selective  $TiO_2$  deposited on the backside (Fig. 2(b)), the hole dark current is blocked. This leads to a further reduction in the dark current and thus an increase in the open-circuit voltage. However, in reality, the Si/TiO<sub>2</sub> interface will have defect states, allowing holes to recombine and thus negating the hole-blocking functionality of the Si/TiO<sub>2</sub> interface (Fig. 2(c)). The interface quality is typically described though an interface recombination velocity S<sub>eff</sub>. We calculated S<sub>eff</sub> for different TiO<sub>2</sub> process conditions by measuring the minority carrier lifetime utilizing the Quasi-Steady State Photoconductance Decay (QSSPCD) method [5].



Fig. 2. Band diagrams of (a) Single-sided PEDOT/n-Si device (b) Double-heterojunction with electron-selective TiO<sub>2</sub> contact blocking hole dark current and (c) Double-heterojunction showing interface defects at Si/TiO<sub>2</sub> interface negating hole-blocking.

To elucidate the importance of interface recombination, one notes that the rate of hole transport in the substrate due to diffusion has to match the rate of recombination at the  $TiO_2$  interface, which is proportional to the hole density at that interface. It is straightforward to show that the hole current  $(J_{0,h})$  is reduced from its short base value  $J_{0,SB}$  (no  $TiO_2$ ) by a "blocking factor" BF, where

$$J_{0,h} = \frac{q n_i^2 D_p}{N_D W} * \frac{1}{BF} = J_{0,SB} * \frac{1}{BF}$$
(1)

with BF =  $[(1+D_p/(W*S_{eff}))]$  [1]. The calculated hole density profile is plotted in Figure 3 for an applied bias of 0.60V in dark (short-base scenario) for different S<sub>eff</sub> values. A lower S<sub>eff</sub> (smaller gradient) implies a higher BF and a smaller J<sub>0</sub>. At S<sub>eff</sub> = 0 cm/s, the gradient is completely flat. For an  $S_{eff} > 10^3$  cm/s there is little effective blocking compared to a direct metal contact. Concomitantly, one can calculate an increase in  $V_{OC}$  from the reduced  $J_0$ :

$$\Delta V_{OC} = kT * \ln\left(\frac{J_{0,no\ TiO2}}{J_{0,TiO2}}\right) = kT * \ln(BF)$$
(2)



Fig. 3. Simulated hole density profile for a 300  $\mu$ m thick wafer for different S<sub>eff</sub> value. The applied bias is 0.60 V. Larger S<sub>eff</sub> values lead to larger gradients

#### **III. RESULTS AND DISCUSSION**

To demonstrate the effect of the passivated TiO<sub>2</sub> contact, the two structures from Figure 2(a) and 2(b) - without and with TiO<sub>2</sub> respectively - were fabricated. Experimental details regarding fabrication are given elsewhere [1], with the exception that an additional step was performed: samples were left in N<sub>2</sub> ambient at room temperature for 48 hours. This step improved the passivation of the Si/TiO<sub>2</sub> interface to the same level as a 250°C anneal (measured by QSSPCD, before cathode deposition) [6]. J-V curves under light (solar simulator at  $\sim 110 \text{ mW/cm}^2$ ) are shown in Figure 4. The increase in V<sub>OC</sub> is consistent with the shift in dark current (inset). The relatively low J<sub>SC</sub> values are due to the lack of an effective AR coating, PEDOT absorption, and the cathode metal coverage. A slight increase in short-circuit current due to the  $TiO_2$  can be attributed to increased collection of long wavelength photons as the Si/TiO2 interface is passivated and thus fewer photogenerated carriers recombine at the cathode.

Figure 5 shows the blocking factor as a function of  $V_{OC}$  (from (2)) and  $S_{eff}$  from the observed  $V_{OC}$  (from (1)). Based on the experimentally observed increase in  $V_{OC}$  of 45 mV, we find a BF of 5.4. Using W = 300 µm and assuming  $D_p = 10$ 

 $cm^2s^{-1}$ , we estimate  $S_{eff}$  to be 75 cm/s. This  $S_{eff}$  value is consistent with calculated  $S_{eff}$  values from QSSPCD measurements of 65 - 85 cm/s at similar light levels.



Fig. 4. J-V characteristics of device without  $TiO_2$  (black) and with  $TiO_2$  (blue) respectively under light. (inset shows dark J-V characteristics for 0 to 0.6 V)

 TABLE I

 Solar Cell Parameters of The Two Devices in Fig. 4



Fig. 5. From  $\Delta V_{OC}$ , one can calculate the blocking factor (reduction in  $J_0$ ) and the recombination velocity value required to achieve said  $\Delta V_{OC}$ .

Figure 6 shows a comparison between  $S_{eff}(\Delta V_{OC})$ , extracted from  $\Delta V_{OC}$  using (1) and (2) and S<sub>eff</sub>(PCD), determined from QSSPCD measurements of the TiO<sub>2</sub>/Si interface left in N<sub>2</sub> ambient for 48 hours at room temperature ('stabilized TiO<sub>2</sub>'). Additionally, comparison between  $S_{eff}(\Delta V_{OC})$  and  $S_{eff}(PCD)$ are made for 250°C annealed TiO<sub>2</sub> ('annealed' TiO<sub>2</sub>') from previous experiments [6,7]. 250°C-annealed and room Tstabilized (this work) TiO<sub>2</sub> have similar S<sub>eff</sub>(PCD) values. However 250°C-annealed TiO<sub>2</sub> has a large and high range for  $S_{eff}(\Delta V_{OC})$ . This indicates that although the 250°C annealing step reduces the recombination velocity measured by QSSPCD compared to as-deposited TiO<sub>2</sub>, which typically has a Seff(PCD) ~5000 cm/s, annealing at 250°C may lead to a morphology change (such as pinholes) which could allow the penetration of the cathode metal and thus increase  $S_{eff}(\Delta V_{OC})$ and limits the effectiveness of 250°C annealed  $TiO_2$  in a device.



Fig. 6. Comparison of recombination velocities calculated from improvement in  $V_{OC}$ ,  $S_{eff}(\Delta V_{OC})$ , and from QSSPCD measurements,  $S_{eff}(PCD)$ , for 'annealed' TiO<sub>2</sub> (250°C anneal) and 'stabilized TiO<sub>2</sub>' (N<sub>2</sub> ambient for 48 hours – this work).

#### **IV. CONCLUSIONS**

We have shown for the first time the use of an electronselective TiO<sub>2</sub> contact to improve the open-circuit voltage of crystalline silicon solar cells by 45 mV to reach a V<sub>OC</sub> of 640 mV with a maximum process temperature of 100°C. The improvement in V<sub>OC</sub> can be attributed to a well-passivated Si/TiO<sub>2</sub> interface with a recombination velocity of 75 cm/s.

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