Measurement of TiO_2/p-Si Selective Contact Performance using a Heterojunction Bipolar Transistor with a Selective Contact Emitter

Janam Jhaveri, Alexander Berg, Sigurd Wagner and James C. Sturm

Department of Electrical Engineering and Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, NJ 08544, USA

***Abstract* — In a photovoltaic device, the evaluation and understanding of carrier-selective contacts are difficult, because in both terminals the current measured represents the sum of both electron and hole currents at that contact. We seek to independently know the electron current and hole current across a carrier-selective contact. In this work, we demonstrate a heterojunction bipolar transistor structure using the selective contact as the emitter-base junction, allowing one to separately measure the electron and hole currents at that contact. The method is then used to evaluate the properties of a TiO_2/p-type crystalline Si electron-selective heterojunction contact, and the information learned is used to understand a TiO_2/p-Si heterojunction PV cell, where the TiO_2/p-Si replaces the n^+-p junction.**

I. Introduction

Dopant-free carrier-selective contacts, utilized to replace p-n or n-n^+ junctions, are of high interest for silicon photovoltaics [1]. Recently, materials such as poly(3,4- ethylene-dioxythiophene):polystyrenesulfonate (PEDOT:PSS) [2], titanium oxide (TiO_2) [3,4] , nickel oxide (NiOx) [5], and molybdenum oxide (MoOx) [6] have been investigated for selective contact purposes. Carrier-selective contacts work by blocking one type of carrier in one direction while allowing the other carrier to pass through in the other direction (thus selecting one carrier). As such, quantifying the electron and hole current components separately across a terminal could be important to optimize selective contacts. Yet understanding the fundamental performance of such contacts in photovoltaic devices is difficult, because the device current at either contact represents the sum of the electron and hole current at that contact. Thus determining which current is dominant, and how small the smaller current is, is not possible.

In this paper we introduce a general method using the selective contact in a heterojunction bipolar transistor, which allows the independent and direct measurement of the electron and hole current components at the contact. The method is used to study TiO_2/p-type crystalline Si contacts. We show that in a Al/TiO_2/p-type Si single junction cell, the electron and hole currents are of similar magnitude.

II. Current Processes at TiO2/p-Si Heterojunctions

Because of its large valence band offset (~ 2 eV), one can consider using the TiO_2/p-Si heterojunction as an electron-selective contact, to replace the n-p junction [3]. This would allow Si-based solar cell fabrication using a low-temperature (~100 °C) CVD step to replace the high-temperature phosphorus diffusion process.

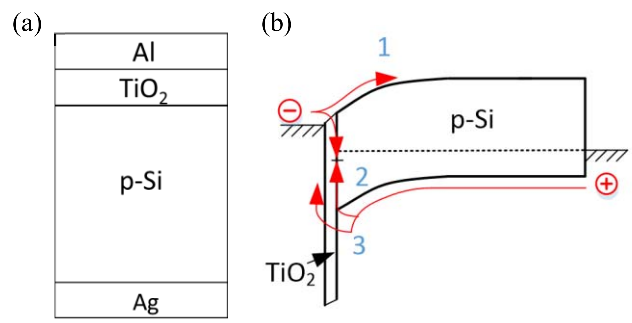

Fig. 1. (a) Device structure and (b) Fundamental current processes at an Al/TiO_2/p-Si selective contact [3]. Process 1 is the ideal electron injection current, process 2 is recombination at the Si/TiO_2 interface and process 3 is hole current through the TiO_2 through tunneling or defect states.

While the high offset should ideally block all hole current from the Si towards the cathode, second-order effects such as recombination at TiO_2/Si interface states and tunneling through the TiO_2 or to TiO_2 defect states (processes 2 and 3 respectively in Fig. 1) would lead to hole current and could negate the blocking effects of the valence band barrier.

Fig. 2 shows the dark I-V curve of an Al/TiO_2/p-Si diode on a high-lifetime FZ substrate. The titanium oxide is deposited using a low temperature chemical vapor deposition method (maximum substrate temperature of 100°C) [7]. Also shown is the ideal injected minority carrier current of electrons, calculated from the following equation:

$$J_{elec,inj} = \frac{qn_i^2 D_n}{N_A W}\left(e^{\frac{qV}{kT}} - 1\right) = J_{0,e} * \left(e^{\frac{qV}{kT}} - 1\right) \qquad (1)$$

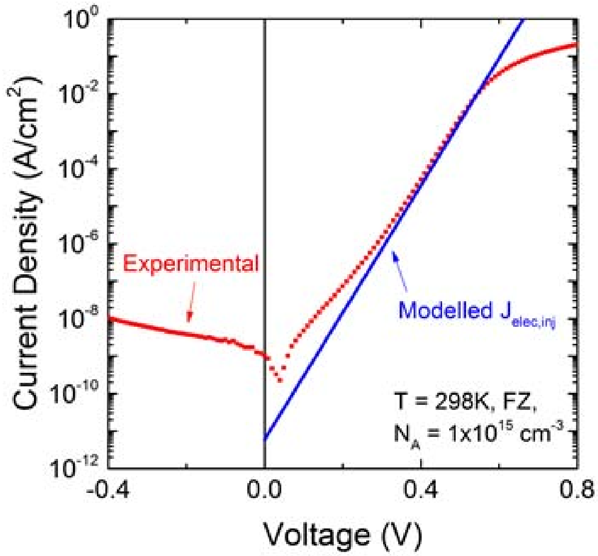

Fig. 2. Measured J-V characteristics of Al/TiO2/FZ p-Si (red) and modelled ideal J-V characteristics for injected electron current (blue) using a diffusion width L_n of 675 um). TiO_2 thickness is 4nm. Positive voltage is on the substrate back contact [3]

We assume carriers can diffuse towards the back of the substrate. The ideal injected minority carrier current is comparable to the experimental current. However, from this we can't learn the magnitude of the hole current. The hole current could be nearly as large as the electron current, or orders of magnitude smaller. This is important for PV, since the addition of an minority carrier electron blocker (a second selective contact) at the back interface would have a major impact on lowering the total current (and raising V_{OC}) only if the hole current at the TiO_2/p-Si contact were very small. The goal of the work is to measure this hole current.

III. TiO_2/P-Si/N-Si Heterojunction Bipolar Transistor

Consider a heterojunction bipolar transistor where the n+ emitter of a conventional n^+/p/n device (Fig. 3a) is replaced with a Al/TiO_2 selective contact (Fig. 3b). As in the conventional device, under forward bias on the emitter-base and reverse/zero bias on the base-collector, electrons are injected into the p-type base as minority carriers, diffuse across the base, and are collected to become collector current (I_C). Hole current from base to emitter ($I_{B)}$ originates from the base contact.

Thus, the hole current, representing processes 2 and 3 in Fig. 1 can be measured as base current I_B, independent of the electron current on the selective contact. This independent measurement of electron and hole currents was not possible with the diode device of Fig. 2.

The HBT device was fabricated by starting with an epitaxial p-type base (doping of $5x10^{14}$ cm^{-3}, width of 6μm) on an n-type

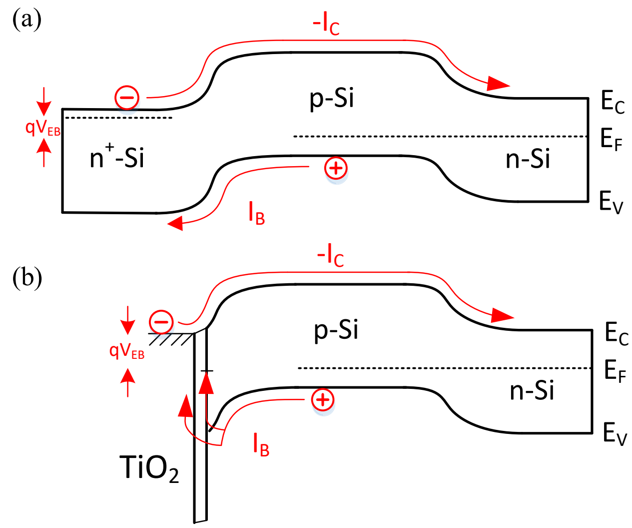

Fig. 3. (a) N/P/N BJT Band diagram and current processes, and (b) TiO_2/P/N HBT Band diagram and current processes

substrate (Fig. 4). The area of the base-collector junction was isolated by mesa etching. Shadow masks were used to define the areas of the silver base contact, the TiO_2 deposition, and the Al emitter contact. The TiO_2 was deposited as with the diode to a thickness of 4 nm. The emitter area was 0.1 cm x 0.1 cm.

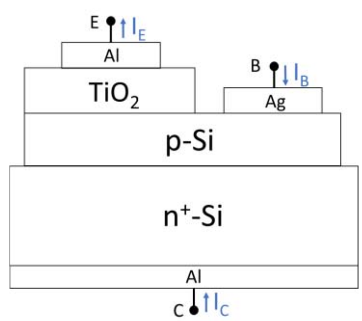

Fig. 4 Cross section of HBT device with n-type Si substrate, p-type Si base and Al/TiO_2 electron-selective contact to the base as the minority carrier emitter.

HBT I-V Gummel plots in forward active mode are shown in Fig. 5. The current gain (collector current /base current ratio) is about 180. Our focus is not to make a practical transistor, but rather to isolate different current mechanisms. The large collector current represents electrons injected from emitter to base and diffusing across the base. A dotted line is shown modeling this current with the classical equation for collector current:

$$I_C = \frac{qn_i^2 D_n A_E}{N_A W_D}\left(e^{\frac{qV}{kT}} - 1\right) = I_{0,e} * \left(e^{\frac{qV}{kT}} - 1\right) \qquad (2)$$

where N_A is the base doping ($5x10^{14}$ cm^{-3}), and W_B is the neutral base width (6 μm). Note that replacing N_A and W_B with substrate doping and substrate thickness would give the diode electron current of (1).

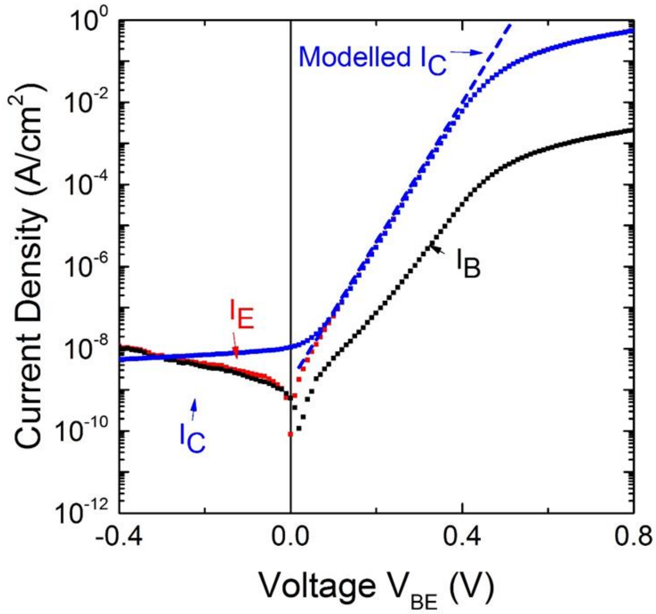

Fig. 5. Gummel plot of I_C and I_B vs base-emitter bias for the HBT of Fig. 4, for $V_{BC} = 0$. I_E is show in red, I_C in blue and I_B in black.

The base current (I_B) of the device is far smaller than I_C, and represents the current of holes from the p-type base to the emitter contact. (Electron recombination in the base can be shown to be negligible). Because the base doping of the HBT and the FZ p-type substrate doping of the diode of Fig. 2 are comparable, the base current of the HBT should thus represent the hole current from substrate to the cathode of the diode device of Fig. 2, specifically recombination at the TiO_2/p-Si interface and/or tunneling into or through the TiO_2 layer (processes 2 and 3 of Fig. 1).

IV. Relevance for Photovoltaics and Minority Carrier Injection Ratio

For devices where the minority carrier current dominates and the majority carrier current component is hard to detect (such as the device shown in Fig. 2), the HBT can be used as a measurement method to see the effect of processing on the majority carrier component. Fig. 6 shows HBT base current (which corresponds to the hole current) for different thicknesses of TiO_2 – demonstrating the utility of the HBT as a majority carrier probe. Note the lack of variation in I_C for different TiO_2

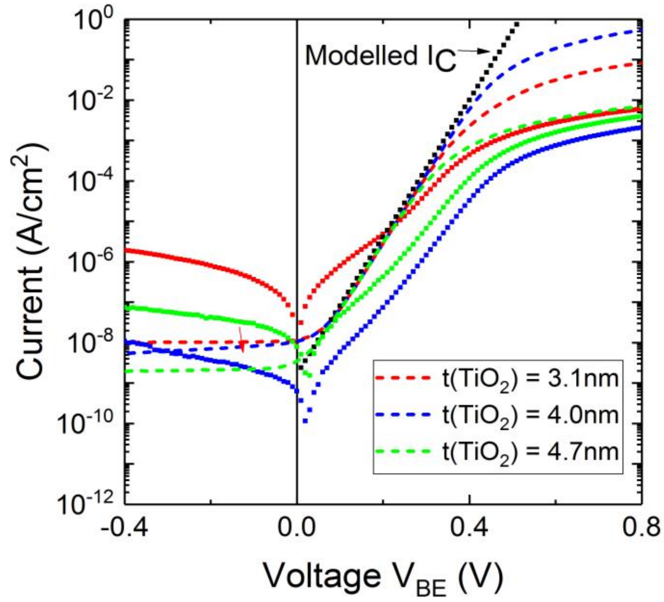

Fig. 6. Comparison of HBT I_C (dotted) and I_B (scatter) for different TiO_2 thicknesses.

thicknesses. This is as expected since I_C is given by (2) and thus is independent from the TiO_2/Si heterojunction characteristics, except at higher voltages when series resistance effects become prevalent.

Furthermore, since we now know the magnitude of the hole, current (I_B of the HBT) corresponding to the diode shown in Fig. 2, we can compare it to the total current of Fig. 2. This is done in Fig 7. It shows the hole current (I_B of the HBT) and the total current of the diode of Fig. 2, both versus bias on the Al/TiO_2/p-Si junction. The roll-off of the HBT I_B above V_{BE} = 0.5V is due to excessive lateral base resistance. One can extrapolate the exponential region of I_B to relevant voltages for PV (≥ 0.6V). In this range, the two current levels are similar. The hole current would be expected to vary somewhat from device to device, because it depends on parasitic mechanisms (such as defects at the TiO_2 interface). Also shown is the modelled line for the electron injection current from Fig. 2. This line could vary depending on the exact substrate doping. However, our results show that for the deposition and fabrication processes in this work, the hole and electron currents are of similar magnitude for 0.4V. At higher voltages, utilizing the extrapolated HBT base current and the modelled electron injection current, we obtain better ratios. For example, at the PV-relevant voltage of 0.6V, the electron current component is six times larger than the hole current component.

In crystalline Si PV, it is well known that for high lifetime substrates that injected minority carrier can easily diffuse across the wafer and recombine at the rear contact. Thus, a barrier for the minority carriers (such as a back-side field) is often

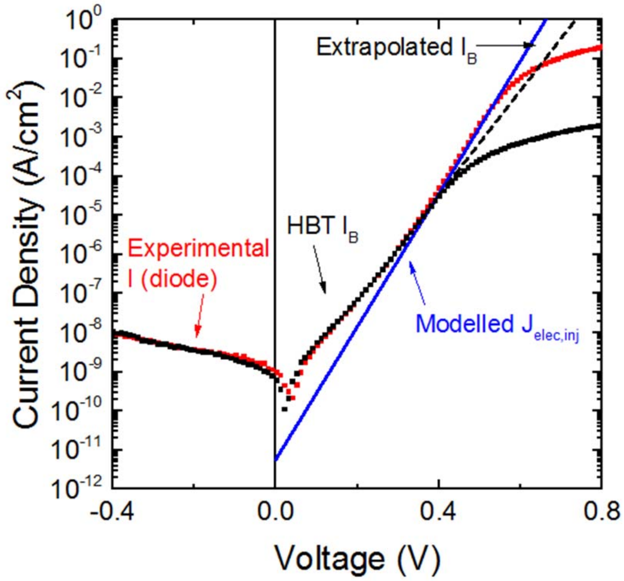

Fig. 7. Comparison of hole current from p-Si to Al/TiO_2 emitter contact (from the HBT) under forward bias with the current in the Al/p-Si diode of Fig's. 1-2.

added at the rear contact to reduce this dark current and raise V_{OC}. This will be effective if the minority carrier current is dominant and other current sources are not significant. This highlights the importance of identifying the magnitude of the hole current at the TiO_2/p-Si interface. Our work suggests that without a back-side field, the electron and hole currents in the structure of Fig. 2 are similar, i.e. the minority carrier injection ratio (ratio of minority carrier current to total current) is on the order of 0.5 for an applied voltage of 0.4V.

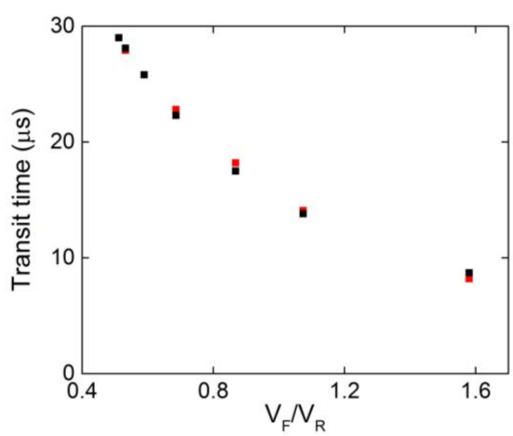

Fig. 8. Experimental reverse recovery data (red) and fit (black) with γ = 0.55.

Reverse recovery experiments further probed this [8], which confirmed that the hole and electron currents are similar. Fig. 8 shows the transit time versus the ratio between forward and reverse current. The fit gives a value of 0.55 for the minority carrier injection ratio γ.

V. Conclusions

In this work we have introduced a new method to distinguish the hole and electron current across selective contacts: the hybrid heterojunction bipolar junction device (HBT). Using the HBT for TiO_2/Si electron-selective contact, we have shown that the hole and electron currents across the interface are similar. Silicon-based heterojunction cells based on p-type substrates have potential. Further work, possible related to reducing TiO_2/Si interface states, is needed to reduce the majority carrier (hole) current and fulfill the desired open-circuit voltage.

Acknowledgement

This work was supported by the National Science Foundation Princeton MRSEC Grant No. DMR-0819860 and the Princeton Institute for the Science and Technology of Materials MRSEC Grant No. DMR-0819860 and the Princeton Institute for the Science and Technology of Materials.

References

[1] S. De Wolf, A. Descoeudres, Z.C. Holman, and C. Ballif, "High-efficiency silicon heterojunction solar cells: A review," green, vol. 2,1, pp. 7-24, 2012.

[2] K. A. Nagamatsu, S. Avasthi, J. Jhaveri, and J. C. Sturm, "A 12% Efficient Silicon/PEDOT:PSS Heterojunction Solar Cell Fabricated at < 100C," IEEE Journal of Photovoltaics, vol. 4, no. 1, pp. 260–264, Jan. 2014.

[3] S. Avasthi, W. E. McClain, G. Man, A. Kahn, J. Schwartz, and J. C. Sturm, "Hole-blocking titanium-oxide/silicon heterojunction and its application to photovoltaics," *Applied Physics Letters*, vol. 102, pp. 203901, 2013.

[4] K. A. Nagamatsu, S. Avasthi, G. Sahasrabuddhe, G. Man, J. Jhaveri, A. H. Berg, J. Schwartz, A. Kahn, S. Wagner, and J. C. Sturm, "Titanium dioxide/silicon hole-blocking selective contact to enable double-heterojunction crystalline silicon-based solar cell," Applied Physics Letters, vol. 106, no. 12, p. 123906, 2015.

[5] C. Battaglia, S.M. De Nicolas, S. De Wolf, X. Yin, M. Zheng, C. Ballif, and A. Javey, "Silicon heterojunction solar cell with passivated hole selective MoOx contact," Applied Physics Letters, vol. 104, no. 11, p 113902, 2014.

[6] R. Islam, G. Shine, K.C. Saraswat, "Schottky barrier height reduction for holes by Fermi level depinning using metal/nickel oxide/silicon contacts," Applied Physics Letters, vol. 105, no. 18, p. 182103, 2014.

[7] J. Jhaveri, A.H. Berg, S. Wagner and J. C. Sturm, "Al/TiO_2/p-Si heterojunction as an ideal minority carrier electron injector for silicon photovoltaics," in 43rd IEEE Photovoltaic Specialist Conference, 2016, pp. 2444-2447.

[8] B. Lax and S. F. Neustadter, "Transient Response of p-n Junction.," Journal of Applied Physics, vol. 25, no. 9, pp. 1148-1154, 1954.