Proc. IEEE Photovoltaic Specialist Conf (PVSC), June 5-10, 2016, Portland, OR

DOI: 10.1109/PVSC.2016.7750081

Al/TiO_2/p-Si Heterojunction as an Ideal Minority Carrier Electron Injector for Silicon Photovoltaics

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

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

***Abstract* — Amorphous titanium dioxide (TiO_2) several nm thick deposited on crystalline silicon at 100°C has been shown to block holes due to a large valence band offset and be transparent to electrons. In this work, using a combination of temperature-dependent I-V measurements and multiple p-type substrate types (CZ, FZ), we demonstrate that the dominant current mechanism in an Al/TiO2/p-Si heterojunction is the injection of electrons into the quasi-neutral silicon, implying a highly effective electron-selective contact.**

***Index Terms*—Silicon, Photovoltaics, Solar, Selective Contact, Metal-oxide, Heterojunction, Titanium dioxide.**

I. Introduction

Passivated selective contacts have recently generated much interest as the next generation silicon photovoltaic technology. Selective contacts enable the collection of one carrier type while obstructing the collection of the other, thus being an alternative to p-n junctions fabricated at high temperatures (>800°C). Additionally, passivated selective contacts can significantly reduce recombination associated with diffused regions and metal/semiconductor interfaces [1].

Amorphous TiO_2 deposited on Si(100) at temperatures no higher than 100°C, for example, has a large valence band offset ($\Delta E_V \geq 2.3$ eV), thus forming a barrier to hole collection while having a small conduction band offset ($\Delta E_C < 0.3$eV), enabling electron collection [1]. Furthermore, annealed TiO_2/Si interfaces have demonstrated effective minority carrier recombination velocities below 10 cm/s [3] and shown to be stable in air for months [4], as measured by Quasi-Steady State Photoconductance Decay (no electrical contacts). Historically, TiO_2 has been used as an antireflection coating due to the fact it absorbs very little in the visible and has a refractive index of ~2.4. The combination of these properties makes TiO_2 a potential choice for an electron-selective contact for high efficiency and low-cost Si-based photovoltaics.

Previously, we showed the use of TiO_2/Si as an electron-selective contact in a double-heterojunction crystalline n-silicon solar [5]. 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. The back-side n+/n junction was replaced by the electron-selective n-Si/TiO_2/Al heterojunction. The electron-selective TiO_2 contact increased V_{OC} by 30-45 mV without degrading short circuit current or fill factor compared to a direct metal back contact to the substrate [5]-[6]. This improvement in V_{OC} was attributed to less hole recombination at the back contact because of the blocking action of the TiO_2 and the formation of Si-O-Ti bonds at the Si/TiO_2 interface leading to a passivated contact [7]. Recently, power conversion efficiencies up to 21.6% for double-heterojunction solar cells has been achieved by inserting a SiO_2 tunneling layer between n-Si TiO_2 [8]

In this work, we focus on the Al/TiO_2/p-Si interface, and its role as a minority carrier electron injector, instead of using the TiO_2 to block minority carrier holes at an n-Si/TiO2 contact. We find effective hole blocking and low parasitic current mechanisms to yield a minority carrier injection efficiency near unity.

II. Current Mechanisms

Fig. 1 shows the structure and band diagram of the TiO_2/p-Si heterojunction. There are five possibilities regarding the current mechanisms across the heterojunction: (1) injection of minority carriers (electrons) from the cathode across the heterojunction into the p-type Si quasi-neutral region, (2) electron injection and subsequent recombination in the space-charge region, (3) electron transport through the TiO_2 to recombine at the TiO_2/Si interface, (4) holes tunneling through the TiO_2 layer, effectively exhibiting a Schottky-barrier-like majority carrier current, and (5) holes passing over the TiO_2/Si

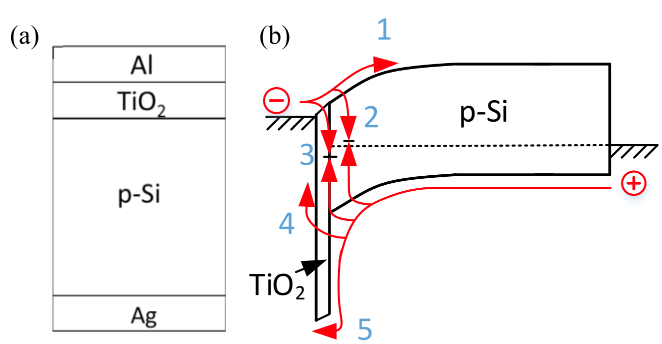

Fig. 1. (a) Device structure and (b) potential current mechanisms in forward bias. The Ag provides an ohmic back contact.

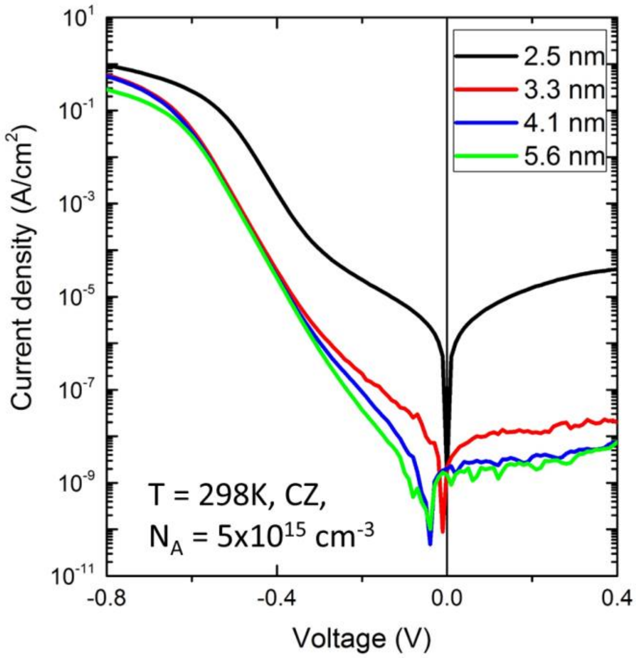

Fig. 2. J-V characteristics TiO_2/p-Si for different thicknesses of TiO_2 for CZ substrates doped 5 x 10^{15} cm^{-3} at ~298K.

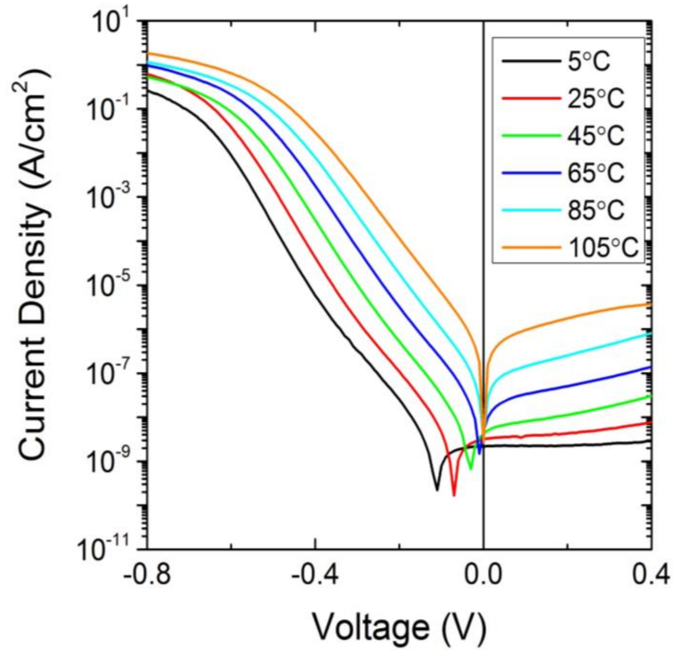

Fig. 3. J-V characteristics TiO_2/p-Si for different temperatures. TiO2 thickness was 4 nm for CZ substrates doped 5 x 10^{15} cm^{-3} at ~298K.

barrier. Only mechanism (1) functions as an minority carrier injector into the substrate; the other mechanisms are parasitic and undesirable for PV applications.

III. Results And Discussion

Fig. 2 shows current versus voltage for several thicknesses of the TiO_2 film on a CZ substrate doped $5x10^{15}$ cm^{-3}. Note that the current gets reduced significantly as the thickness increases to 3nm, implying that as the TiO_2 layer gets thicker fewer holes are able to tunnel through the TiO_2 layer. Further increasing the TiO_2 thickness does not lead to further reduction in current.

In I-V measurements for 4 nm of TiO_2 at different temperatures (Fig. 3), two regimes are visible: a low-current regime at < 10^{-6} A/cm^2 (disappears at higher temperatures) and a high-current regime. Saturation current densities (J_0's) for both regimes plotted versus inverse temperature (Fig. 3) yield an activation energy (E_A) for the low-current regime of 0.53 eV (Fig. 4), indicating that this current regime is due to space-charge region recombination (current mechanism (2)). The fact that the activation energy for the high-current regime is 1.12 eV is consistent with electrons being injected into the silicon (mechanism (1)):

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

in the long-base limit with n_i^2 being proportion to exp(-E_G/kT) and E_G of 1.12 eV. The high-current and low-current regimes are consistent with the double diode model common in Si PV, with corresponding saturation current densities J_{01} and J_{02}.

However current mechanism (1) is not the only possibility for the high current mechanism. Current mechanism (4), Schottky barrier majority carrier current, has an activation energy equivalent to the Schottky barrier height. Fig. 5 shows capacitance-voltage measurements for the TiO_2/p-Si heterojunction, with an extracted built-in voltage of 0.74 eV giving a Schottky barrier height is 0.99 eV, implying the

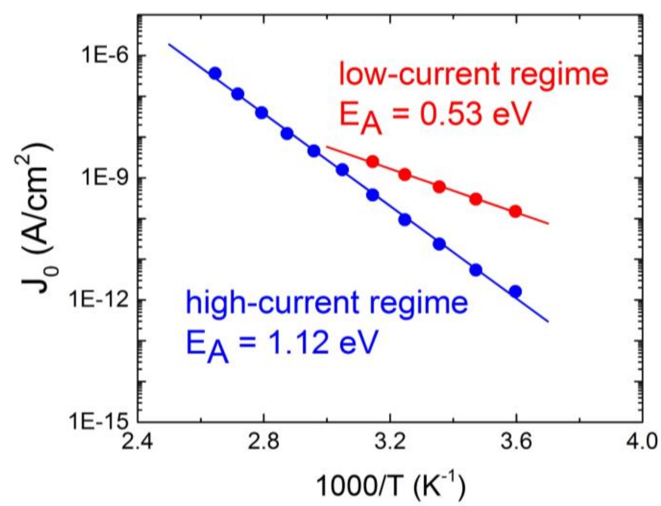

Fig. 4. J_0 versus inverse temperature for the high-current and low-current regimes of Fig. 3.

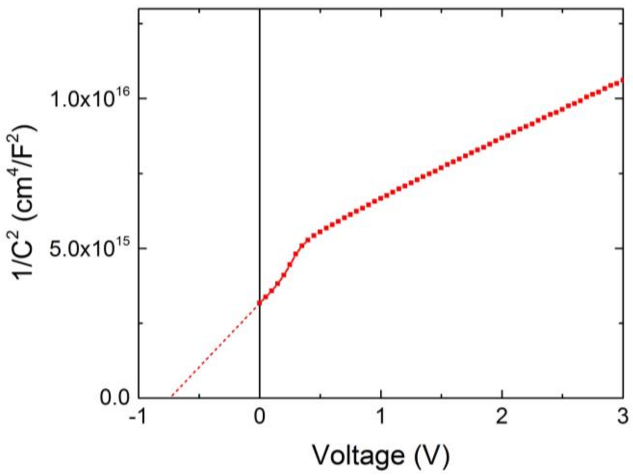

Fig. 5. C-V characteristics of Al/TiO_2/CZ p-Si at 1MHz.

combination of the low Al work function and thin nature of the TiO_2 set the Fermi level at the Si surface near the conduction band. The kink in the C-V data is from to a well-known effect of H-passivation of boron dopants at the Si surface due to RCA cleaning [9]. Assuming all current to be due to mechanism (4), and using a $T^2\exp(-\Phi_B/kT)$ prefactor for Schottky barrier current, the data in Fig. 4 would be consistent with a Schottky barrier of 1.07 eV, close to that predicted by the C-V data.

However, Fig. 2 showed the TiO_2 barrier thickness > 3 nm had no effect on current implying mechanism (4) – which includes holes tunneling through the TiO_2 – is unlikely. Mechanism (5), holes going over the TiO_2 barrier, is unlikely due to the large Si/TiO_2 band offset (~3 eV). The remaining possible parasitic mechanism would be interface recombination, mechanism (3). Using SRH formalism, the lack of an electron barrier would imply a large electron density at the Si/TiO_2 interface, leading to a large activation energy which could be consistent with the data in Fig. 4

Modelling current based on (1) requires knowledge of L_n for CZ substrates, which is unknown but less than wafer thickness W = 525 µm. Modelling with W = 525 µm underestimates the current (Fig. 5). Thus the current is dominated by either ideal electron injection with Ln ≈ 200 µm or interface recombination.

To resolve this uncertainty, Fig. 6 was reproduced with an FZ silicon wafer (doping 1.0 x 10^{15} cm^{-3}), which was measured to have diffusion length $L_n = (\sqrt{D\tau}) > 1$ mm, in excess of wafer thickness, so (1) can be used with the wafer thickness substituted for L_n (short base model). The very close fit between the ideal electron injection current and the actual J-V curve in Fig. 7 indicates that current mechanism (1) dominates. To further illustrate this point, we utilize the concept of minority carrier injection efficiency γ. A γ-factor of 1 implies all the current is due to current mechanism (1), while a γ-factor of 0 would imply none of the current is due to minority carrier

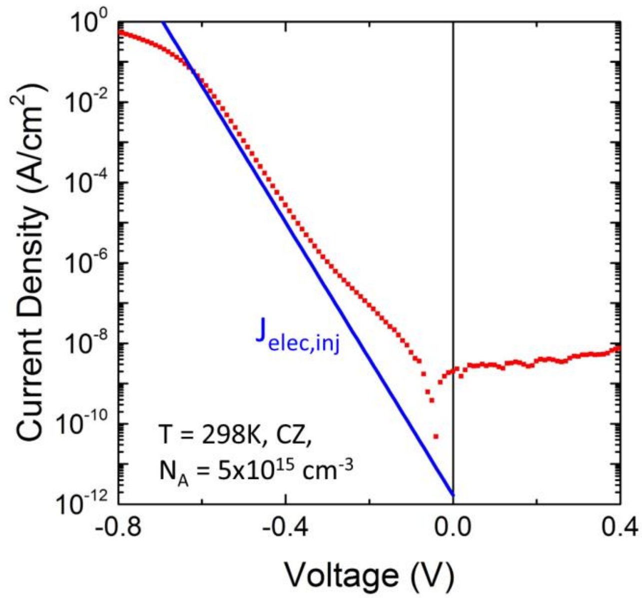

Fig. 6. J-V characteristics of Al/TiO_2/CZ p-Si (red) and model (1) using the maximum possible L_n of the wafer thickness (525 um), which as expected underestimates the current. TiO_2 thickness is 4nm.

injection. In Fig. 8, we show total current for γ = 0.1 and γ = 1. As can be seen, the actual γ-factor is close to unity, implying an ideal minority carrier injection. The J-V curves in our experiments are well over 10 times lower than those in similar structures in [1]. We attribute the higher currents in [1] to a high level of interface recombination (mechanism (3)), which is not significant in the work presented here because of a refined cleaning procedure and improved deposition system.

IV. Conclusions

We have shown that the dominant current mechanism in an Al/TiO_2/p-Si heterojunction is the minority carrier electron injection into the silicon. Further work is needed to quantify the actual magnitude of the parasitic mechanisms, and if γ would remain the same if the electron injection mechanism were reduced, for example, by a back surface field or hole-selective contact on the backside of the substrate. Silicon-based heterojunction cells based on p-type substrates may be an attractive alternative to those on n-type substrates.

Acknowledgement

This work was supported by the DOE Sunshot Grant No. DE-EE0005315, 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.

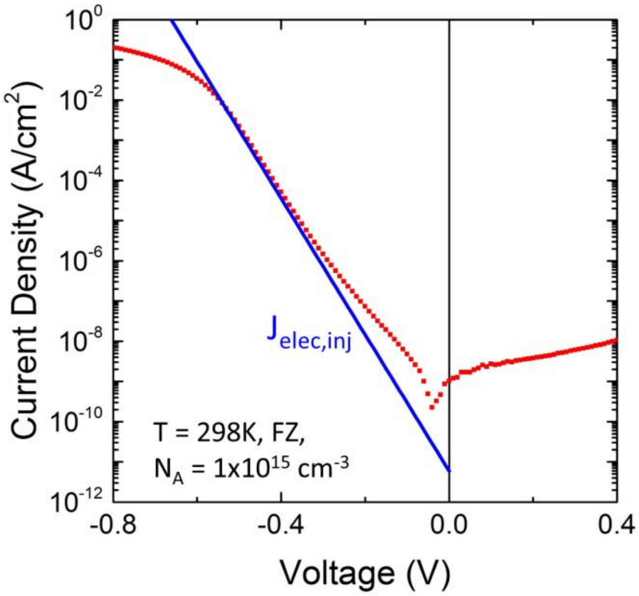

Fig. 7. J-V characteristics of Al/TiO_2/FZ p-Si (red) and ideal J-V characteristics for injected electron current (blue) using Ln of the wafer thickness (675 um). TiO_2 thickness is 4 nm.

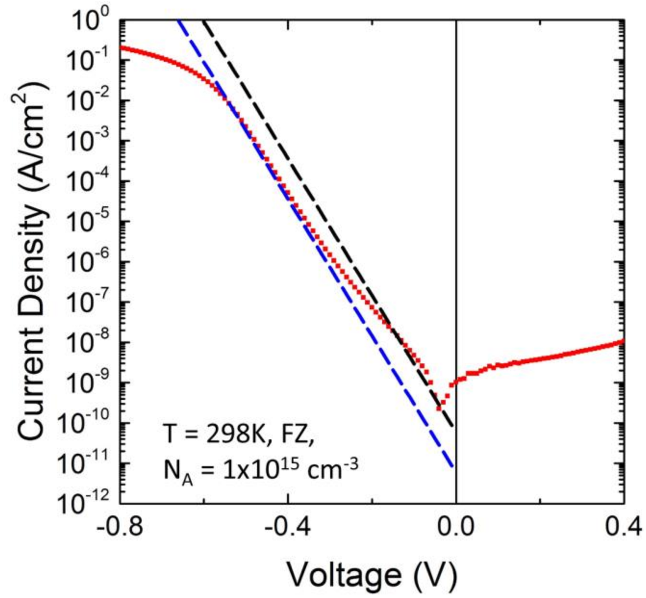

Fig. 8. J-V characteristics of Al/TiO_2/FZ p-Si (red) and ideal J-V characteristics for injected electron current (blue) using Ln of the wafer thickness (675 um). TiO_2 thickness is 4 nm.

REFERENCES

[1] C. Battaglia, A. Cuevas, and S. De Wolf. "High-efficiency crystalline silicon solar cells: status and perspectives," *Energy & Environmental Science*, vol. 9, no. 5, pp. 1552-157, 2016

[2] 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.

[3] B. Liao, B. Hoex, A. G. Aberle, D. Chi, and C. S. Bhatia, "Excellent c-Si surface passivation by low-temperature atomic layer deposited titanium oxide," *Applied Physics Letters*, vol. 10, no. 25, p. 253903, 2014.

[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] J. Jhaveri, S. Avasthi, K. A. Nagamatsu, and J. C. Sturm, "Stable Low-Recombination n-Si/TiO2 Hole-blocking Interface and Its effect on Silicon Heterojunction Photovoltaics," in *40th IEEE Photovoltaic Specialist Conference*, 2014, pp. 1525-1528

[6] J. Jhaveri, K. A. Nagamatsu, A. H. Berg, G. Man, G. Sahasrabuddhe, S. Wagner, J. Schwartz, A. Kahn, and J. C. Sturm, "Double-Heterojunction Crystalline Silicon Solar Cell with Electron-Selective TiO2 Cathode Contact Fabricated at 100°C with Open-Circuit Voltage of 640 mV," in *42nd IEEE Photovoltaic Specialist Conference*, 2015, pp. 1-4.

[7] G. Sahasrabudhe, S. M. Rupich, J. Jhaveri, A. H. Berg, K. A. Nagamatsu, G. Man, Y. J. Chabal, A. Kahn, S. Wagner, J. C Sturm, and J. Schwartz, "Low-Temperature Synthesis of a TiO2/Si Heterojunction," *Journal of the American Chemical Society,* vol.137, no. 47, pp. 14842-14845, 2015.

[8] X. Yang, B. Qunyu, A. Haider, D. Kristopher, W. V. Schoenfeld, and K. Weber. "High Performance TiO2-Based Electron-Selective Contacts for Crystalline Silicon Solar Cells." *Advanced Materials*, 2016.

[9] J.P. Sullivan, W.R. Graham, W. R., R. T. Tung, and F. Schrey. "Pitfalls in the measurement of metal/p-Si contacts: The effect of hydrogen passivation," *Applied Physics Letters,* vol. 62, no. 22, p. 2804, 1993.