Hole-blocking TiO_2/Silicon Heterojunction for Silicon Photovoltaics

Sushobhan Avasthi[1], Will McClain[2], Jeffrey Schwartz[2], and James C. Sturm[1]
Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton NJ
[1]Department of Electrical Engineering. [2]Department of Chemistry

Narrow bandgap heterojunctions on crystalline silicon such as $Si/Si_{1-x}Ge_x$ are now in widespread use, but to date there has been little progress on widegap heterojunctions on silicon. In this abstract, we report:

(i) TiO_2/Si heterojunction with a band alignment which blocks holes from silicon but freely passes electrons, and

(ii) the application of this heterojunction to form a photovoltaic cell on silicon with <u>no p-n junction</u>, and all fabrication below a temperature of 75 °C.

TiO_2 is a widegap semiconductor with bandgap 3.2 eV, with conduction and valence bands at 4.0 and 7.2 eV below the vacuum level, respectively [1]. Thus, the TiO_2/Si interface is expected to have a large valence-band (VB) barrier (ΔE_V>>0) and a small conduction band offset (Fig. 1a). To experimentally test the band-offsets at the TiO_2/Si interface, test diodes were fabricated on p-type and n-type Si (100) wafers (structure and band-diagrams shown in Fig. 1b-d) by depositing 2-3 nm of TiO_2 by CVD at 75 °C, followed by a top metal electrode. As a control, diodes without the TiO_2 layer, having a Al/Si Schottky structure, were also fabricated. Ohmic Ag contacts at the bottom of the substrate served as the second electrode. Devices made on p-Si without TiO_2 showed ohmic I-V characteristics, typical of a Schottky barrier with a very low barrier for holes. Devices made on p-type Si with a TiO_2 layer showed rectifying (diode-like) I-V characteristics with a J_0 of ~10^{-8} A/cm^2 (Fig. 2). Since the currents in Schottky-type diode on p-Si are dominated by holes, the change in characteristics from ohmic to rectifying shows that TiO_2 blocks the holes in Si from moving to the top electrode, arguably due to the large hole barrier (ΔE_V>>0) at TiO_2/p-Si interface. In comparison, devices fabricated on n-Si showed ohmic characteristics even with the TiO_2 layer (Fig. 3). Since for n-type Si the majority carriers are electrons, the ohmic characteristics show that TiO_2/Si interface does not block electrons and ΔE_C is indeed small at TiO_2/n-Si. Assuming that the band-offsets at the TiO_2/Si interface do not change with Si doping type, the I-V characteristics qualitatively confirm the band-alignment posited in Fig. 1a.

We now describe one application of the thin hole-blocking TiO_2/Si heterojunction – Si photovoltaics. One possible approach to low-cost photovoltaics is though a merged TiO_2/crystalline-silicon solar cell in which the silicon p-n junction is replaced by the TiO_2/p-Si heterojunction (Fig. 4a). The light absorption still occurs in silicon, but instead of p-n junction, the cathode/TiO_2/p-Si heterojunction provides the electric field to separate the photogenerated carriers (Fig 4b). Such a TiO_2/Si structure is technologically interesting because it can be fabricated by a very simple low-temperature (~ 75 °C) CVD process, instead of high-purity high-temperature (900 °C) dopant diffusion process required for p-n junction. Motivated by similar arguments, we recently demonstrated a 10% efficient solar cell using an electron-blocking wide bandgap heterojunction on Si, which was fabricated by spin-coating a layer of the organic semiconductor, polythiophene, on n-type Si [2]. The present work demonstrates the complimentary technology, a hole-blocking heterojunction using TiO_2, fabricated by low-temperature CVD.

In this initial work, the transparent conductor is a thin layer of Al metal, 15 ± 5 nm thick. The bottom electrode and TiO_2 were deposited as before (Fig 4a). We also examined methods to the reduce J_0 of the TiO_2/p-Si solar cell because reduction in J_0 is the key to improvement in solar cell efficiency. In a metal/p-Si device, the hole current is the dominant part of J_0. However, TiO_2 blocks holes without affecting the electron, so it is possible that electron injection from cathode into Si (via TiO_2) is the dominant component in the J_0 of TiO_2/p-Si diodes (Fig 4b). To confirm, devices were fabricated on 10^{15} and 10^{16} cm^{-3} doped p-Si wafers. Assuming that the minority carrier diffusion lengths are of the same order in the two wafers, the higher doped devices should have lower electron injection and hence show lower J_0. I-V characteristics in dark (Fig. 5c) clearly show that devices on 10^{16} cm^{-3} Si indeed have a lower J_0 (10^{-9} A/cm^2 instead of 10^{-8} A/cm^2). Under 200 mW/cm^2 of illumination from a halogen lamp, this reduction in J_0 translates to a increase in open-circuit voltage from 0.47 V to 0.54 V (Fig. 5d). Due to unintended variation in the thickness of the semi-transparent top electrode, the short-circuit current varies from 9 mA/cm^2 to 18 mA/cm^2.

In conclusion, we demonstrate a novel low-temperature wide bandgap TiO_2/Si heterojunction, that selectively blocks holes but passes electrons and which could lead to low-cost but efficient crystalline Si solar cells.

[1] D. Gebeyehu, *et al*. *Synthetic Metals* **125**, 2001, 279.
[2] S. Avasthi, *et al*. *Advanced Materials* **23**, 2011, 5762.

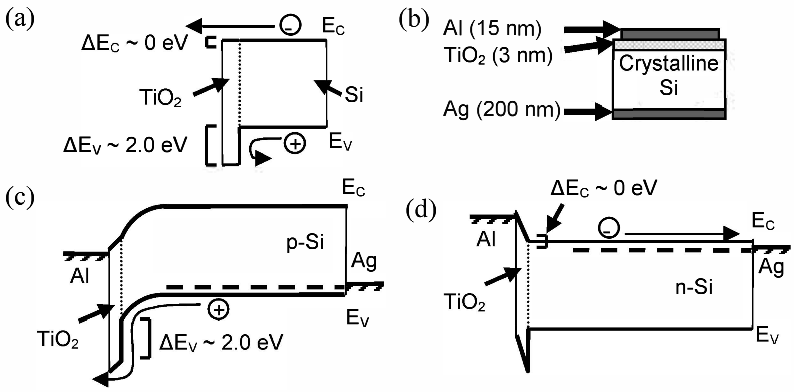

Fig. 1: (a) The expected band-offsets at a TiO_2/Si interface [1]. (b) Structure of the test diodes to experimentally measure the offsets. Band diagrams of the TiO_2/Si heterojunction test diodes on (c) p-Si and (d) n-Si, showing the flow of majority carrier in dark under positive bias on Ag electrode.

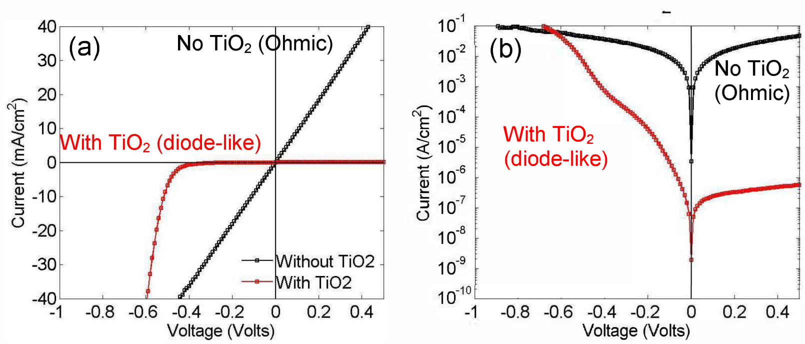

Fig. 2: The dark I-V characteristics of Al/TiO_2/p-Si heterojunction diode compared to Al/p-Si Schottky diode on a (a) linear and (b) semilog scale. Without TiO_2 the junction is ohmic but with TiO_2 the junction is rectifying, indicating that the TiO_2/Si junction blocks holes ($\Delta E_V >> 0$ eV).

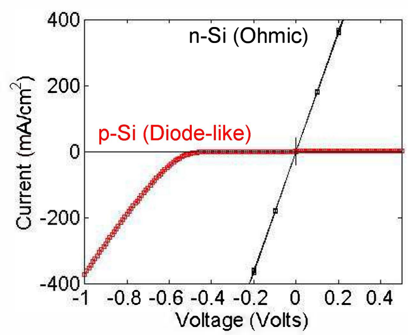

Fig. 3: The dark I-V characteristics of Al/TiO_2/n-Si heterojunction diode (black). Unlike TiO_2/p-Si (red), TiO_2/n-Si interface forms an ohmic contact, indicating that the TiO_2/Si junction does not block electrons

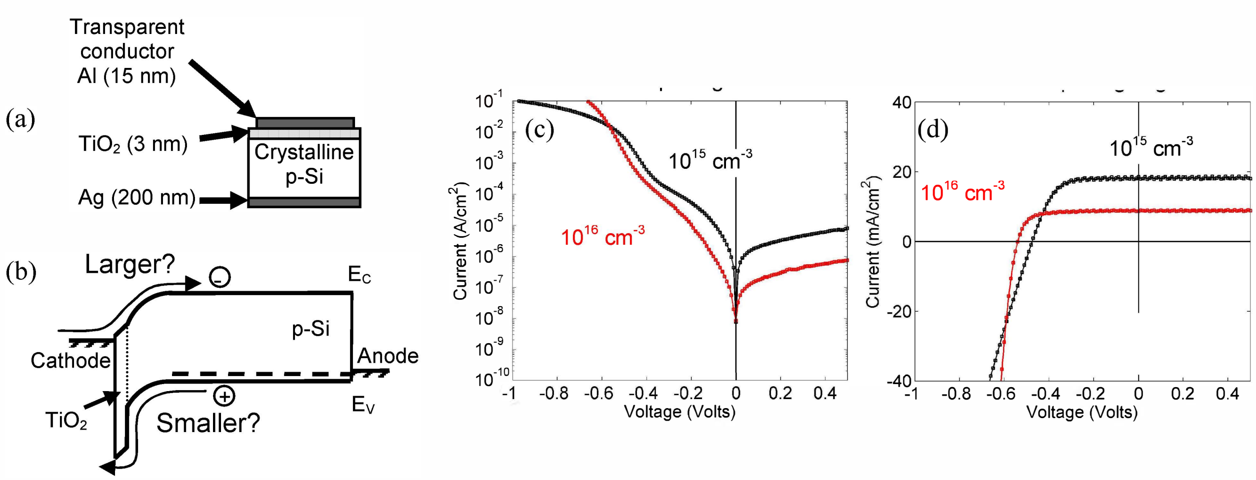

Fig. 4: (a) Structure of the TiO_2/pSi heterojunction solar cell (b) band-diagram of the solar cell, in dark and under forward-bias, showing the hole and electron currents. The I-V characteristics for 10^{15} and 10^{16} cm^{-3} doped Si wafers (c) in dark and (d) under 200 mW/cm^2 halogen lamp illumination. The variation in short-circuit current is probably due to unintended variation in the thickness of the Al electrode.