

Wide Bandgap Heterojunctions on Crystalline Silicon

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We describe the use of organic and metal oxide semiconductors to form wide-bandgap heterojunctions to crystalline silicon. We use these semiconductors to demonstrate a heterojunction which both blocks electrons and passes holes, and a complementary heterojunction which blocks holes and passes electrons and blocks holes. The carrier transport functions are demonstrated through simple device structures as well as a photovoltaic application. In both cases, the ability to deposit layers at low-temperature (< 100 °C) is attractive for low-cost applications. The ability of organic molecules to passivate silicon surface states is also presented.

Introduction

For 30 years there has been extensive research on pseudomorphic strained $\text{Si}_{1-x}\text{Ge}_x$ semiconducting layers grown on the (100) surface of crystalline silicon. This technology provides a narrow bandgap compared to silicon, and has long been established in industrial production to make heterojunction bipolar transistors. On the other hand, despite the great wishes of the designers of silicon-based devices, there has been little progress to date on wide-bandgap heterojunctions on silicon. This problem has largely been due to the lack of an appropriate lattice-matched semiconductor: the diamond phase of carbon has a wide bandgap of 5.5 eV, but a lattice constant of only 0.40 nm vs. 0.54 nm for silicon. The β -phase of SiC has a bandgap of 2.4 eV, but the lattice is only 0.44 nm, still nearly 20% less than that of silicon. In both cases this is far too large to achieve pseudomorphic growth, as compared to the $\text{Si}_{1-x}\text{Ge}_x$, where the mismatch is only 1% for $x = 0.25$. Furthermore, even if pseudomorphic growth were possible, the high temperatures often used in diamond or silicon-carbon growth would severely degrade any existing device profiles in the silicon.

In this work we examine the use of amorphous semiconductors to form heterojunctions to silicon. Because the overlying layers generally do not have crystalline structure, the lack of a lattice match does not necessarily lead to defects in the overlying layers. Previous work on wide-band gap heterojunctions on silicon focused mostly on amorphous Si (a-Si, $E_G = 1.8$ eV), although that work does not allow independent tuning of valence band and conduction band offsets [1]. The semiconductors examined in this work are organic semiconductors (both small molecules and polymers) and metal-oxide semiconductors (such as ZnO, TiO_2 , etc.), both of which can be deposited by fairly simple methods at low temperatures (< 100 °C). In addition to examining electron-

blocking and hole-blocking properties of the heterojunctions, we also examine their ability to passivate silicon surface states.

Electron-Blocking Heterojunctions

In device engineering, one of the main roles of a heterojunction is to enable selective injection of carriers – for example holes can flow in one direction under bias but electrons will not flow in the opposite direction. To achieve such an electron-blocking function with a wide bandgap material on silicon, one seeks a semiconductor with a low electron affinity – a conduction band high in energy close to the vacuum level. To pass electrons, the valence bands of the two materials should be an equal distance from the vacuum level. Organic semiconductors, which may be either small organic molecules or polymers, generally have a bandgap based on the energy level splitting based on the π -interaction of p-orbitals in adjacent carbon atoms, typically in the range of 2-3 eV. Because the lower (filled) and upper (empty) energy states do not broaden into wide bands, they are generally referred to as the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) instead of valence band and conduction band, respectively. Fig. 1 shows the HOMO and LUMO levels (distance between being the bandgap) of a wide range of organic semiconductors. Also shown are the conduction band edge (E_C) and valence band edge of silicon (E_V). For an “electron blocker,” the LUMO should be much higher in energy than the conduction band edge (E_C of Si) but, to not impede holes, the HOMO should align with E_V . From inspection of Fig. 1, one sees the polymer polythiophene (P3HT) to be a good choice for such a

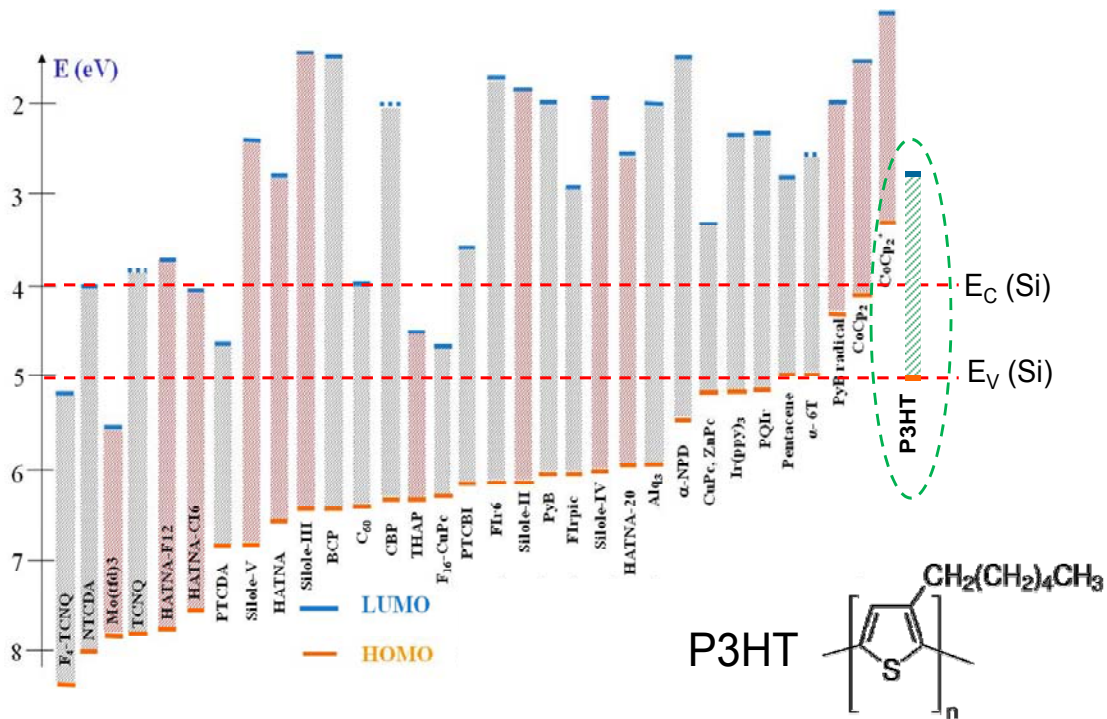


Figure 1. Energy level alignment for a wide range of organic semiconductors, along with the conduction and valence band edges of silicon for comparison. The polymer polythiophene (P3HT) is identified as a potential electron blocker and its chemical structure is indicated.

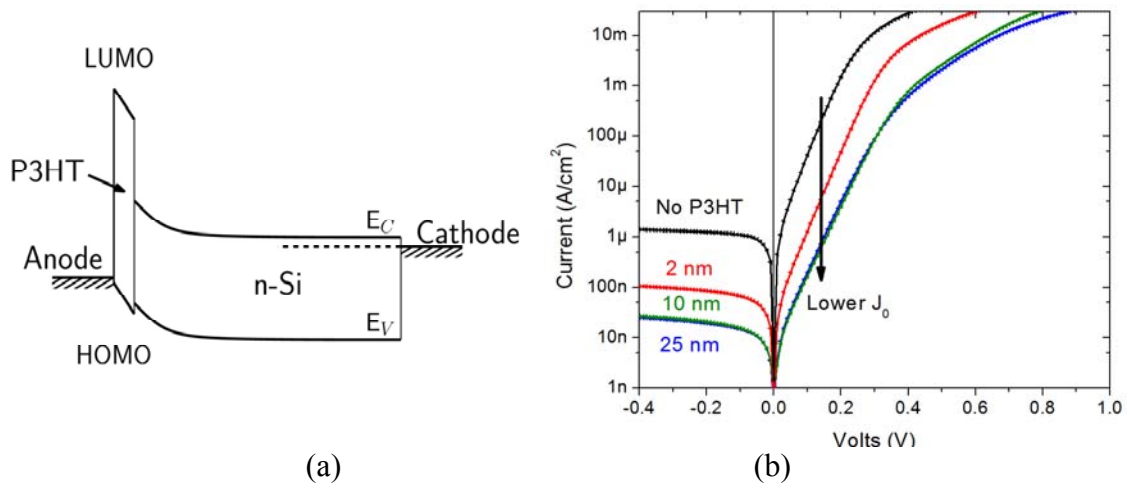


Figure 2. (a) Ideal band diagram for undoped P3HT on n-type silicon, with a Pd top contact. (b) Dark I-V curves for various P3HT thicknesses [2].

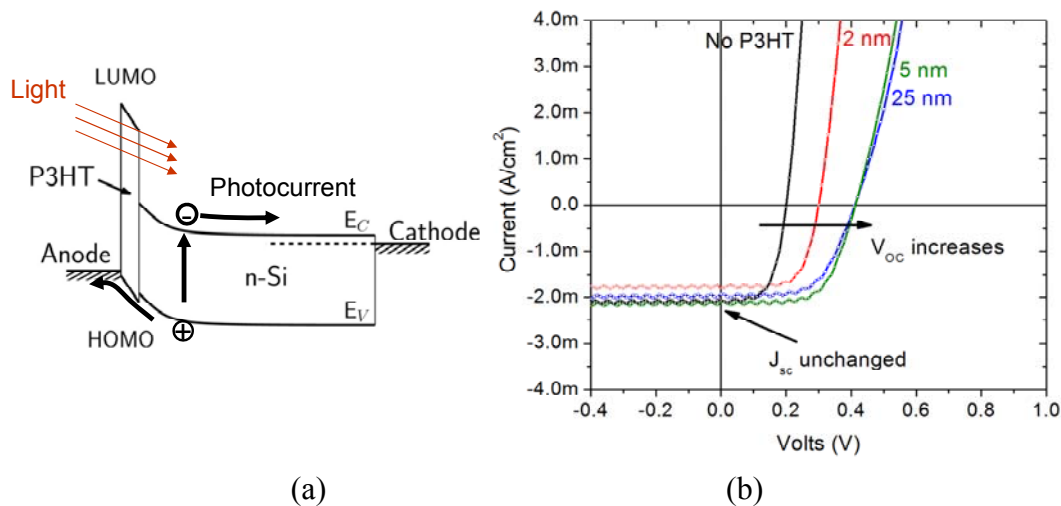


Figure 3. (a) Band diagram for structure of Fig. 2 under illumination and paths of photo-generated carriers [2].

heterojunction on silicon. It has a bandgap over 2 eV, a HOMO closely-aligned to the valence band edge of silicon, and a LUMO ~ 1 eV higher than the conduction band edge of silicon.

Fig. 2(a) shows the I-V curves of thin layers of undoped P3HT deposited on n-type silicon by spin-coating. A high work function metal (Pd) was used on top of the P3HT to create band bending in the silicon under zero bias, similar to a Schottky barrier. In a Schottky barrier on n-type silicon, electron current from the silicon to the metal dominates the current in forward bias. As the P3HT thickness is increased from 0 to 25 nm, the current in forward bias drops by orders of magnitude, clearly indicating the electron-blocking properties of the P3HT layer.

To examine the ability of the junction to pass holes freely, light was shined through a semitransparent (thin) Pd anode to create electron-hole pairs in the silicon (Fig 3(a)). Electrons would then be moved by the electric field into the silicon, and holes to the Si/P3HT interface. If the HOMO of the P3HT were significantly lower than the valence band edge of silicon, the holes would be blocked and pile up and recombine with electrons at the interface, leading to a reduced photocurrent. Fig. 3(b) shows no change in photocurrent as P3HT is added to the structure, confirming that the Si/P3HT interface is “electron transparent.”

One also notes that the open circuit voltage (V_{OC}) increases as the P3HT is added, which results from the decrease of dark current shown in Fig. 2. This suggests that the P3HT structure may be used for low-cost “hybrid” photovoltaics on crystalline silicon, without the need for any high-temperature processes to form a p-n junction in the silicon. To avoid the absorption of light by the anode, doped PEDOT can be used as a transparent conductive layer on top of the P3HT, and then only narrow metal fingers are required to conduct the photocurrent to external wires. Unlike all-organic solar cells, the light is absorbed primarily in the silicon, so there are no problems associated with separating excitons, which is a problematic issue in organic solar cells. Efficiencies of 10% under AM1.5 conditions are obtained in the P3HT/Si hybrid structure [2].

PEDOT is an organic semiconductor with a work function similar to that of Pd. Our recent work indicates it has a HOMO close to that of the valence band edge of silicon, and a LUMO much higher than the conduction band edge of silicon. Thus in principle the P3HT layer may be omitted. There have been a number of efforts to make PEDOT/Si solar cells by this method [3-5], and recently AM1.5 efficiencies of 12% have been reported [6].

Because band alignments at interfaces are complicated in practice and often deviate from ideal principles, interface spectroscopy was used to examine the offsets of a P3HT/Si interface. P3HT layers of only a few nm were deposited so the probe (or escaping) electrons could penetrate the P3HT layers to measure energy levels near the interface. X-ray Photoelectron Spectroscopy (XPS) was used to determine the position of valence band states and HOMO levels, and Inverse Photo-Electron Spectroscopy (IPES) was used to measure the position of conduction band states and LUMO levels. Fig. 4(a) shows the resulting band alignment. The high LUMO of P3HT relative to E_C in silicon is confirmed, and the HOMO is actually slightly higher than the E_V of Si. There is also a small interface dipole (0.3 eV). The simplified view (Fig. 4(b)) yields a band diagram consistent with the device operation under illumination shown in Fig. 2.

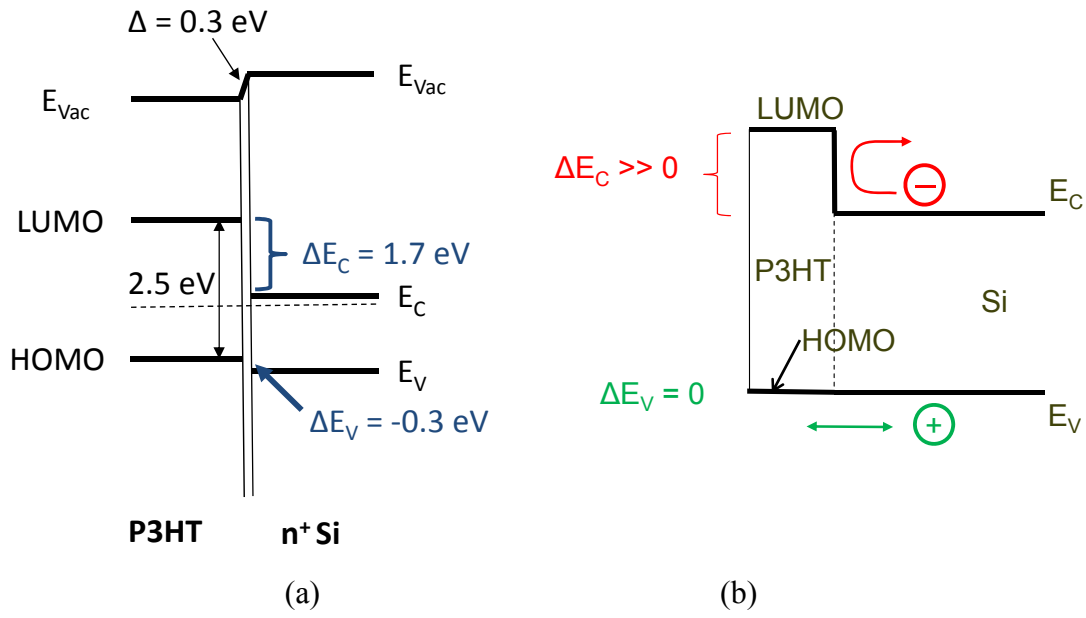


Figure 4. (a) Energy level alignment measured at the P3HT/n-Si interface, and simplified band diagram showing electron-blocking property of the interface and the ability of holes to pass from the silicon to (and through) the P3HT.

Hole-Blocking Heterojunctions

For the device engineer's toolbox, we also seek a hole-blocking interface (which still allows the passage of electrons) as a complement to the electron-blocking interface presented above. In this case we seek a semiconductor with an E_C close to that of silicon, and with a much lower E_V than that in silicon. Fig. 5 shows the relevant energy levels of several organic as well as metal oxide semiconductors compared to those of silicon. ZnO, TiO₂ and related materials have recently received wide attention for thin film transistors [8,9]. For our work we chose titanium dioxide (TiO₂). Titanium dioxide is normally a crystalline material. However, we developed a CVD process for depositing amorphous TiO₂ layers, with a maximum deposition temperature of only 100 °C [10].

UPS and IPES measurements of the TiO₂/Si interface were used to confirm that the TiO₂ layers form a hole-blocking wide bandgap heterojunction with silicon (Fig 6). The valence and conduction band edges were measured at 3.8 eV and 0.8 eV from the Fermi-level. This gives the TiO₂ thin film a bandgap of 4.6 eV, which is substantially larger than 3.8 eV that has been reported for crystalline TiO₂ (rutile phase). The difference could be due to amorphous nature of the thin-film [10].

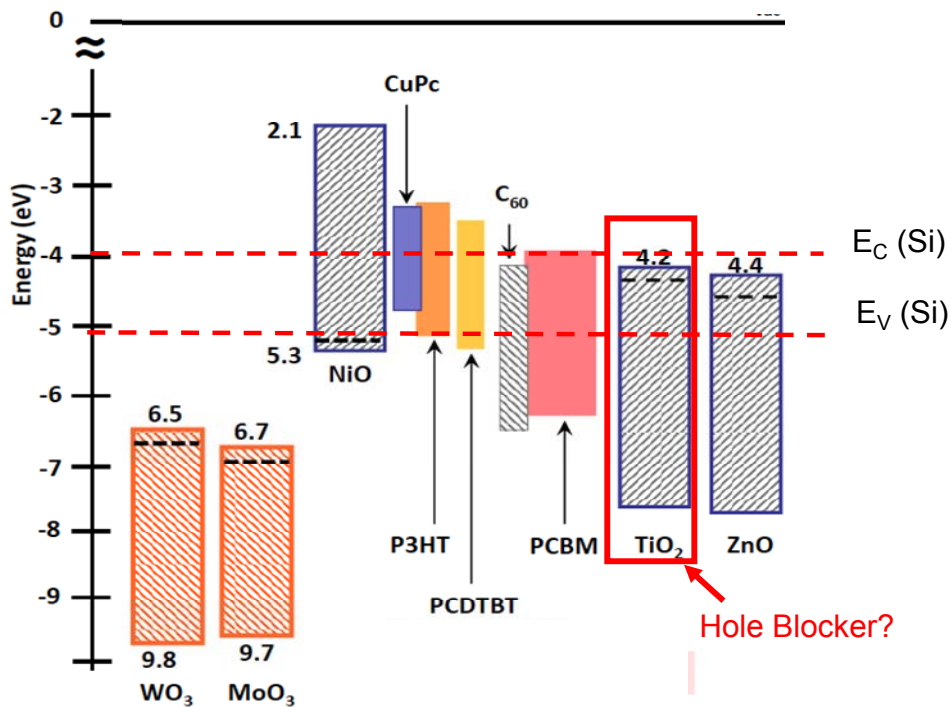


Figure 5. Energy level alignment for a range of organic and metal oxide semiconductors compared to valence and conduction band edges of silicon [7]. TiO₂ was chosen for our experiments.

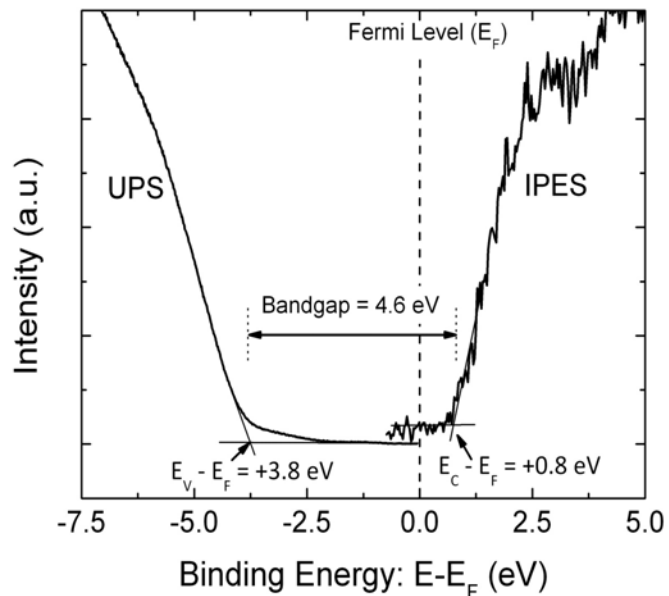


Figure 6. Combined UPS and IPES spectrum of TiO₂ on p⁺Si, showing the bandgap of the of TiO₂ layer along with the conduction/valence band offsets. [10]

The electrical properties of the TiO₂/Si interface were also investigated by fabricating TiO₂/Si heterojunction diodes on n and p-type Si with Al as the top electrode and silver as the Ohmic back electrode (Fig. 7(a)). The band diagrams of these structures are shown in Fig. 7(b). On p-Si, without the TiO₂, the barrier was so low that the characteristics were Ohmic (not shown here). With TiO₂, the barrier increases and diode-like characteristics are obtained with a turn-on voltage of 0.5V – clearly indicating that the TiO₂ layer blocks transport of holes from Si to TiO₂ (Fig 7(c)). On n-Si, the I-V characteristics are Ohmic even with TiO₂ – indicating the TiO₂ layer does not block transport of electrons from Si to TiO₂ (Fig 7(c)). This electron-transparent and hole-blocking TiO₂/Si heterojunction can also be used as a photovoltaic structure that is complementary – reversing n with p-Si, high to low work-function metal – to the one described in Fig. 3 [11].

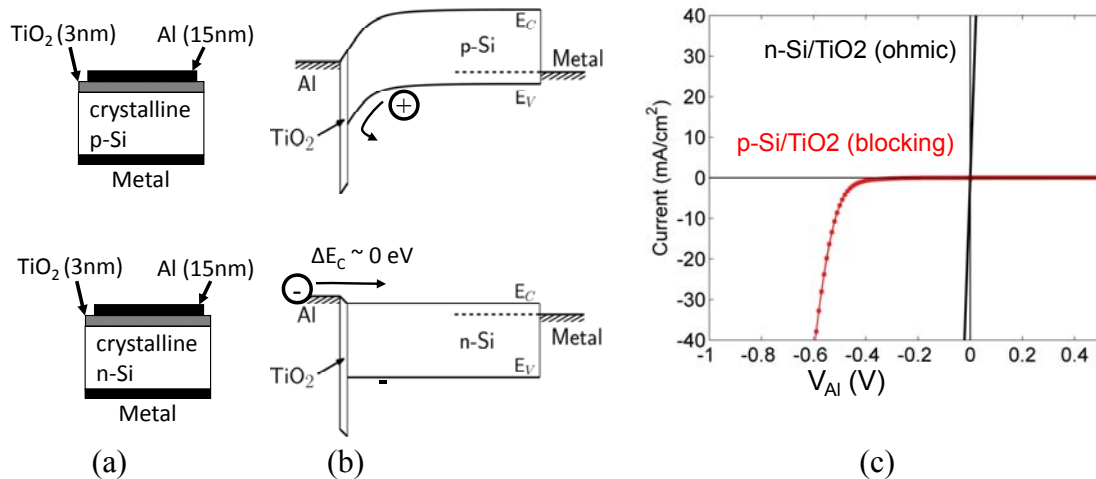


Figure 7. (a) Device structure and (b) band diagrams of the TiO₂/Si heterojunction test diodes on p-Si and n-Si showing the flow of majority carriers in dark under negative-bias on the Al electrode. (c) Dark I-V characteristics of the two devices showing rectifying behavior on p-Si and Ohmic behavior on n-Si. The voltage is applied to the top electrode and positive current flows from metal to Si. Also shown are the dark I-V characteristics [11].

Surface Passivation

Surface passivation is an important consideration at the heterointerfaces. An unpassivated silicon surface has a high density of midgap states due to the silicon dangling bonds, which might lead to undesirable effects such as carrier recombination and Fermi-level pinning. For optimal device performance and reliability it is important that these midgap surface states be reduced, i.e. surface be passivated.

Organic molecules typically interact only through weak Van der Waals bonds and not through strong covalent ones. Silicon on the other hand bonds via strong covalent bonds. Thus the interaction between an organic and silicon at the Si/organic heterojunction is not

guaranteed to reduce the silicon dangling bonds. Novel methods could include a bridging molecule which bonds to Si on one side and exhibit organic semiconductor behavior on the other side. We have proposed one such molecule, 9,10-phenanthrenequinone (PQ) [12-14]. It had been previously shown that PQ reacts with silicon dangling bonds in UHV conditions to form a covalently bonded adduct [12]. Our surface spectroscopic measurements (UPS, IPES, etc.), used to probe the energy level alignment, show that the Si/PQ interface is a Type-I heterojunction – band-offsets at both conduction and valence bands - which confines that both electrons and holes in Si [13]. The passivating properties of PQ were confirmed using quasi steady-state photoconductance measurements. On both n and p-type Si surfaces, PQ reduces the interface recombination velocity from $> 10^6$ cm/s to ~ 200 cm/s [14]. This corresponds to a reduction in silicon surface defect density from 10^{15} cm⁻² to $< 10^{12}$ cm⁻². The PQ-passivated Si surfaces can even be used to make field-effect transistors that do not need high-quality SiO₂ as the gate dielectric, thereby reducing the processing temperatures from ~ 900 °C to < 100 °C. N-channel MISFETS made on PQ-passivated Si with an organic dielectric, instead of thermal-oxide, show mobilities of ~ 600 cm²/Vs, similar to a control device that used SiO₂ as the gate dielectric [14]. Future work will extend this idea to other passivating molecules with the goal of reducing the conduction and valence band offsets.

For the TiO₂/silicon system, one might imagine that interface O could serve a bridging role between Si and the TiO₂, just as it does between Si and SiO₂, thereby passivating the Si surface without the need of any intermediate molecule. Future work will be necessary to examine this.

Summary

In summary, we have shown how organic semiconductors (P3HT and PEDOT) and metal-oxide semiconductors (TiO₂) can be used to create both electron-blocking/hole-transparent and complementary hole-blocking/electron-transparent heterojunctions to crystalline silicon. These materials are amorphous, so the approach is not restricted by lattice-matching requirements. Additionally, the metal-oxides and organic semiconductors can be deposited at or near room temperature, and hence might be low-cost. The hybrid interfaces are electronically well-behaved, and have potential photovoltaic applications in which the blocking of majority carriers leads to high open circuit voltages. Future directions include understanding the interplay between the exact interface structure, band alignments and dipoles, and residual interface defects.

Acknowledgements

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