

# Dopant-free Silicon Solar Cells and need for Fermi Level De-pinning layers

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## 1. Abstract

Dopant-free solar cells are favored to reduce costs and can achieve efficiencies of 19% and over [1-4]. They use electrodes of extreme n- and p-type work function, known as selective asymmetric electrodes. It is assumed that they supply an equivalent surface potential to the Si sandwiched in between. We show that inserting ultra-thin insulating layers under the electrodes is critical for Fermi level de-pinning, otherwise cell voltages tend to be very small.

## 2. Introduction

The traditional design of photovoltaic cells used p-n junctions to separate the carriers and define the cell's output voltage. These played to the strengths of Si, than it can be easily doped. On the other hand, OLEDs have taken years to be successful because organic semiconductors could not easily be doped. They needed to use electrodes of very different work function to inject carriers into their valence and conduction bands, and these electrodes were often reactive or unstable.

Recently there has been a desire to make solar cells without dopants, to avoid high processing temperatures of poisonous gases in order to reduce costs [1-3]. This is possible because stable electrode materials like Al/LiF and MoO<sub>3</sub> are now available [5]. This design relies on the idea that the surface potential felt by the Si under these contacts is the bare work function, following the electron affinity rule, giving band diagrams like Fig 1(a). (this happens naturally for organic molecules in OLEDs). However, this rule does not hold on Si surfaces, instead the metal Fermi levels are strongly pinned [6] (Fig. 2) with pinning factor  $S = d\phi_n/d\Phi \sim 0.03$ , which results in band diagrams like Fig 1(b). Here  $\phi_n$  is the electron Schottky barrier height (SBH) and  $\Phi_M$  is the metal work function. Thus for a functioning solar cell we must de-pin  $E_F$  and return  $S$  to a value nearer 1.

## 3. Results.

Some years ago, it was noted that Fermi level de-pinning could be achieved experimentally by inserting an ultra-thin layer of insulator, such as SiN<sub>x</sub>, or Al<sub>2</sub>O<sub>3</sub> [7,8]. The basic idea was that at the interface between a metal and a semiconductor (Schottky barrier), the travelling wave states of the metal continue into the semiconductor as evanescent metal-induced gap states (MIGS) which have sufficient number and extent that they pin the metal  $E_F$  to an energy called the charge neutrality level (CNL), Fig. 3 [6]. The MIGS are intrinsic to the semiconductor. The insulator

layer has a wider band gap, which makes MIGS decay quickly, so that they exit into the Si with less pinning effect and a larger  $S$  value. This was used to allow better control of SBHs and reduce contact resistances in CMOS [7,8].

Here we calculate the  $S$  value due to inserting different thicknesses of oxide between the metals and Si using density function supercell models. We insert 1 or 2 unit cell thicknesses of cubic HfO<sub>2</sub>. HfO<sub>2</sub> is chosen because it is lattice matched to Si. The SBH values  $\phi_p$  are extracted from the local density of states as the energy from the valence band top of Si to the metal  $E_F$ . This is slightly complicated by the fact that  $\phi_p$  also depends the atomic termination of the oxide layer [9,10], however we only need the slope  $S$ . We use metals of various work functions. The interfaces and their terminations are shown in Fig 5,6. The resulting SBH values are shown in Fig. 7. The result is that a monolayer of HfO<sub>2</sub> raises  $S$  from 0.03 to  $\sim 0.30$ . Two layers increases  $S$  to 0.50. This gives band diagram like Fig 1(b).

Further thicknesses of oxide will increase  $S$  more, however this will not only lower the MIGS density, it also decreases severely the current flow. Thus, there is an optimum thickness at which depinning and lower  $\phi_n$  value is out-weighed by the lower tunneling current. For solar cells, this is  $\sim 2$  monolayers or  $\sim 1$  nm, as found experimentally [2]. We can also link our model with the 'compact model' of Agrawal [11] which models this cross-over well.

A key point is that current densities in CMOS are very high, so the trade-off between de-pinning and tunneling barely increases overall current densities. On the other hand, solar cells have much lower current densities so the trade-off is very successful.

## 4 Summary

It is shown that Fermi level de-pinning is essential for the operation of carrier selective asymmetric electrodes and dopant-free solar cells. De-pinning is modeled by density functional calculations showing an optimum oxide thickness of 1 nm is suitable.

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## References

1. J Bullock, ... A Javey, Nature Energy 1 (2016)
2. Y Wan, ... A Cuevas, Adv Energy Mats 7 1601863 (2017)
3. J Bullock, ... A Javey, ACS Energy Letts 3 508 (2018)
4. J Melskins et al, IEEE J Photovoltaics 8 373 (2018)
5. J Huang, A Wan, A Kahn, Mat Sci Eng 64 1 (2009)
6. J Tersoff, Phys Rev Lett 52 465 (1984); J Robertson, J Vac Sci Tech B 18 1785 (2000)
7. M Kobayashi, et al, J App Phys 105 023702 (2009)

8. T Nishimura, et al, APX 1 051406 (2008)
9. P W Peacock, J Robertson, PRL 92 057601 (2004)

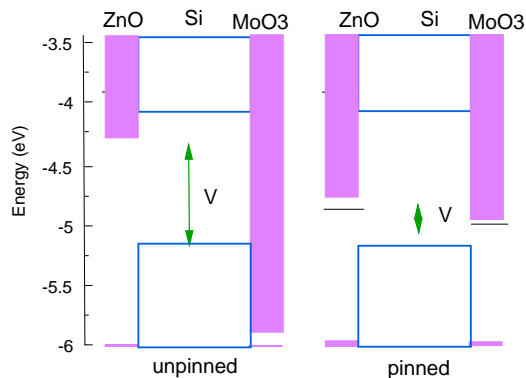


Fig. 1. Band diagram in (a) desired unpinned limit, (b) pinned limit. V is cell's output voltage.

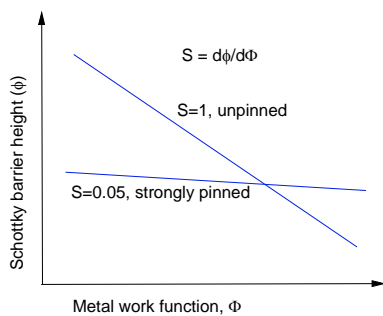


Fig. 2 Illustrating the unpinned and pinned limits.

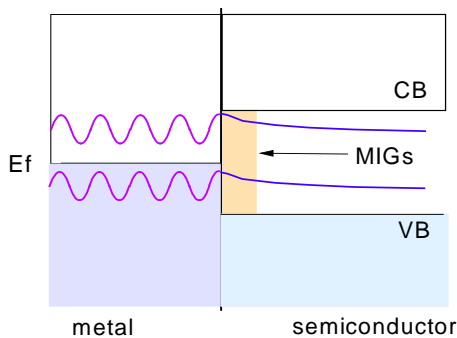


Fig. 3. MIGs are an extension of metal states into the semiconductor's band gap, which pin  $E_F$ .

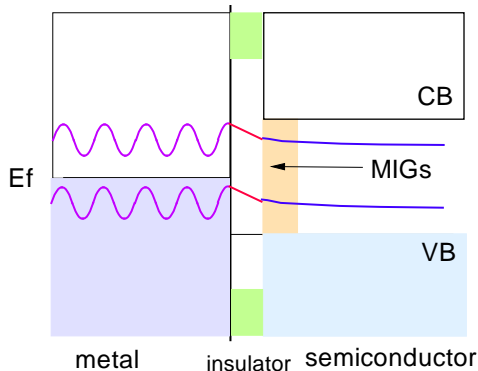


Fig. 4. Inserting a wide gap oxide layer makes MIGs decay faster so their pinning effect is less, and S larger.

10. K Y Tse, J Robertson, PRB 81 035325 (2010)
11. A Agrawal et al, APL 101 042108 (2012)

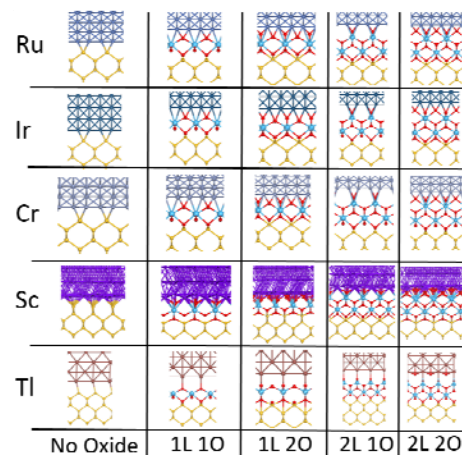


Fig. 5. Illustration of lattice matched Si, oxide and metal layer, showing different oxide terminations, and layer thickness.

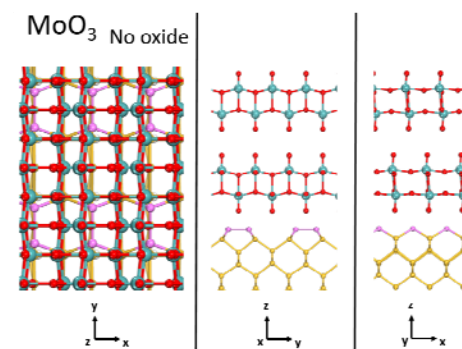


Fig. 6. Illustration of lattice matched Si, HfO2 and MoO3 layers.

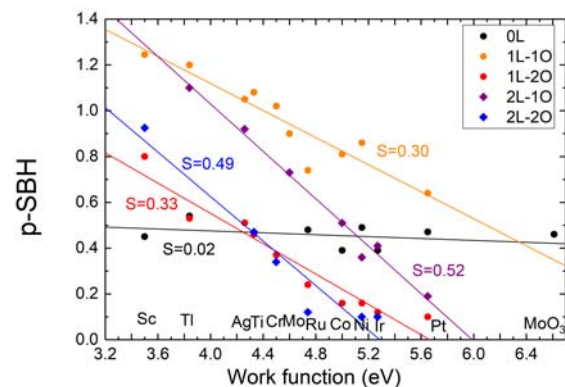


Fig. 7. Calculated Schottky barrier heights for metals on Si and various thickness of HfO2 layers.