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Electron-blocking NiO/Crystalline n-Si Heterojunction
Formed by ALD at 175°C

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Introduction

Silicon heterojunction solar cells have been the subject of growing research interest. Such cells replace the typical p^+nn^+ or n^+pp^+ structure of standard devices with selective heterojunction contacts, which block one type of carrier while allowing the other to pass freely (Fig. 1) [1-3]. Previously [4], we demonstrated a PEDOT/n-Si/TiO$_2$ heterojunction cell fabricated below 100°C with no p-n junctions in the Si. However, the organic polymer PEDOT is known to be unstable over long periods of time; furthermore, recent data indicates that the PEDOT/n-Si interface might be a non-ideal minority carrier emitter, leading to a high J_0 and low upper limit to V_{OC}. Therefore, we are currently investigating inorganic electron-blockers on crystalline silicon. Nickel oxide (NiO), because of its large conduction band offset and small valence band offset with silicon (Fig. 2) [5], is a potential candidate for electron-blocking on n-Si. Here, we report atomic layer deposited (ALD) metal/15nm-i-NiO/Si diodes. We find that the NiO film leads to a heterojunction which blocks electrons compared to diodes with the NiO omitted. The characteristics depend on the top metal, indicating that the NiO passivates the Si surface so that the Fermi level is depinned and diodes with a higher Schottky barrier height can be fabricated. Devices with Ag have electron-blocking and hole-transmitting behavior.

Growth and Methods

NiO films were grown by reactions of water vapor and nickel bis(N,N'- ditertialbutylacetamidinate at 175°C, with film growth of 0.4 Å/cycle. Previous work demonstrated reduced contact resistance using sputtered NiO on p-Si compared to metal/Si devices[6]; compared to that, we expect ALD-deposited films to result in less Si surface damage and fewer interface states. Films were grown to 15nm and metallized via thermal evaporation on top of the NiO and for an Ohmic back contact.

Device Measurements

XPS of the ALD-NiO films (Fig. 3) showed two clear nickel peaks, at 871 eV and 854 eV. These are associated with the 2p$_{1/2}$ and 2p$_{3/2}$ orbitals, respectively, and are characteristic of Ni^{2+} as opposed to Ni^{3+}, which would be indicated by a peak in the 856-857 eV range [7]. This implies a stoichiometric and thus insulating undoped NiO film.

Devices (Fig. 4) with Ag and Al deposited directly onto lightly-doped n-Si (without NiO) showed usual rectifying behavior, with $J_{0,Ag} = 4.8 \times 10^{-5}$ and $J_{0,Al} = 8.2 \times 10^{-6}$, consistent with pinning of the Si Fermi level near midgap causing barrier heights of $\phi_{B,n,eff} \approx 660\text{-}700$ meV. Adding 15-nm of NiO before the metal changed the *I-V* barrier heights to $\phi_{B,n,Al} < 500$ meV ($J_{0,n,Al} > 5 \times 10^{-2}$) and $\phi_{B,n,Ag} = 820$ meV ($J_{0,Ag} = 6.8 \times 10^{-8}$) with Ag, indicating that the NiO passivated the Si surface, depinning the Fermi level and making the Schottky barrier height dependent on the metal work function. With respect to holes, Ag/NiO/p-Si devices had near-Ohmic behavior, consistent with a low hole barrier for a carrier-selective heterojunction.

C-V measurements (Fig. 6) support this picture. The $1/C^2$-*V* curve for an Ag-contacted device shifts right with the addition of the NiO, indicating a larger built-in voltage V_0. This larger V_0 is enabled by Fermi level depinning and is consistent with the implied *I-V* value from a Schottky barrier model to within 20 meV. Combined *I-V* and *C-V* allow us to reconstruct the interface (Fig. 7). Note this band diagram matches the desired diagram of the PEDOT/Si band alignment in Fig. 1. The effective forward bias *I-V* barrier suggests that electrons overcome the built-in potential of the Schottky barrier and immediately recombine at the NiO/Si interface (due to a high density of traps) or travel through the nickel oxide via defect states inside it. Holes can easily travel from the Si to the NiO in the valence band.

Conclusion

The ALD-deposited NiO/heterojunction is able to block electrons compared to metal/n-Si devices without NiO, a first step for a high-performance selective heterojunction contact to silicon. Future work on NiO/silicon integration will focus on annealing and other methods to reduce defects in the NiO and at the NiO/Si interface, so that the NiO/Si conduction band offset can more effectively block majority-carrier current.

[1] De Wolf *et al.*, *Green* vol. 2, pp. 7, 2012. [2] Battaglia *et al..*, *Nano Lett..*, vol. 14, pp. 967, 2014. [3] Erickson *et al.*, *Adv. Energy Mat.*, vol. 4, 2014 [4] Nagamatsu *et al.*, *Appl. Phys. Lett.*, vol. 106, pp. 123906, 2015. [5] Irwing *et al.*, *PNAS,* vol. 105, pp. 2783, 2008 [6] Islam *et al.*, *Appl. Phys. Lett.*, vol. 105, pp. 182103, 2014. [7] Wagner *et al.*, *Handbook of x-ray photoelectron spectroscopy*. Eden Prairie: Perkin-Elmer, 1979.
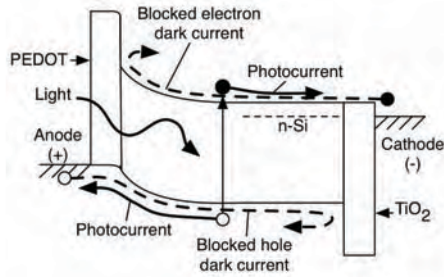
Fig. 1: Schematic of a silicon heterojunction solar cell [4]. This work seeks to replace the organic electron-blocker PEDOT with a NiO/Si heterojunction.
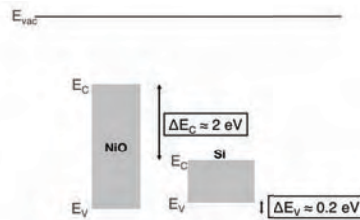

Fig. 2: Ideal band lineups of NiO and Si [5]; the large ΔE_C and small ΔE_V are conducive to a hole-selective/electron-blocking contact.
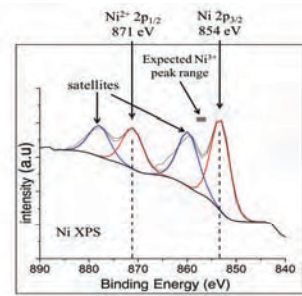

Fig. 3: XPS spectrum of ALD-NiO film, demonstrating the stoichiometric nature of the film.
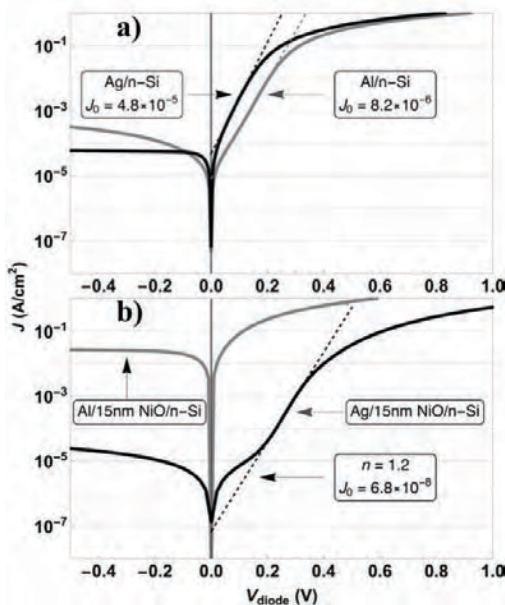

Fig. 4: a) *I-V* curves of Schottky diodes on lightly-doped n-Si. **b)** *I-V* curves of metal/NiO diodes.

Top metal	15nm NiO layer?	$\phi_{B,n\text{-Si}}$ (eV)	$\phi_{B,p\text{-Si}}$ (eV)
Al	No	0.7	N/A (Ohmic)
Ag	No	0.66	N/A (Ohmic)
Al	Yes	< 0.5	0.77
Ag	Yes	0.82	< 0.52

Fig. 5: Summary of fabricated diodes. Those with a NiO layer show increased dependence on the choice of top metal.
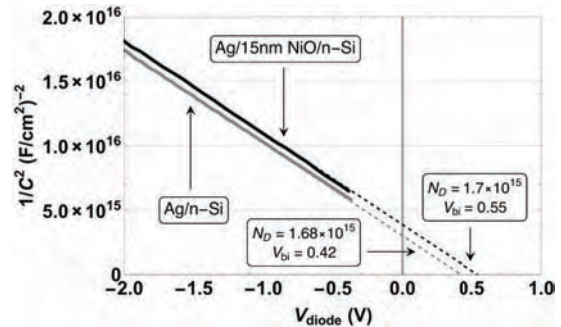

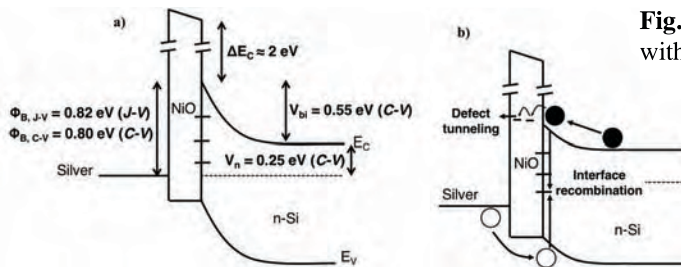**Fig. 6:** $1/C^2$-V curves of Ag-contacted n-Si diodes with and without NiO.

Fig. 7: a) Reconstruction of the Ag/NiO/n-Si interface by combined *I-V* and *C-V* measurements. Note the band diagram resembles the desired electron-blocking hole-selective PEDOT-Si heterojunction in Fig. 1. **b)** Conduction mechanisms in forward bias: defect-assisted tunneling and/or interface recombination