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ABSTRACT

Passivating metal/silicon contacts combine low carrier recombination with low contact resistivities, enabled by a low gap state density at their interface. Such contacts find applications in high-efficiency solar cells. We perform first-principles calculations based on density functional theory to investigate the surface defect and metal-induced gap state density of silicon in close contact with metals (Al and Ag). We confirm that surface hydrogenation fully removes surface-defect gap states of (111)-oriented silicon surfaces. However, the metal-induced gap state density increases significantly when metals are closer than 0.5 nm to such surfaces. These results highlight the importance of the tunneling-film thickness in achieving effective passivating-contact formation.

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With improving silicon wafer quality and surface passivation technologies, carrier recombination in metal/silicon contact regions has now been identified as the most prominent remaining limiting factor in high efficiency silicon solar cells.¹ When directly in contact with silicon substrates, metals introduce very high densities of surface states within the bandgap of silicon, resulting in a very high recombination velocity (10^6 – 10^7 cm/s), which can amount to up to 50% recombination losses in high efficiency solar cells,² limiting the solar cell efficiency well below 24%.³ The most efficient way to combat this issue is through the application of the so-called passivating contacts, where, for example, a tunnel oxide and a thin layer of, say, poly-Si are introduced before the contact for better passivation and for blocking either electrons or holes, and so, the recombination at the poly-Si/metal interface does not affect device behavior. Such contacts simultaneously enable low contact resistivity (ρ_c) and excellent surface passivation in the contact regions. To this end, for silicon solar cells, a series of thin films, either doped silicon layers or metal oxides and nitrides with extremely high or low work functions or suitable band offsets with silicon, have been investigated and developed.^{4–13} These

thin films, which are also frequently used as hole/electron transport interlayers for organic and thin film solar cells, are easily deposited, potentially at low cost, by thermal evaporation, spin-on coating, atomic layer deposition (ALD), brush painting, and even printing.^{14,15} The application of a full-area passivating contact contributes significantly to the recent cell efficiency improvements as well as fabrication simplification.^{4–13}

To optimize these passivating contacts for silicon solar cells, besides chemical passivation of interface states, the tunneling film thickness is often the most critical factor, determining both the surface passivation and the ρ_c value in the contact regions. Generally, the thicker the film, the better the surface passivation, but the higher the ρ_c , as demonstrated on TiO_2 ,^{10,11} LiF ,¹² MoO_x ,¹⁶ and MgO ¹⁷ contacts. At the device level, the passivating contacts' thickness has to be balanced to provide good surface passivation and allow for low ρ_c simultaneously. A thinner film may also be beneficial from the optical perspective, minimizing parasitic absorption in the contact stack. Moreover, thinner films require shorter deposition times and hence a potentially simpler process at lower cost, but could as well lead to homogeneity, reproducibility, and yield issues.

In this letter, we apply density functional theory (DFT) to calculate the electronic properties of Si(111) slabs, fully passivated with H (denoted here, for simplicity, as HSiH) in close contact with either Al(111) or Ag(111) slabs, as representative metal contacts used in solar cells, as shown in Fig. 1. Conduction at the metal/semiconductor contact is mainly governed by the metal-induced gap states (MIGS), which are tails of the Bloch states reaching from the metal into the semiconductor.¹⁸ However, the passivation of semiconductor surface dangling bonds suppresses the influence of MIGS considerably, resulting in a diode-like behavior.¹⁹ In our DFT model, first, we passivate the surface dangling bonds with H atoms. Next, we bring the metal and Si slabs in increasingly close proximity to examine the effect on the density of states and the MIGS density to understand the possible fundamental limitations of passivating contacts.

We perform the DFT calculations using the Vienna Ab-initio Simulation Package²⁰ and treat the exchange correlation functional in the generalized gradient approximation (Perdew-Burke-Ernzerhof). The cutoff energy of the plane wave basis is set to 400 eV. We consider the Al 3s² and 3p¹ electrons, the Ag 4d¹⁰ and 5s¹ electrons, and the Si 3s³ and 3p² electrons as valence states. $2 \times 2 \times 1$, $4 \times 4 \times 1$, and $6 \times 6 \times 1$ k-meshes are employed for the structural relaxation, self-consistent calculation, and non-self-consistent calculation, respectively. The structural relaxation is considered to be converged when the Hellmann-Feynman forces have declined below 0.001 eV/Å for all atoms.

In the structural model, a slab of Si(111) consisting of six Si layers is placed on top of an Al(111)/Ag(111) slab having eight Al/Ag layers. We do not include dopants in our model because it has been shown that the electronic conduction in such thin slabs is determined by the interaction of interface states with the Si band structure instead of bulk dopants.^{21,22} We construct $4 \times 4 \times 1$ and $3 \times 3 \times 1$ supercells of Al(111)/Ag(111) and Si(111), respectively, giving rise to lattice mismatch less than 1%. A 30 Å thick vacuum is added to avoid artificial interaction due to the periodic boundary conditions (see Fig. 1). The H-Si bond length is 1.50 Å, consistent with the experimental value of 1.48 Å.²³ The optimized displacements (d) between the centers of the top Al atoms and H atoms are 2.82 Å and 2.50 Å for the Al(111)-HSiH and Ag(111)-HSiH systems, respectively.

The density of states (DOS) is shown in Fig. 2 for bare and passivated Si(111) surfaces. For bare Si(111), there are many states

FIG. 1. Structural model of metal(111) and hydrogen passivated silicon(111). The region enclosed within the dashed lines is one silicon layer, and a total of six silicon layers is considered. The arrow line gives the separation displacement (d) between metal and passivated silicon. Metal, hydrogen, and silicon atoms appear in green, red, and blue colors.

FIG. 2. Density of states for bare and hydrogen passivated Si (111). The Fermi level is set to 0 eV. For the surface state density, the data on bare silicon within the bandgap of the passivated silicon are used.

within the bandgap which account for a high surface state density of $1.72 \times 10^{15} \text{ cm}^{-2} \text{ eV}^{-1}$ in agreement with a previous report [$2 \times 10^{15} \text{ cm}^{-2} \text{ eV}^{-1}$ (Ref. 24)]. Experimentally, these deep states act as recombination centers for the charge carriers, lowering the operating voltages of the devices, and cause Fermi level pinning (FLP), impairing charge selectivity of overlaying contact structures.^{25,26} In the case of H passivation, these states disappear and, hence, will un-pin the Fermi level, as proven in experiment.²⁷ Moreover, H passivation results in p-type silicon with a bandgap of 0.62 eV, smaller than the experimental value of 1.12 eV (Ref. 28) for bulk silicon. This theoretical bandgap underestimation compared to experiment is well known for the exchange correlation potential used here.

Although the silicon surface dangling bonds are saturated with H, the metal subsequently placed on silicon gives rise to the MIGS penetrating into the bandgap, as evident in Fig. 3, representing the partial DOS at various displacements between the metal and silicon. As the metal moves closer to the passivated silicon surface, the magnitude of these states increases. This clearly indicates that a fully hydrogenated surface can still feature plenty of deep states due to the close proximity of a contact structure. Using a thicker tunneling film between the metal and the semiconductor will suppress the MIGS and, consequently, the FLP. Although this increase may rise ρ_c , one can find a suitable thickness to balance ρ_c and FLP, which has a key effect on the quantum transport. For practical tunnel oxide passivating contacts, Kale *et al.*²⁹ have demonstrated that the carrier recombination parameter (J_0) decreases with the increasing tunnel oxide or polycrystalline silicon thickness, which is consistent with our simulation results. An optimized tunnel oxide thickness of 1.4–1.6 nm was determined to simultaneously yield low J_0 and ρ_c . Experimentally, most silicon solar cells will feature Si(111) surfaces as the facets of random pyramids of textured Si(100) wafers. Nevertheless, Si(100) surfaces may also be present in devices. In this context, we obtain a similar trend for Si(100) as well. We further calculate the density of MIGS over the entire bandgap as a function of metal separation from the passivated silicon surface, as given in Fig. 4. For the optimized geometries (the structures obtained after structural optimization), the MIGS density is $9.10 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ for Ag, which is slightly higher than the value of $6.91 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ obtained for Al. This

FIG. 3. Density of states for silicon placed at various displacements from Al(111) (top) and Ag(111) (bottom). The solid circles and boxes represent the valence band maxima and the conduction band minima, respectively. The Fermi level is set to 0 eV.

FIG. 4. MIGS density within the bandgap as a function of displacement (d) between metal (blue: Al; black: Ag) and passivated silicon.

comes from the higher electronegativity of Ag as compared to that of Al due to which Ag remains closer to Si, which is consistent with Fig. 3 where the magnitude of MIGS is lower for Al. According to optical absorption measurements, the defects in poly-Si are present as exponential band tails.^{30,31} Therefore, we implement exponential fitting of the MIGS density data. The decaying trend in the MIGS density suggests that a thicker tunneling film suppresses the MIGS and FLP.

In summary, the electronic DOS and MIGS density within the bandgap of passivated Si(111) placed at various displacements from the metals Al(111) and Ag(111) are calculated. The high surface state density of the un-passivated Si(111) disappears by saturating dangling bonds with H, giving rise to a p-type silicon character at the silicon surface. However, the presence of a metal placed on top of such a perfectly passivated silicon surface induces MIGS within the bandgap. This trend decays by moving the metal away from silicon. Our results demonstrate that one needs an optimal thickness of the tunneling film between the metal and the semiconductor for achieving a passivating metal/semiconductor contact, as otherwise MIGS will pin the Fermi level.

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