

Accurate Solar Cell Efficiency from First Principle

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Although the Shockley–Queisser limit is a sound estimate of the maximum theoretical efficiency of a cell, this upper estimate can be significantly higher than the practically achievable efficiency [1]. In reality, parallel non-radiative processes affect the device efficiency. The effect of parallel non-radiative processes can be described in terms of external radiative efficiency, where devices with lower non-radiative recombination processes have higher external radiative efficiencies and thus their efficiency limit approaches the Shockley–Queisser limit [2].

One key element to determine solar cell efficiency limited by non-radiative processes from first principle is to determine the energy levels of defects limiting such solar cells. The energy level, in combination with the capture rates, allows to determine the minority carrier lifetime which directly influences the external radiative efficiency, open-circuit voltage, voltage at maximum power point and ultimately efficiency of solar cell devices. Recent advances have indicated that all relevant defect parameters can be obtained from first principles [3]–[6], however the accuracy of such calculations remains unclear. Here we demonstrate that defect parameters can be obtained accurately from first principle by using hybrid functionals in combination with large enough supercells and appropriate correction scheme. This advance enables to determine the practical efficiency potential of novel solar materials from first principle.

Theoretical formulation and methodology

There are a wide range of absorbers such as III-Vs, II-VIs, perovskites or transition metal dichalcogenides to validate the accuracy of defect energy levels calculated from first principles. However, experimental data of defect energy levels are scarce in such materials and thus we choose silicon as one of the most studied materials with very well-defined defect energy levels as measured by Deep Level Transient Spectroscopy and Hall measurements [7], [8]. We use the data of Graff as reference to assess the accuracy of our calculations [9].

We calculate the total energy of bulk materials with and without impurities using the projector augmented-wave (PAW) method [10] of the Density Functional Theory (DFT) [11], [12]. We use the hybrid exchange-correlation functional, Heyd-Scuseria-Ernzerhof (HSE06) [13] to describe the atomic and the electronic structure of the bulk and defective structure. Hybrid functionals allows to add a portion of Fock exchange (here screened by a parameter $\mu = 0.2 \text{ \AA}^{-1}$) to the exchange described by the generalized gradient approximation functional of Perdew, Burke, and Ernzerhof (PBE) [14], which significantly improves the determination of the defect energy levels, the bandgap and the band structure [13]. As commonly performed, we tune the value of exchange [15], [16] to reproduce the low-temperature bandgap value of silicon [17].

To calculate the defect formation, we use a $2 \times 2 \times 2$ supercell expansion (64 atoms) of the unit cell and use gamma-point sampling. For all our calculations we use a kinetic energy cutoff of 400 eV. The resulting lattice parameters of 5.46 Å is in good agreement with the experimental value of 5.43 Å [18]. All our calculations are performed using the VASP code [19], [20].

The calculation of the defect formation energy level is performed as follows [21]

$$E^f[X^q] = E_{tot}[X^q] - E_{tot}[Si, bulk] - n_{impurity}\mu_{impurity} + n_{Si}\mu_{Si} + q[E_{VBM} + E_F] + \Delta q + E_{finite\ size\ correction}$$

$E_{tot}[X^q]$ is the total energy of the defect supercell, $E_{tot}[Si, bulk]$ is the total energy of the bulk supercell, n_{Si} and $n_{impurity}$ indicate the number of impurities that have been added from the supercell and μ_{Si} and $\mu_{impurity}$ is their respective chemical potentials. E_{VBM} indicates the energy of the minimum of the valence band, E_F is the Fermi level and Δq indicates the charge of the supercell. For all calculations we use the finite-size corrections as proposed by Freysoldt [22].

Substitutional impurities are placed in the centre of the supercell. There are several interstitial sites in silicon [23], here we find that most transition metals relax in tetrahedral or hexagonal interstitial sites as shown in Figure 1. With the lattice parameter a , the tetrahedral site is located at $(a/2, a/2, a/2)$ and has four equally distanced silicon nearest neighbours, while the hexagonal interstitial is located at $(3a/8, 3a/8, 5a/8)$ and has six silicon nearest neighbours.

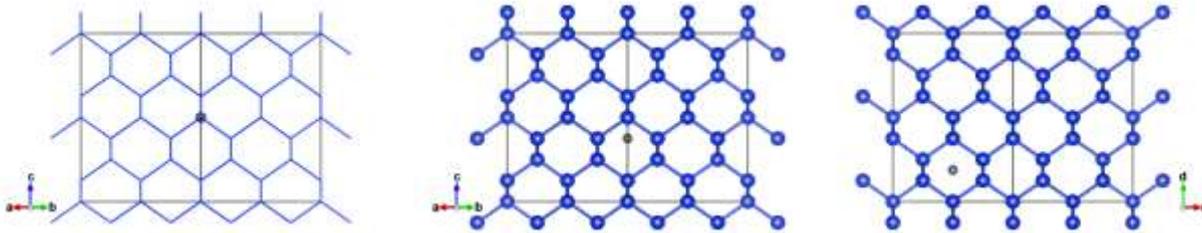


Figure 1. Wireframe and ball and stick representation of the (a) substitutional site, (b) tetrahedral site and (c) hexagonal site within the 64 atom supercell used for our calculations.

Results

Figure 2 shows the result of our calculation on defects relevant to the operation of silicon solar cells. Our results show excellent agreement between experimental defect activation energies and calculated activation energies in this work.

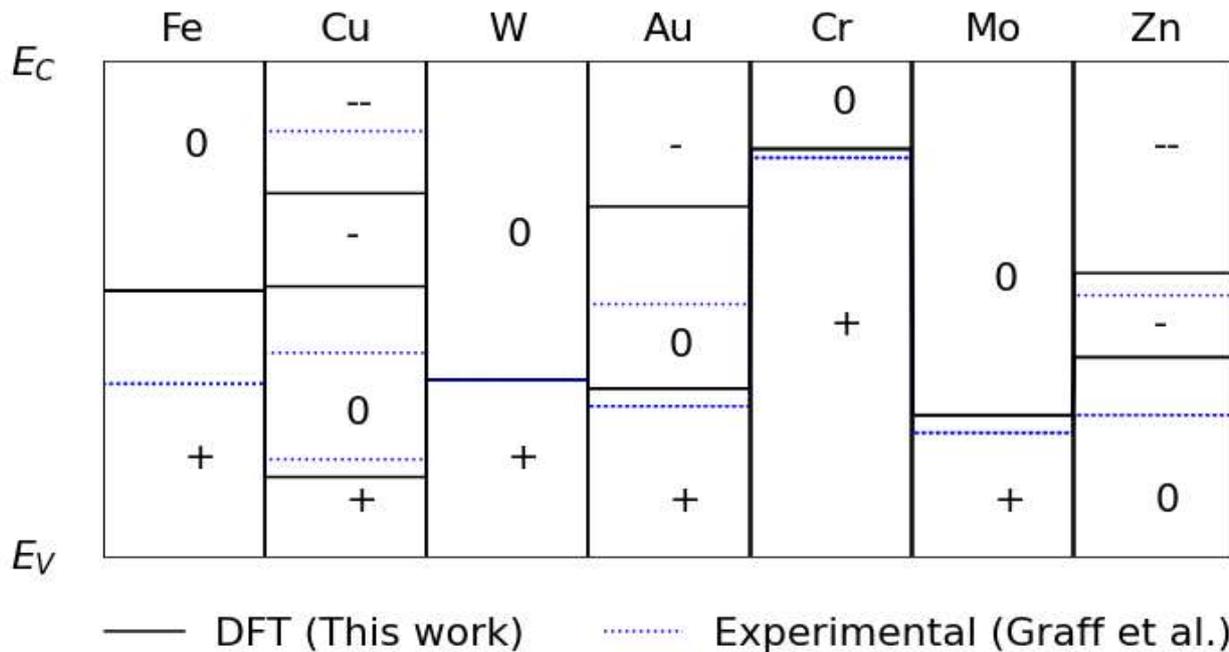


Figure 2. Exeperimental (Graff [9]) and calculated (this work) activation energies of interstitial and substitutional transition metals (charge states are indicated as ++/+/0/-/-).

Conclusions

For the first time we show that first principle calculations can reliably estimate the configuration (substitutional, interstitial...) of defect as well as their charge states and their respective activation energies. This is a significant step forward for the calculation of efficiency from first principle. In the final presentation, we will also show the accuracy of capture rates calculated from first principle and present our full procedure for predicting the efficiency from first principle in any material system.

Conclusions

This research project was undertaken with the assistance of resources and services from the National Computational Infrastructure (NCI), which is supported by the Australian Government. The access to NCI was supported by UNSW. This work was also supported by the Australian Research Council (ARC) Discovery Early Career Researcher Award (DECRA) and ACAP projects, R4FR01. We thank Prof. Alison Lennon for fruitful discussions.

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