

Al-Ani OA, Goss JP, Al-Hadidi M, Briddon PR, Rayson MJ, Cowern NEB.

[Impact of grain boundary structures on trapping iron.](#)

*Journal of Crystal Growth* (2017)

DOI: <https://doi.org/10.1016/j.jcrysgr.2017.01.033>

**Copyright:**

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

**DOI link to article:**

<https://doi.org/10.1016/j.jcrysgr.2017.01.033>

**Date deposited:**

05/05/2017



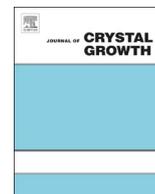
This work is licensed under a  
[Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International licence](http://creativecommons.org/licenses/by-nc-nd/4.0/)



ELSEVIER

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: [www.elsevier.com/locate/jcrysgro](http://www.elsevier.com/locate/jcrysgro)

## Impact of grain boundary structures on trapping iron

Oras A. Al-Ani<sup>a,b,\*</sup>, J.P. Goss<sup>a</sup>, Meaad Al-Hadidi<sup>a</sup>, P.R. Briddon<sup>a</sup>, M.J. Rayson<sup>a</sup>, N.E.B. Cowern<sup>a</sup>

<sup>a</sup> School of Electrical and Electronic Engineering, Newcastle University, UK

<sup>b</sup> Electrical Engineering Technical College, Baghdad, Iraq

### ARTICLE INFO

MSC:  
00–01  
99–00

**Keywords:**

A1. Defects  
A1. Impurities  
A1. Surface structure  
A1. Planar defects  
A1. Segregation  
B3. Solar cells

### ABSTRACT

Density-functional theory has been used to study the segregation of iron at  $\Sigma 3$ -(110) and  $\Sigma 5$ -(001) twist grain boundaries. We find both grain boundaries bind interstitial iron by less than 0.4 eV, and modify the equilibrium spin state. Although interstitial Fe binds relatively weakly at fully bonded grain boundaries, it is more strongly trapped by vacancies at the grain boundary, and perhaps more critically, by Fe already trapped there. We conclude that precipitation of Fe at grain boundaries is energetically favourable, even in the absence of direct chemical bonding afforded by the substitution of Si by iron.

### 1. Introduction

Low cost Si-based materials, including multi-crystalline silicon (mc-Si), is promising for use in photovoltaic (PV) applications [1]. mc-Si generally contains extended defects and contamination by transition elements present during module fabrication [2]. Among these elements, iron is arguably the most important detrimental impurity in lower grade Si [3], with interstitial iron ( $\text{Fe}_i$ ) being a recombination centre, reducing the operating efficiency of solar cells [4,5]. Iron and its complexes in bulk silicon have previously been investigated both theoretically and experimentally [6,7]. There is some evidence of Fe gettering at grain boundaries (GBs) is a viable route to reduction of the deleterious effects of Fe in mc-Si solar cells [8,5]. Various experimental studies [9–11] indicate the strong dependence of iron segregation in Si at GBs upon both misorientation of grains and upon the inclination of the GBs.

In this work, quantum-chemical simulations have been employed, with systems modelled using periodic boundary conditions and large supercells, to evaluate the binding of  $\text{Fe}_i$  at  $\Sigma 5$ -(001) and  $\Sigma 3$ -(110) twist GBs. These GBs exhibit considerable bond-strain, although all atoms are fully co-ordinated. There is relatively little understanding of the mechanism of segregation of iron at these GBs types at an atomistic level, possibly because modelling of GBs is challenging in terms of system size required, and that the detailed structure of GBs in mc-Si remains a matter of some debate [12]. However, it is important to develop a fundamental understanding of the mechanism of any

attractive interaction (gettering) between GBs structures in mc-Si and diffusing Fe atoms.

We have previously reported preliminary calculations showing that  $\Sigma 5$ -(001) GBs represent binding sites for  $\text{Fe}_i$  [13]. In addition, there is experimental evidence that  $\Sigma 3$ -(110) GBs contains large amounts of segregated iron [10,14]. In this paper, we report further data for the  $\Sigma 5$ -(001) GB, and introduce data for the  $\Sigma 3$ -(110) case. We first present a description of the methodology used.

### 2. Methodology

Density-functional theory, as implemented in AIMPRO [15], has been employed, with systems modelled using periodic boundary conditions for  $\Sigma 5$ -(001) and  $\Sigma 3$ -(110) twist GBs. We use norm-conserving separable pseudo-potentials [16], and the Kohn-Sham eigen-functions are expanded using atom-centred Gaussian basis sets [17] consisting of independent sets of *s*-, *p*- and *d*-type functions with 4 and 6 different widths for the Si and Fe, respectively. Matrix elements of the Hamiltonian are calculated using a plane wave expansion of the density and Kohn-Sham potential [18] with a cutoff of 150 Ha. Structures are optimised by conjugate gradients requiring forces to be  $< 10^{-3}$  au, and the final optimisation step is required to be  $< 10^{-5}$  Ha. The Brillouin-zone is sampled using Monkhorst-Pack grids [19], with meshes chosen such that each point represents approximately a cubic section of reciprocal space. The sampling yields total energies converged to the order of  $10^{-5}$  eV/atom.

\* Corresponding author at: School of Electrical and Electronic Engineering, Newcastle University, UK.  
E-mail address: [o.a.s.al-ani@ncl.ac.uk](mailto:o.a.s.al-ani@ncl.ac.uk) (O.A. Al-Ani).

<http://dx.doi.org/10.1016/j.jcrysgro.2017.01.033>

0022-0248/ © 2017 The Authors. Published by Elsevier B.V.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Bulk silicon is modelled using primitive and 512 atom cells (lattice vectors of  $[400]a$ ,  $[040]a$  and  $[004]a$ ). For the  $\Sigma 5$ -(001) and  $\Sigma 3$ -(110) coincidence-site-lattice twist GBs, the periodic boundary conditions along the  $[001]$ - and  $[110]$ -directions respectively produce two, equivalent GBs. Our model  $\Sigma 5$ -(001) GB system with 24 layers, may be viewed as six atomic layers either side of each boundaries. For the decorated form of the  $\Sigma 5$ -(001) GB, we have repeated the in-plane foot-print in each in-plane direction, yielding 20 atoms per layer, and 480 silicon atoms overall. This separates Fe atoms from their periodic images whilst maintaining a feasible overall simulation size. For the  $\Sigma 3$ -(110) GB, we repeated the in-plane foot-print in each in-plane direction to yield 24 atoms per layer, 16 layers and 384 silicon atoms overall. For both forms of GB, the lattice parameter normal to the boundary-plane has been varied to minimise the total energy, and the in-plane vectors fixed to the lengths determined for bulk silicon. These GBs exhibit considerable strain, but all silicon atoms are fully co-ordinated.

The binding energies of Fe to the GBs ( $E^b$ ) are the energy differences between sites within the GB and those in bulk regions of the supercells.

### 3. Results and discussions

#### 3.1. Interstitial iron in bulk silicon

It is generally agreed that  $Fe_i$  has a high diffusivity in pure silicon [7]. We reported previously [13] the migration energy is 0.80 eV (0.7 eV) and for the neutral(positive) charge state, in line with previous calculations [20]. We also reproduced the electronic spin energies of  $Fe_i$  from the literature [21,20]. The positive outcomes obtained for  $Fe_i$  in bulk Si provides the basis for the extension of the study to the more complex problem of Fe attached to twist GBs.

#### 3.2. Grain boundaries

Schematics of the  $\Sigma 5$ -(001) and  $\Sigma 3$ -(110)twist GBs are shown in Fig. 1. The labels indicate sites examined.

Areal energy-densities ( $\sigma$ ) may be calculated using  $\sigma = (E_{GB} - E_{bulk})/2A_{GB}$ , where  $E_{GB}$  is the total energy supercell,  $E_{bulk}$  is the total energy of the same number of bulk Si atoms, and  $A_{GB}$  is the interface area (the factor of 2 is because there are two GBs per cell). We find  $\sigma(\Sigma 5)$  and  $\sigma(\Sigma 3)$  to be 1.289 and 0.786 J/m<sup>2</sup>, respectively, which compare well with the literature [22,23].

Based upon these data, we view our methodology to be sufficient for modelling Fe-GB interactions, where for each of the two GB structures,  $Fe_i$  has been introduced at a range of non-equivalent sites (Fig. 1). At each site, the structure has been optimised for different charge and spin states.

#### 3.3. $Fe_i$ -GBs complexes

For the majority of sites examined within the  $\Sigma 5$ -(001) GB (sites  $a'$ – $d'$ ), the neutral charge state favours the spin-triplet state, in line with behaviour in bulk silicon [20,21]. However, at the  $a'$  site, which is lower in energy than the other sites, the spin singlet and triplet states are degenerate to the accuracy of the calculation. All the sites within the  $\Sigma 3$ -(110) GB favour the  $S=1$  configuration for  $Fe_i^0$ , with site  $e''$  being the most stable site, where the  $S=0$  and  $S=2$  configurations lie 0.17 eV and 0.76 eV above the spin triplet. At sites  $i'$  and  $i''$  the spin state energies resemble the energetics from bulk silicon simulations, confirming that these sites can be considered as a reference for  $Fe_i$  in a bulk-like environment.

We have also examined the  $S = 1/2$  and  $S = 3/2$  configurations for the positive charge states, where we find that the doublet state is favoured for both GBs in the stable sites. For all sites examined, we find a deep level arising from the Fe  $3d$ -orbitals, and thus the electrical activity of  $Fe_i$  is predicted to remain irrespective when if segregated to

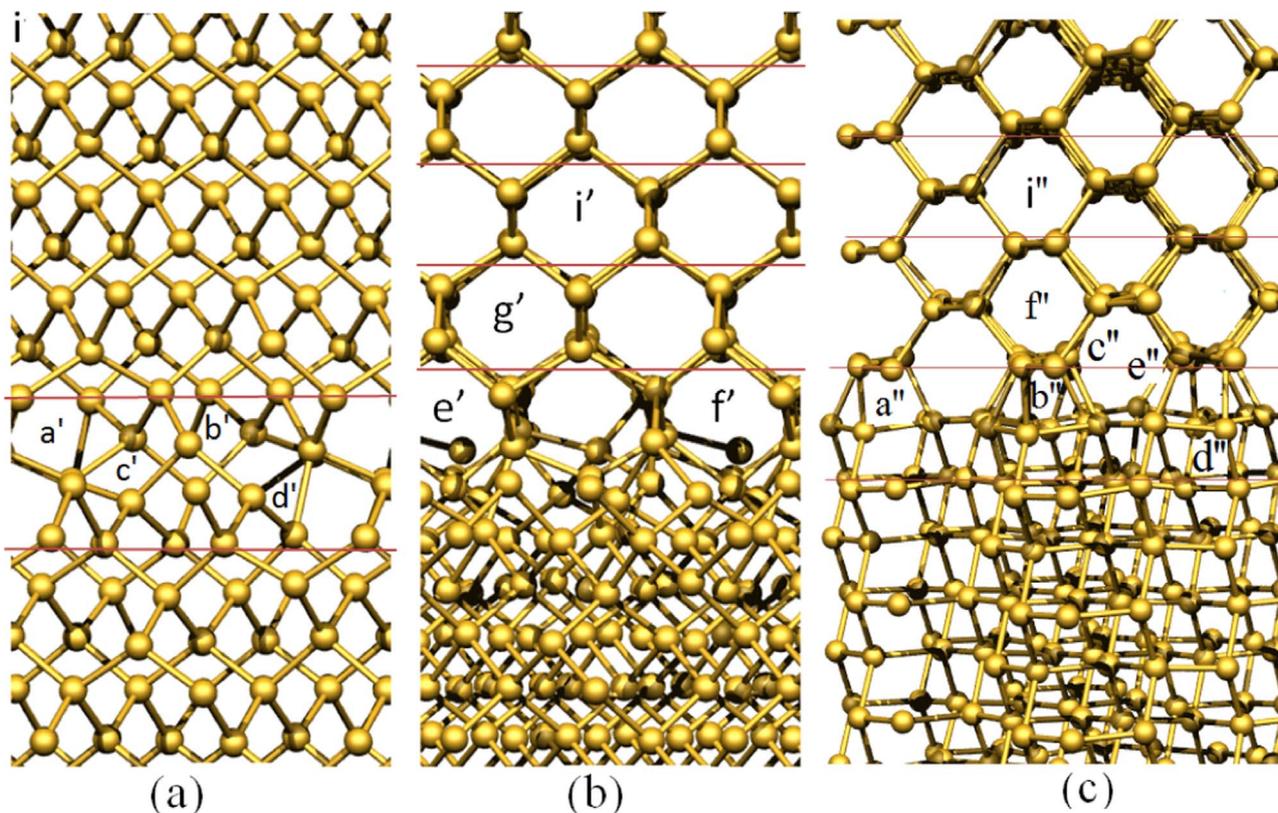
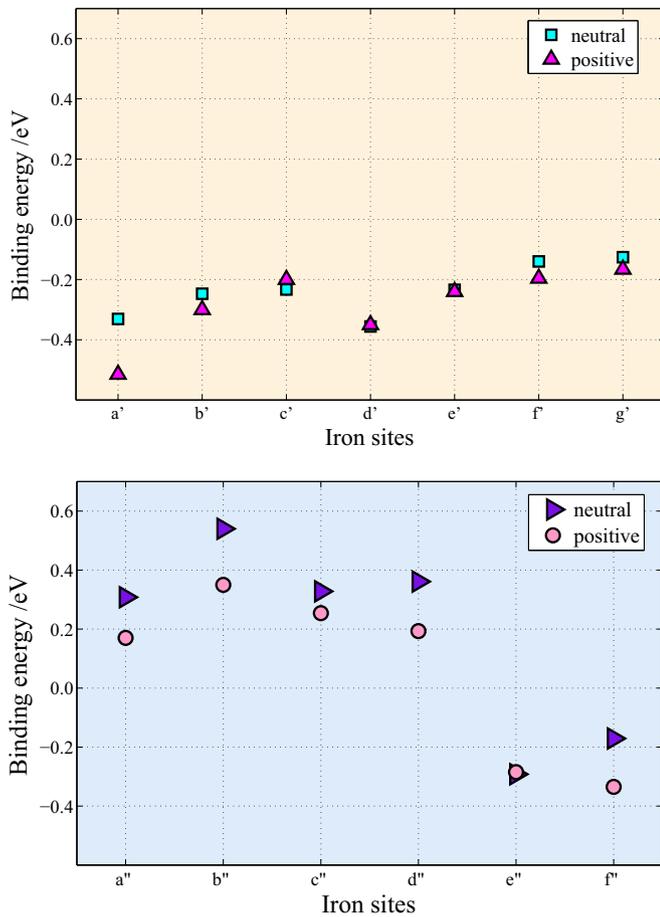


Fig. 1. Optimised structures of (a)-(b)  $\Sigma 5$ -(001) and (c)  $\Sigma 3$ -(110) twist GBs. (a) and (b) illustrate the GB from different directions to facilitate identification of the GB layer.  $a'$ – $i'$  and  $a''$ – $i''$  show the interstitial sites investigated.  $i'$  and  $i''$  are references for  $Fe_i$  in a bulk-like environment.



**Fig. 2.** Binding energies (eV) of iron to the (top)  $\Sigma 5$ -(001) and (bottom)  $\Sigma 3$ -(110) twist grain-boundaries as a function of site (Fig. 1) and charge state. Negative values correspond to an attraction between the GB and Fe, while positive values indicate that segregation is not favourable.

either of these GBs.

Fig. 2 shows a plot of  $E^b$  for the two GBs. Negative values correspond to an attraction between the grain boundary and iron, while positive ones indicate that segregation is not favourable.

We find Fe is bound to the  $\Sigma 5$ -(001) GB by around 0.4 eV, and to the  $\Sigma 3$ -(110) GB by about 0.3 eV. The positive values for sites a''–d'' in the case of the  $\Sigma 3$ -(110) GB can be understood in terms of the space available to the Fe impurity at these sites. For example, the average Fe–Si separation at site b'' is around 3% shorter than the reference site (i''), whereas the average distance is around 2% greater than the reference site for f''. This hints that

an important part of the stabilisation of interstitial Fe at GBs is the existence of open volume sites at the extended defects.

Where  $Fe_i$  is located at its equilibrium sites in the GBs (a' and e''), the Fe atom has a higher co-ordination than in the tetrahedral form in bulk silicon. The inter-nuclear distances and angles are indicated in Fig. 3, which resemble  $FeSi_2$  co-ordination [24], with eight Fe–Si distances of 2.35 Å.

### 3.4. Fe pairs– $\Sigma 5$ -(001) complexes

In addition to  $Fe_i$ , for the  $\Sigma 5$ -(001) GB we have examined incorporation of  $Fe_i$  at a vacancy, and the formation of  $Fe_i$ -pairs.

#### 3.4.1. Iron–vacancy pairing

GBs may contain voids that trap mobile  $Fe_i$ . If diffusing  $Fe_i$  encounters a neutral vacancy at the  $\Sigma 5$ -(001) GB, initially a near-neighbour  $Fe_i$ -V pair may be formed. Indeed, the NL19 EPR centre has been suggested to arise from such a structure [7]. We investigated many sites inside the boundary, and find for the neutral charge state the  $S=1$  configuration is marginally favoured over  $S=0$ . The reaction to form ( $Fe_i$ -V) from  $Fe_i$  in the grain and a vacancy in the GB reduces the energy by 1.6 eV, which is close to previous estimates for a similar reaction in bulk Si [25].

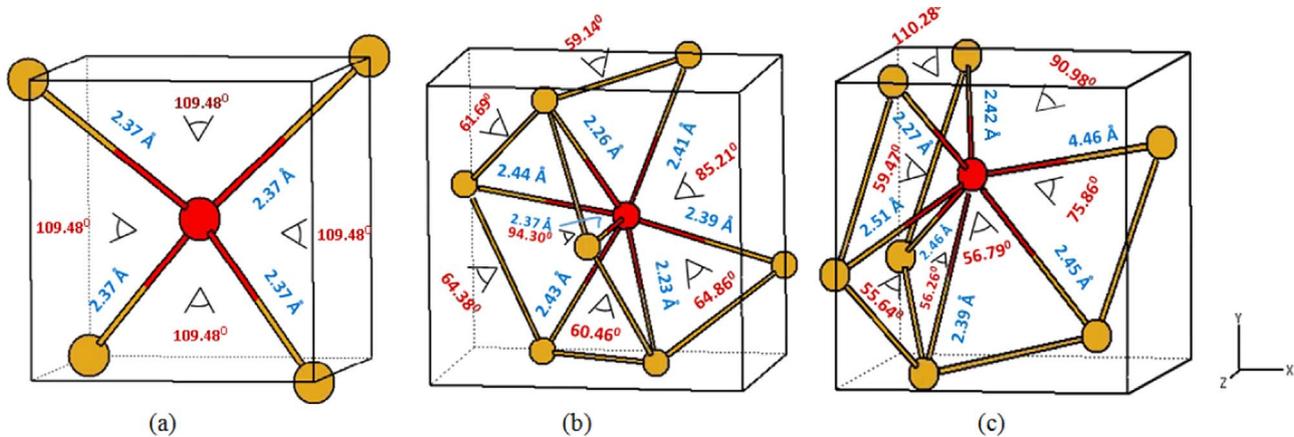
When the  $Fe_i$  moves into the vacancy, substitutional Fe ( $Fe_s$ ) is formed, which is found to have a  $S=0$  ground state. The nearest-neighbour  $Fe_i$ -V pair is 0.8 – 2.4 eV higher in energy than  $Fe_s$ , depending upon the site in the GB. Again the upper limit of the reaction energy compares favourably with the comparable bulk reaction estimated to release 2.6 eV [25].

#### 3.4.2 Iron pairs

We have reported elsewhere that  $Fe_i$ -pairs [26] are both bound (in contrast to an earlier report [25]) and mobile. This being the case it is plausible that Fe atoms would arrive at the GBs in pairs, or, should they arrive individually, that pairs would be formed in the GB. The binding of a second  $Fe_i$  atom to the GB is found to be greater than the first, being 1.5 eV. The energy gained by taking an iron-pair from the grain and locating it at the GB is estimated to be 1.6 eV.

## 4. Conclusion

Based upon our calculations, we conclude that interstitial Fe binds with a modest energy (<0.5 eV) to a fully bonded  $\Sigma 5$ -(001) or  $\Sigma 3$ -(110) twist grain boundary. This binding is greatly increased by  $Fe_i$  being trapped at vacancies at the GB, or perhaps more critically, by Fe already trapped there. The latter result indicates that precipitation of Fe at GBs is strongly energetically favourable, even in the absence of direct chemical bonding afforded by the substitution of Si by iron.



**Fig. 3.** Schematic showing the high coordination of iron at the ground state site of (b)  $\Sigma 5$ -(001) and (c)  $\Sigma 3$ -(110) twist GBs. (a) shows the calculated geometry of  $Fe_i$  in the bulk Si.

## Acknowledgement

The first author would like to thank HCED for sponsoring her PhD study as well as Dr Ahmed Sabaawi for his support.

## References

- [1] J.F. Nijs, J. Szlufcik, J. Poortmans, S. Sivonthaman, R.P. Mertens, Advanced manufacturing concepts for crystalline silicon solar cells, *IEEE Trans. Electron Devices* 46 (10) (1999) 1948–1969.
- [2] S. Myers, M. Seibt, W. Schröter, Mechanisms of transition-metal gettering in silicon, *J. Appl. Phys.* 88 (7) (2000) 3795.
- [3] A. Istratov, H. Hieslmair, E. Weber, Iron contamination in silicon technology, *Appl. Phys. A* 70 (5) (2000) 489–534.
- [4] G. Coletti, P.C. Bronsveld, G. Hahn, W. Warta, D. Macdonald, B. Ceccaroli, K. Wambach, N. le Quang, J.M. Fernandez, Impact of metal contamination in silicon solar cells, *Adv. Funct. Mater.* 21 (5) (2011) 879–890.
- [5] O.A. Al-Ani, A.M. Sabaawi, J.P. Goss, N.E.B. Cowern, P.R. Briddon, R., M.J. Rayson. Investigation into efficiency-limiting defects in mc-si solar cells, *Solid State Phenomena*, 242, 2010, pp. 96–101.
- [6] A.A. Istratov, H. Hieslmair, E.R. Weber, Iron and its complexes in silicon, *Appl. Phys. A* 69 (1) (1999) 13–44.
- [7] S.H. Muller, G.M. Tuynman, E.G. Sieverts, C. Ammerlaan, Electron paramagnetic resonance on iron-related centers in silicon, *Phys. Rev. B* 25 (1) (1982) 25.
- [8] M. Rumler, M. Rommel, J. Erlekampf, M. Azizi, T. Geiger, A.J. Bauer, E. Meißner, L. Frey, Characterization of grain boundaries in multicrystalline silicon with high lateral resolution using conductive atomic force microscopy, *J. Appl. Phys.* 112 (3) (2012) 034909.
- [9] M.C. Schubert, H. Habenicht, W. Warta, Imaging of metastable defects in silicon, *IEEE J. Photovolt.* 1 (2) (2011) 168–173.
- [10] J. Chen, T. Sekiguchi, D. Yang, F. Yin, K. Kido, S. Tsurekawa, Electron-beam-induced current study of grain boundaries in multicrystalline silicon, *J. Appl. Phys.* 96 (10) (2004) 5490–5495.
- [11] J. Chen, B. Chen, W. Lee, M. Fukuzawa, M. Yamada, T. Sekiguchi, Grain boundaries in multicrystalline si, in: *Solid State Phenomena*, Vol. 156, 2010, pp. 19–26.
- [12] C.V. Ciobanu, C.-Z. Wang, K.-M. Ho, *Atomic Structure Prediction of Nanostructures, Clusters and Surfaces*, Wiley, Germany, 2013.
- [13] O.A. Al-Ani, J.P. Goss, N.E.B. Cowern, P.R. Briddon, M. Al-Hadidi, R. Al-Hamadany, M.J. Rayson, A density functional study of iron segregation at ISFs and  $\Sigma 5$ -(001) GBs in mc-Si, *Solid State Phenom.* 242 (2016) 224–229.
- [14] M. Knörlein, A. Autruffe, R. SondenÅ, M. Di Sabatino, Internal gettering of iron at extended defects, *Energy Procedia* 55 (2014) 539–544.
- [15] R. Jones, P.R. Briddon, *The ab initio cluster method and the dynamics of defects in semiconductors*, Vol. 51A of *Semiconductors and Semimetals*, Academic Press, Boston, 1998, Ch. 6.
- [16] C. Hartwigsen, S. Goedecker, J. Hutter, Relativistic separable dual-space gaussian pseudopotentials from H to Rn, *Phys. Rev. B* 58 (7) (1998) 3641.
- [17] J.P. Goss, M.J. Shaw, P.R. Briddon, Marker-method calculations for electrical levels using gaussian-orbital basis sets, *Top. Appl. Phys.* 104 (2007) 69.
- [18] M. Rayson, P. Briddon, Highly efficient method for kohn-sham density functional calculations of 500–10000 at systems, *Phys. Rev. B* 80 (20) (2009) 205104.
- [19] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* 13 (12) (1976) 5188–5192.
- [20] H. Takahashi, M. Suezawa, K. Sumino, Charge-state-dependent activation energy for diffusion of iron in silicon, *Phys. Rev. B* 46 (1992) 1882–1885.
- [21] M. Sanati, N.G. Szwacki, S.K. Estreicher, Interstitial Fe in Si and its interactions with hydrogen and shallow dopants, *Phys. Rev. B* 76 (12) (2007) 125204.
- [22] M.C. Payne, P.D. Bristowe, J.D. Joannopoulos, Ab initio determination of the structure of a grain boundary by simulated quenching, *Phys. Rev. Lett.* 58 (13) (1987) 1348.
- [23] B. Ziebarth, M. Mrovec, C. Elsässer, P. Gumbsch, Interstitial iron impurities at grain boundaries in silicon: a first-principles study, *Phys. Rev. B* 91 (2015) 035309.
- [24] B. Egert, G. Panzner, Bonding state of silicon segregated to  $\alpha$ -iron surfaces and on iron silicide surfaces studied by electron spectroscopy, *Phys. Rev. B* 29 (4) (1984) 2091.
- [25] M. Sanati, S. Estreicher, First-principles study of iron and iron pairs in Si, *Physica B C* 401 (2007) 105–108.
- [26] O.A. Al-Ani, J. Goss, P. Briddon, M. Rayson, N. Cowern, Interstitial Fe-pairs in silicon, *J. Cryst. Growth* (2016).