Phosphorus $\delta$-doped silicon: mixed-atom pseudopotentials and dopant disorder effects

Damien J Carter$^{1,2}$, Nigel A Marks$^1$, Oliver Warschkow$^3$ and David R McKenzie$^3$

$^1$ Nanochemistry Research Institute, Curtin University, PO Box U1987, Perth WA 6845, Australia
$^2$ iVEC, Technology Park, Kensington WA 6151, Australia
$^3$ Centre for Quantum Computer Technology, School of Physics, The University of Sydney, Sydney, NSW 2006, Australia

E-mail: d.carter@curtin.edu.au

Received 22 September 2010, in final form 18 November 2010
Published 7 January 2011
Online at stacks.iop.org/Nano/22/065701

Abstract
Within a full density functional theory framework we calculate the band structure and doping potential for phosphorus $\delta$-doped silicon. We compare two different representations of the dopant plane; pseudo-atoms in which the nuclear charge is fractional between silicon and phosphorus, and explicit arrangements employing distinct silicon and phosphorus atoms. While the pseudo-atom approach offers several computational advantages, the explicit model calculations differ in a number of key points, including the valley splitting, the Fermi level and the width of the doping potential. These findings have implications for parameters used in device modelling.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Silicon semiconductor nanofabrication has now advanced to the point where it is possible to make devices by the direct placement of phosphorus dopants in two-dimensional structures [1–7]. This includes recent experiments which characterized a few-electron quantum dot device with atomically abrupt changes in the doping profile [8]. Phosphorus $\delta$-doped silicon, i.e. confinement of phosphorus atoms into a single atomic plane, is an important structural element in these devices. These experiments are complemented by computational studies of $\delta$-doping in silicon, in which a variety of methods [9–14] have been employed. These calculations yield quantities such as the doping potential, the donor electron density and the valley splitting; these in turn are important inputs into device-scale models used to characterize and optimize experimental devices.

Initial descriptions of $\delta$-doped silicon were based on the effective-mass approximation [9, 10]. In subsequent work, Qian et al [11] developed a conduction band model based on density functional theory (DFT), while Cartoxià and Chang [12] presented a tight-binding model. A more sophisticated tight-binding treatment was recently reported by Ryu et al [14] using the NEMO package [15], while a full DFT treatment of $\delta$-doped silicon was reported by ourselves [13]. While there is general agreement between the various models, open questions include the role of disorder, the validity of mixed-atom pseudopotentials and the effect of computational approximations such as basis set size, $k$-point sampling and the tight-binding formalism. While tight-binding and effective-mass models will invariably be needed for the large-scale description of ‘real’ devices, a full DFT treatment provides the justification for these approximations and a sound theoretical basis.

Building upon our earlier work [13], we report here calculations using a mixed-atom pseudopotential, enabling a direct comparison between full DFT and the earlier model of Qian et al [11]. Mixed-atom pseudopotentials offer considerable computational advantages, allowing us to treat a wide range of dopant concentrations without having to enlarge the DFT unit cell. We also examine to what extent such pseudopotentials are a meaningful representation of dopant...
disorder in the δ-plane. In section 2 we outline and test our computational methodology, placing particular emphasis on our mixed pseudopotential, k-point sampling and convergence of the doping potential. Section 3 reports how the electronic properties are affected by the doping concentration. Also discussed is the surprising variability of the valley splitting and band structure when different models of dopant disorder are used. This effect has not previously been recognized, and represents an important consideration when choosing parameters for device-scale modelling [3–7].

2. Computational model

As in our previous study [13], we describe δ-doped silicon using a highly asymmetric periodic superlattice. A large repeat length in the [001] direction of between 40 and 200 atomic layers (denoted 40L and 200L, respectively) separates individual δ-layers from their periodic images. For the in-plane directions, we use p(1 × 1), c(2 × 2), and c(4 × 4) unit cells, with 2, 4, and 16 atoms per atomic plane. Calculations using an explicit description of the dopant layer require relatively large unit cells (figures 1(a) and (b)), while with a mixed pseudopotential approach (see below), all doping levels can be described using the smallest possible unit cell, namely p(1 × 1) (figure 1(c)). Studies of explicit disorder necessarily use the large unit cell, an illustration of a quasi-random structure is shown in figure 1(b).

Our calculations are performed using the SIESTA software [16] which employs localized atomic basis sets to describe the electronic eigenfunctions. To access very large systems, the majority of the calculations use single numerical plus polarization basis sets together with norm-conserving Troullier–Martins pseudopotentials [17]. All basis sets are radially confined using an orbital energy shift of 0.01 Ryd (see [16] for further detail). We further increase the scope of our calculations by describing the atoms of the dopant plane using mixed pseudopotentials, thereby enabling use of the smaller p(1 × 1) unit cell (figure 1(c)). With this approach, known as the virtual crystal approximation [18, 19], the constituent atoms in the dopant plane are effectively alloyed into a single type of quasi-atom with a fractional nuclear charge intermediate between silicon and phosphorus; the extent of the alloying corresponds to the doping level. In the present work, mixed pseudopotentials between 1/16 monolayer (ML) and 1 ML phosphorus in silicon are generated by combining standard phosphorus and silicon pseudopotentials using a SIESTA utility.

Geometry optimization of the coordinates was found to have a minimal effect on the physical and electronic structure, and hence all calculations were single-point using bulk lattice positions. A test was performed using a 40L slab with 1/4 ML doping and a mixed pseudopotential; geometry optimization of the internal coordinates changed the atomic distances by less than 0.01 Å, the Fermi energy by less than 2 meV, and the valley splitting by less than 1 meV. Even without geometry optimization, the single-point calculations are still costly, requiring extremely small mixing parameters (≪0.001) and many cycles (>200) in order to achieve self-consistent field (SCF) convergence. By contrast, SCF convergence in typical SIESTA calculations uses a mixing parameter of 0.25. This requirement for a very small mixing parameter reflects the large spatial extent in the direction normal to the δ-plane.

Exchange–correlation energies are calculated using the generalized gradient approximation (GGA; Perdew–Burke–Ernzerhof functional [20]) and are evaluated on a real-space grid with a cutoff of 300 Ryd. As the system is essentially metallic, we use Methfessel–Paxton smearing (polynomial of order 5, T = 298 K; see [21] for further detail) to accelerate the convergence. In discussing our results, we report all band energies and the Fermi energy (EF) relative to the bulk conduction band minimum (CBM). This necessitates a band alignment between δ-doped and bulk (undoped) silicon which is achieved by matching the plane-averaged electrostatic potentials in the atomic plane most distant from the δ-layer. This alignment method assumes that the δ-doping potential has vanished at the matching plane, justification for which is provided in the following section. The doping potential itself is calculated as the electrostatic potential difference between δ-doped and undoped supercells.

2.1. Bulk silicon

Given the heavy computational cost to describe δ-doped silicon, it is important to use the smallest possible basis set that qualitatively reproduces the bulk properties of silicon. We performed bulk calculations using four different basis sets: single-zeta (SZ), double-zeta (DZ), single-zeta plus polarization (SZP), and double-zeta plus polarization (DZP). A 16 × 16 × 16 k-point grid was used to sample the Brillouin zone of the primitive two-atom unit cell. Tests at higher sampling densities confirmed that k-point convergence was achieved.

Table 1 reports as a function of the basis set the optimized lattice parameter (a), the bulk modulus (B), and several band structure parameters, including the band gap. The number of basis functions and the angular momentum components are listed for each basis set. The calculated lattice
Maximum.

All band structure energies are measured relative to the valence band maximum.

Table 1. Bulk properties of silicon as a function of basis set quality. All band structure energies are measured relative to the valence band maximum.

<table>
<thead>
<tr>
<th>Basis</th>
<th>a (Å)</th>
<th>B (GPa)</th>
<th>$E_{\text{gap}}$ (eV)</th>
<th>$E_F$ (eV)</th>
<th>$E_X$ (eV)</th>
<th>$E_L$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ (4; sp)</td>
<td>5.63</td>
<td>69</td>
<td>1.53</td>
<td>1.87</td>
<td>2.53</td>
<td>1.53</td>
</tr>
<tr>
<td>DZ (8; 2s2p)</td>
<td>5.56</td>
<td>82</td>
<td>1.43</td>
<td>2.37</td>
<td>1.77</td>
<td>1.62</td>
</tr>
<tr>
<td>SZP (9; sp)</td>
<td>5.58</td>
<td>80</td>
<td>0.85</td>
<td>2.51</td>
<td>0.99</td>
<td>1.34</td>
</tr>
<tr>
<td>DZP (13; 2s2pd)</td>
<td>5.49</td>
<td>88</td>
<td>0.63</td>
<td>2.50</td>
<td>0.78</td>
<td>1.41</td>
</tr>
<tr>
<td>Expt.</td>
<td>5.43$^a$</td>
<td>102$^b$</td>
<td>1.12$^c$</td>
<td>3.4$^d$</td>
<td>1.2$^e$</td>
<td>2.0$^f$</td>
</tr>
</tbody>
</table>

$^a$ Reference [22]. $^b$ Reference [23]. $^c$ Reference [24].

parameters are all slightly larger than the experimental value and the calculated bulk moduli are smaller; this behaviour is commonly observed when using a GGA exchange–correlation functional. The corresponding band structures in figure 2 illustrate how the choice of basis set influences the electronic structure of silicon. For the smallest and least accurate SZ basis (figure 2(a)) the band structure is qualitatively incorrect, predicting the conduction band minimum at the L-point. Inclusion of a second zeta in the basis (figure 2(b)) doubles the number of basis functions and moves the conduction band minima to the correct position in the Brillouin zone; the values of $E_L$ and $E_{\text{gap}}$, however, remain similar. A much more effective improvement of the SZ basis is achieved by adding polarization functions (figure 2(c)). Requiring only one more basis function than DZ, the SZP basis set provides an essentially correct description of the silicon band structure, aside from a broadly uniform reduction of the band gap that is very familiar for density functional theory. The inclusion of polarization functions in the DZP set (figure 2(d)) increases the computational cost by about a factor of three, but results in only a minor improvement of the band structure parameters. Consequently, an SZP basis is used throughout this work as an optimum compromise between computational accuracy and efficiency.

Mixed pseudopotentials are not commonly used in DFT calculations, and hence it is instructive to first quantify their effect in doped bulk silicon. We generated a mixed pseudopotential comprised of 7/8 of a silicon and 1/8 of a phosphorus atom. Band structures for these two representations of phosphorus-doped silicon are compared to that of bulk silicon in figure 3.

The bulk band structure in figure 3(a) shows the Fermi level midway between the valence and conduction bands, with an indirect band gap between the valence band maximum at the $\Gamma$-point, and the $\Delta$ minima of the conduction band, partway between $\Gamma$ and X. Note that the band structures are for the full eight-atom cell, and therefore contain folded bands with respect to the primitive (fcc) cell used in figure 2. Due to this folding, the minimum in the $\Delta$ band appears at 0.15 in the direction of X, rather than at 0.85, as in figure 2. In all subsequent band structures reported here, the $\Delta$ minimum will similarly appear at this folded position.

With explicit doping (figure 3(b)), the Fermi level is raised into the conduction band and a defect level appears, corresponding to a conduction band which is pulled into the mid-gap. A number of other changes and splitting of bands can be seen, reflecting the large perturbation of the band structure due to the heavy doping. In contrast, the band structure for the mixed pseudopotential (figure 3(c)) is very similar to that of the bulk, with the main difference being that the Fermi level is simply shifted to higher energy. This difference between the explicit and mixed band structures reflects the reduction in symmetry associated with explicit donor atoms, as these have a deeper Coulomb potential than their silicon counterparts. Use of the mixed pseudopotential, however, retains the symmetry of the bulk crystal, and hence the overall band structure remains essentially unchanged. As we will show, maintaining symmetry can provide significant computational advantages, however, the lack of band splitting or explicit defect levels in

Figure 2. Band structures of bulk silicon using (a) SZ, (b) DZ, (c) SZP, and (d) DZP basis sets. The dotted line denotes the Fermi level ($E_F$).

Figure 3. Band structures of (a) bulk silicon, (b) an eight-atom cell containing seven silicon atoms and one phosphorus atom, and (c) an eight-atom cell where all atoms are described by a mixed pseudopotential comprised of 7/8 of a silicon and 1/8 of a phosphorus atom. The dotted line denotes the Fermi level ($E_F$).
the mixed representation is a considerable approximation. In reality, doped silicon will lie intermediate between these two conceptual reference points, possessing neither the imposed periodicity of a small unit cell with explicit dopants, nor the homogenized representation of the mixed pseudopotential.

2.2. Convergence in \( \delta \)-layer calculations

In this section we examine in detail several computational parameters and their effect on the calculated electronic properties of \( \delta \)-doped silicon. As described by Qian et al [11], the \( \delta \)-layer doping potential pulls several conduction bands into the band gap, breaking the six-fold degeneracy of the band minima. The lowest two bands (1\( \Gamma \) and 2\( \Gamma \)) have their minima at the \( \Gamma \)-point while the four-fold degenerate 1\( \Delta \) band is higher in energy and has its minima at around 0.15 in the direction of \( X \). We use the energies of these band minima as well as the self-consistent doping potential and donor electron distribution to assess convergence. As we show here, a particularly sensitive point is the density of \( \kappa \)-points used to sample the Brillouin zone. With hindsight, our earlier brief report [13], being focused primarily on convergence with respect to slab thickness, used an overly coarse \( \kappa \)-point grid. Here, we quantify both \( \kappa \)-point and slab thickness effects and their mutual interdependence. Our tests also include a comparison between explicit and mixed pseudopotential representations of the \( \delta \)-layer.

To quantify convergence in the \( \kappa \)-point grid, we use an 80L \( p(1 \times 1) \) supercell and mixed pseudopotentials to represent a 1/4 ML phosphorus \( \delta \)-layer. For a sequence of \( \kappa \)-point meshes between \( 6 \times 6 \) and \( 14 \times 14 \), we report in table 2 a range of characteristic parameters of the electronic structure, namely the Fermi level \( (E_F) \), three band minima (1\( \Gamma \), 2\( \Gamma \), and 1\( \Delta \)) the valence band maximum (VBM), as well as the full-width at half-maximum of the self-consistent doping potential \( (\text{FWHM}_\text{potential}) \) and the donor electron density \( (\text{FWHM}_\text{density}) \).

<table>
<thead>
<tr>
<th>( \kappa )-point density</th>
<th>( E_F ) (eV)</th>
<th>1( \Gamma ) (eV)</th>
<th>2( \Gamma ) (eV)</th>
<th>1( \Delta ) (eV)</th>
<th>VBM (eV)</th>
<th>( \text{FWHM}_\text{potential} ) (( \text{Å} ))</th>
<th>( \text{FWHM}_\text{density} ) (( \text{Å} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 6 \times 6 )</td>
<td>-0.043</td>
<td>-0.221</td>
<td>-0.108</td>
<td>-0.860</td>
<td>5.07</td>
<td>7.74</td>
<td>8.23</td>
</tr>
<tr>
<td>( 8 \times 8 )</td>
<td>-0.050</td>
<td>-0.252</td>
<td>-0.133</td>
<td>-0.860 - 0.860</td>
<td>5.72</td>
<td>8.23</td>
<td>8.48</td>
</tr>
<tr>
<td>( 10 \times 10 )</td>
<td>-0.062</td>
<td>-0.285</td>
<td>-0.156 - 0.156</td>
<td>-0.860 - 0.860</td>
<td>6.08</td>
<td>8.48</td>
<td>8.53</td>
</tr>
<tr>
<td>( 12 \times 12 )</td>
<td>-0.048</td>
<td>-0.289</td>
<td>-0.160 - 0.160</td>
<td>-0.861 - 0.861</td>
<td>6.14</td>
<td>8.53</td>
<td>8.47</td>
</tr>
<tr>
<td>( 14 \times 14 )</td>
<td>-0.059</td>
<td>-0.280</td>
<td>-0.154</td>
<td>-0.861</td>
<td>6.13</td>
<td>8.47</td>
<td>8.47</td>
</tr>
</tbody>
</table>

To quantify convergence in the \( \kappa \)-point grid, we use an 80L \( p(1 \times 1) \) supercell and mixed pseudopotentials to represent a 1/4 ML phosphorus \( \delta \)-layer. For a sequence of \( \kappa \)-point meshes between \( 6 \times 6 \) and \( 14 \times 14 \), we report in table 2 a range of characteristic parameters of the electronic structure, namely the Fermi level \( (E_F) \), three band minima (1\( \Gamma \), 2\( \Gamma \), and 1\( \Delta \)) the valence band maximum (VBM), as well as the full-width at half-maximum of the self-consistent doping potential \( (\text{FWHM}_\text{potential}) \) and the donor electron density \( (\text{FWHM}_\text{density}) \).

Table 2. Electronic structure parameters of a 1/4 ML mixed pseudopotential \( \delta \)-layer as a function of the \( \kappa \)-point density. Calculations performed using a 80L system with a \( p(1 \times 1) \) unit cell.

For \( \kappa \)-points of \( 10 \times 10 \) and above. Use of a lower \( \kappa \)-point density leads to a narrowing of the potential profile as illustrated in figure 4. Similar behaviour is observed for the donor density profile (not shown).

It is instructive to compare these \( \kappa \)-point data with our earlier work [13] in which a \( 4 \times 4 \) \( \kappa \)-grid was employed in a \( c(2 \times 2) \) cell. Accounting for the differing unit cell size, this corresponds to a nominal \( \kappa \)-point density of \( 4\sqrt{2} \times 4\sqrt{2} = 5.7 \times 5.7 \) in a \( p(1 \times 1) \) unit cell. In light of the above results, such a calculation is not satisfactorily converged.

We performed a similar convergence test in which a 1/4 ML \( \delta \)-layer was described using explicit silicon and phosphorus atoms in a \( c(2 \times 2) \) unit cell (table 3). Similar convergence trends are observed, with electronic levels and potentials/density profiles converged to within 0.01 eV and 0.1 Å above a \( \kappa \)-point sampling of \( 8 \times 8 \), corresponding to a nominal equivalent \( \kappa \)-point density \( 8\sqrt{2} \times 8\sqrt{2} = 11.3 \times 11.3 \) in a \( p(1 \times 1) \) unit cell. Taking into account this equivalence, we compare in figure 5 the \( \kappa \)-point dependence of the doping potential width using explicit and mixed representations. The figure highlights three important points: (i) mixed and explicit pseudopotentials converge to significantly different widths, with the mixed pseudopotential about 20% wider, (ii) both systems converge at approximately the same \( \kappa \)-point density, above \( 10 \times 10 \) in the \( p(1 \times 1) \), corresponding to a nominal \( 7.1 \times 7.1 \) grid in the \( c(2 \times 2) \) cell, and (iii) at lower \( \kappa \)-point densities, the mixed and explicit representations behave in an opposite sense; the same reversal can be seen in the band minima and associated properties in tables 2 and 3.

Table 3. Electronic structure parameters of a 1/4 ML explicit pseudopotential \( \delta \)-layer as a function of the \( \kappa \)-point density. Calculations performed using a 80L system with a \( c(2 \times 2) \) unit cell.

For \( \kappa \)-points of \( 10 \times 10 \) and above. Use of a lower \( \kappa \)-point density leads to a narrowing of the potential profile as illustrated in figure 4. Similar behaviour is observed for the donor density profile (not shown).

It is instructive to compare these \( \kappa \)-point data with our earlier work [13] in which a \( 4 \times 4 \) \( \kappa \)-grid was employed in a \( c(2 \times 2) \) cell. Accounting for the differing unit cell size, this corresponds to a nominal \( \kappa \)-point density of \( 4\sqrt{2} \times 4\sqrt{2} = 5.7 \times 5.7 \) in a \( p(1 \times 1) \) unit cell. In light of the above results, such a calculation is not satisfactorily converged.

We performed a similar convergence test in which a 1/4 ML \( \delta \)-layer was described using explicit silicon and phosphorus atoms in a \( c(2 \times 2) \) unit cell (table 3). Similar convergence trends are observed, with electronic levels and potentials/density profiles converged to within 0.01 eV and 0.1 Å above a \( \kappa \)-point sampling of \( 8 \times 8 \), corresponding to a nominal equivalent \( \kappa \)-point density \( 8\sqrt{2} \times 8\sqrt{2} = 11.3 \times 11.3 \) in a \( p(1 \times 1) \) unit cell. Taking into account this equivalence, we compare in figure 5 the \( \kappa \)-point dependence of the doping potential width using explicit and mixed representations. The figure highlights three important points: (i) mixed and explicit pseudopotentials converge to significantly different widths, with the mixed pseudopotential about 20% wider, (ii) both systems converge at approximately the same \( \kappa \)-point density, above \( 10 \times 10 \) in the \( p(1 \times 1) \), corresponding to a nominal \( 7.1 \times 7.1 \) grid in the \( c(2 \times 2) \) cell, and (iii) at lower \( \kappa \)-point densities, the mixed and explicit representations behave in an opposite sense; the same reversal can be seen in the band minima and associated properties in tables 2 and 3.

Figure 4. Doping potentials for a 1/4 ML mixed pseudopotential using a 80L \( p(1 \times 1) \) supercell, where the \( \kappa \)-point densities of the \( \delta \)-layer are \( 6 \times 6 \) and \( 14 \times 14 \).

Figure 5. Doping potentials for a 1/4 ML explicit pseudopotential using a 80L \( p(1 \times 1) \) supercell, where the \( \kappa \)-point densities of the \( \delta \)-layer are \( 6 \times 6 \) and \( 14 \times 14 \).
Having determined the effect of \( k \)-point sampling on the \( \delta \)-layer properties, we now consider the effect of slab thickness. Convergence with respect to slab thickness indicates the point at which successive \( \delta \)-layers become decoupled from their periodic images. Calculations were performed using mixed pseudopotentials for cell lengths between 40L and 200L together with a \( p(1 \times 1) \) unit cell. Given the size of these systems, we use the smallest \( k \)-point grid for which convergence is seen, namely \( 10 \times 10 \).

Table 4 reports the Fermi level, band minima, and FWHM of the doping potential and donor density. The data show rapid convergence with the \( \delta \)-layer separation, bearing close similarity to earlier effective-mass calculations [9]. At 80L, band energies and the dopant/potential width are converged to better than 0.005 eV and 0.1 Å, respectively. Even the smaller 40L slab delivers a qualitatively correct picture of the electronic structure, albeit with a slightly larger error. While a 200L slab is excessive for a 1/4 ML system, at lower dopant concentrations the doping potential and donor distributions become significantly wider. Thus the capacity to run a 200L system with our methodology is important.

### 3. Properties of phosphorus \( \delta \)-doped silicon slabs

Having established the foundation of our methodology, we now consider how mixed pseudopotentials can be employed in practice. Specifically, they allow us to examine an arbitrary range of doping concentrations within the same \( p(1 \times 1) \) unit cell setup. In contrast, an explicit dopant treatment is computationally more expensive, requiring a unit cell that is enlarged as the doping concentration is reduced. For example, a 1/16 ML doping concentration requires a minimum 16 atoms in the in-plane repeat, which is eight times larger, and a nominal 512 times more expensive, than the two-atom \( p(1 \times 1) \) repeat used for a mixed representation.

Here we consider the electronic structure of \( \delta \)-doped layers for phosphorus concentrations between 1/16 and 1 ML. At a fixed concentration of 1/4 ML we also examine how well the mixed pseudopotential is a representation of disorder in the dopant plane. Both of these comparisons highlight the strength of the full DFT treatment used in this work.

#### 3.1. Effect of dopant concentration

We show in figure 6 the band structure of phosphorus \( \delta \)-doped silicon for a sequence of dopant concentrations. These band structures were calculated using a large 200L supercell and a \( 10 \times 10 k \)-point grid. The left-hand panel shows the full in-plane band structure in the absence of doping. This corresponds to the band structure of bulk silicon folded into the elongated supercell that is used for \( \delta \)-doping. In this representation, the two plane-perpendicular (\( \pm z \)) conduction band minima are folded to the \( \Gamma \)-point and the four in-plane minima (\( \pm x, \pm y \)) remain along the \( \Delta \) axis. The corresponding bands are labelled 1\( \Gamma \), 2\( \Gamma \), and 1\( \Delta \), respectively. Dopant concentrations of 1/16, 1/8, 1/4, 1/2, and 1 ML are considered in subsequent panels (figures 6(b)–(f)). Here, the band structure focuses on the \( \Delta \) axis in which the relevant band minima occur. With increasing doping concentration the 1\( \Gamma \), 2\( \Gamma \), and 1\( \Delta \) bands are progressively lowered in energy and the degeneracy between these bands is lifted. The trends in the band structure in figure 6 are a reflection of changes in the doping potential as the density of phosphorus atoms in the \( \delta \)-plane is increased. Figure 7 shows the self-consistent doping potential, highlighting a gradual deepening and narrowing of the potential with dopant concentration. The FWHM of the potential and other associated electronic structure properties are summarized in table 5. The potential width varies considerably as a function of concentration, from nearly 9 Å for 1/16 ML down to 3 Å for 1 ML. Note that the FWHM of the potential for 1/16 ML is significantly wider than the 1/4 ML case, justifying the use of the large 200L cell. A similar trend is seen for the donor electron distribution, decreasing from 9 Å at low concentrations down to 2.5 Å at high concentrations. This reduction in width occurs despite there being considerably more electrons in the high concentration \( \delta \)-layers. A graphical representation of the strong confining effect of the potential is shown in figure 8.

There are a number of areas where our full DFT approach can be directly compared to earlier tight-binding and effective-mass treatments. Firstly, the convergence with respect to
the $\delta$-layer separation is very similar to the effective-mass treatment of Scolfaro et al [9]. For example, at a dopant concentration of $6.5 \times 10^{13}$ cm$^{-2}$ (approximately 1/11 ML) they found significant broadening below 100 Å separation (about 70L), and effectively no interaction between $\delta$-layers for separations above 150 Å (about 110L). Scolfaro et al also found that the precise values for non-interacting $\delta$-layers depend on the dopant concentration, with high concentrations resulting in convergence at small separations due to the deeper and narrower doping potential. All of these trends are observed in our DFT treatment, and the convergence in the 1/4 ML system above 80L (table 4) is entirely consistent.

Another area of contact between our work and Scolfaro et al [9] concerns the splitting between the 1$\Delta$ and the 1$\Gamma$/2$\Gamma$ bands. Scolfaro et al [9] illustrated in their figures 1–3 that the lowest two bands are separated by at least 0.015 eV, with the exact value of the splitting becoming larger with increasing concentration. Their lowest band ($E_{0l}$) corresponds to the $\Gamma$
band (two-fold degenerate in their treatment), while the second lowest band \((E_0)\) corresponds to the ground state of the four-fold degenerate \(\Delta\) band. The energy difference between these two bands for non-interacting layers can be directly compared to our values in Table 5. For concentrations of 1/85, 1/52, and 1/10 ML, Scolfaro et al.\(^9\) report \(\Delta-G\) energy differences of 0.015, 0.025, and 0.068 eV.\(^4\) Our calculations find the same trend, and are quantitatively similar with \(\Delta-G\) differences of 0.037 and 0.070 eV at 1/16 and 1/8 ML, respectively.

Cartoxià and Chang\(^12\) performed a detailed tight-binding analysis of the relationship between the Fermi level and the doping concentration. They reported oscillatory behaviour in which the Fermi level changes non-monotonically with doping concentration. Our calculations are consistent with this finding. As seen in Table 5 the Fermi level initially becomes more negative with increasing concentration, but then rises at 1/2 ML before sharply decreasing again to its most negative value at 1 ML. Cartoxià and Chang attributed this sharp change at high concentrations to filling of the 3\(\Gamma\) and 4\(\Gamma\) sub-bands. This is visually confirmed in Figure 6 in which higher energy bands at 1/2 ML and above are seen to intersect with the Fermi level. Another manifestation of different behaviour above 1/2 ML is seen in Figure 7(b). Here, the doping potential for 1 ML is distinctly different to the lower concentrations, exhibiting sharp side-lobes which are spatially coincident with the atomic layers either side of the \(\delta\)-layer.

Qian et al.\(^11\) used a plane-averaged pseudopotential treatment of the conduction band to examine phosphorus concentrations between 1/1024 and 1/4 ML. Their model agrees closely with that of Cartoxià and Chang\(^12\), finding a steady monotonic trend towards more negative Fermi levels with increasing concentrations. Qian et al.\(^11\) reported in their Table II that the 1/4 ML case has a Fermi level 0.049 eV more negative than that for 1/16 ML. In our DFT treatment using the mixed pseudopotential a similar difference of 0.061 eV is observed (Table 5). One point of difference between our work and that of Qian et al and Cartoxià and Chang is that our Fermi energies are less negative by about 0.060 eV. We speculate that these differences reflect the various treatments of the doping potential. This hypothesis is supported by the results of Cartoxià and Chang showing that the position of the Fermi level strongly depends on the width of the Gaussian-shaped dopant distribution used in their model (Figure 4 in \(12\)).

While not considering the effect of varying the dopant concentration, the recent tight-binding simulations of Ryu et al.\(^14\) using the NEMO code\(^15\) can also be directly compared to our work. Using explicit phosphorus and silicon atoms in the dopant plane they reported a Fermi level of \(-0.087\) eV and a donor band minimum of \(-0.367\) eV. These values compare reasonably to our corresponding values of \(-0.035\) and \(-0.374\) eV, calculated using an explicit model (Table 3). We note, however, that Ryu et al.\(^14\) use a \(p(2 \times 1)\) repeat in their dopant distribution pattern, whereas our data in Table 3 is based upon a \(c(2 \times 2)\) repeat.

\(^4\) Energies of the various sub-bands were graphically extracted from figures 1–3 in \(9\).
ordered from left to right in order of decreasing valley splitting. Six different cases are shown, with schematics above the band structures illustrating the dopant distribution and grey shading highlighting the dopant repeat unit within each representation. All calculations were performed in the same \( (4 \times 4) \) unit cell, and hence any differences reflect the donor placement. We do not attempt to rationalize the quantitative dependence of the band structure on the dopant placement, save to note that the relationship is very complex. There are, however, a number of general qualitative trends and points of interest. Firstly, an avoided crossing between the \( 1/\Gamma_1 \) and \( 1/\Delta_1 \) bands occurs in two of the structures (ordered and 100 line), while no interaction is seen in the other four. Secondly, the \( 1/\Gamma_1/2/\Gamma_1 \) valley splitting changes considerably across the series. Thirdly, the flat band in the 110 line structure (figure 10(a)) is not a localized defect level as significant dispersion occurs further out in the Brillouin zone. Finally, the 100 line structure (figure 10(f)) has the same dopant repeat unit as Ryu et al [14] and accordingly the band structures are broadly similar. For the 100 line dopant distribution we also computed the band structure in the symmetry-inequivalent line-parallel direction, but found that the band structure was essentially the same.

The extent of the variation in the valley splitting as a function of the concentration and dopant ordering pattern is shown in figure 11. This diagram contrasts the range of valley splittings arising from a variation of the dopant concentration using mixed pseudopotentials (square data points), with the range obtained for explicit dopant placements at 1/4 ML (triangle data points). We see that the latter far outweighs the former. At a concentration of 1/4 ML the splitting for explicit doping varies between 0.050 and 0.266 eV, while the coverage dependent splitting using mixed pseudopotentials varies by less than 0.1 eV. Also included in the figure are the splittings reported for the Qian et al [11] and Ryu et al [14] models at 1/4 ML, which are closest to our mixed potential result. This is as expected for the work of Qian et al due to their use of an averaged potential, but is surprising for the Ryu et al calculations as their model uses an explicit dopant distribution. That said, our calculation with the same dopant repeat unit as Ryu et al, namely 100 line, has the smallest valley splitting amongst the explicit distributions considered. We thus see that the model used to describe the \( \delta \)-layer has an enormous effect on the band structure at the \( \Gamma \)-point, and this factor must be taken into account when comparing various models in the literature.

The valley splitting is closely related to the potential as demonstrated in figure 12 where we correlate the valley splitting as a function of the dopant concentration. Circles denote literature data from Qian, Chang, and Tucker [11] (QCT) and Ryu, Lee, and Klimeck [14] (RLK). Squares and triangles are from this work. Squares denote mixed pseudopotential calculations as a function of doping concentration. Triangles denote 1/4 ML calculations using an explicit description of disorder for various phosphorus placements as illustrated in figure 10.
splitting with the FWHM of the potential. As before, the square data points show the mixed pseudopotential results for which an increased doping concentration leads to a narrowing of the doping potential and a commensurate monotonic increase in the valley splitting (cf table 5). For the case of explicit doping at 1/4 ML, the triangle data points show again an inverse relationship between the valley splitting and the width of the potential. There are two important differences, however, firstly that the slope is markedly steeper and, secondly, the trend is much more ‘noisy’. This demonstrates that the confining properties of the potential are not entirely described by the FWHM of the potential. Different distributions of phosphorus atoms in the dopant plane presumably create very different confining potentials leading to spatial inhomogeneity within the dopant plane. In contrast, homogenization of the potential as embodied in the mixed pseudopotential approach leads to a reduction of the valley splitting and a broadening of the potential. As noted earlier, further homogenization of the atoms in the form of a plane-averaged potential is another level of approximation. This suggests that an element of caution needs to be applied when extracting valley splitting parameters from computational studies.

4. Conclusions

In presenting a comprehensive DFT analysis of phosphorus δ-doping in silicon we have shown that the details of the calculation are more significant than previously recognized. We carefully tested the computational parameters used and analysed their effect on the calculated properties. Our approach compares well with earlier, more empirical treatments, yet offering distinct advantages through its first-principles approach. We demonstrate that mixed pseudopotentials offer considerable computational advantages, allowing calculations for arbitrary dopant concentrations with a minimum number of atoms in the unit cell. However, this atom-averaged treatment of the dopant plane alters the band structure with respect to an explicit representation. We find that important parameters such as the valley splitting, the Fermi level and the position of the band minima depend strongly on the distribution of phosphorus atoms within the dopant plane. We postulate that an averaged representation of the dopant distribution leads to a doping potential that is less confining, thereby leading to band splittings that are significantly reduced. These effects are particularly important for quantum device-scale modelling where the valley splitting is an important input parameter [8].

Acknowledgments

This work is supported by the Australian Research Council, the Australian Government, and the US Advanced Research and Development Activity, National Security Agency, and Army Research Office under Contract No. DAAD19-01-1-0653. Computing support was provided by the Australian National Computational Infrastructure.

References