Surface-phosphorus interaction in Si nanocrystals

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Abstract. The properties of phosphorus-related defects in freestanding silicon nanocrystals with different surface compositions are investigated using density functional theory models. Both hydrogen (H-) and hydroxyl (OH-) covered surfaces are considered. The dependence of the formation energy of substitutional phosphorus on the distance to the surface is found to be stronger in hydroxyl-covered crystals. The formation of tricoordinated defects, energetically favourable in hydrogenated nanocrystals, is less likely in nanocrystals with hydroxylated surfaces. Further, the ionisation energy level of P-doped nanocrystals is found to be deeper in OH-covered nanocrystals than in H-covered nanocrystals.

1. Introduction
Freestanding silicon nanocrystals (Si-NCs) offer exceptional potential for electronic structure manipulation through the control of confinement effects and the hybridisation of surface and silicon states. Si nanoparticles grown using plasma deposition techniques can be dispersed in a variety of liquids to form inorganic inks, and printing-based film deposition techniques are currently under development[1, 2]. In order to exploit this class of materials, it is necessary to achieve a detailed understanding of the influence of the surface radicals and adsorbed molecules on the properties of Si-NCs.

Especially in small nanocrystals, surface atoms can have an important contribution to the highest occupied (HO) and lowest unoccupied (LU) molecular orbitals, changing the electronic energy levels and the optical absorption spectra[3, 4, 5, 6]. The effect of oxygen on hydrogen-terminated crystals has been explored by previous studies, showing that both surface hydroxylation and silane groups lead to a redshift of the optical absorption threshold[3, 6], whereas oxidation of the core can either lead to a blueshift or to a redshift[4, 6]. Here we show, using theoretical calculations, that the surface composition also affects the properties of impurities, even at the nanocrystal core, changing the respective potential for segregation and ionisation energy. As a case study, we will consider substitutional phosphorus, an n-type dopant which shows limited doping efficiency in silicon nanocrystals and quantum dots [7, 2].

2. Modelling details
The simulations were carried out within the framework of density functional theory, as implemented in the aIMPRO code[8, 9]. Core electrons were accounted for using the dual space
separable pseudopotentials of Hartwigsen, Goedecker and Hutter\cite{10}. A Padé parametrisation of a functional based on the local density approximation was employed for the exchange and correlation energy\cite{11}, with spin polarisation for paramagnetic systems. The basis set consists of Cartesian $s$, $p$ and $d$-type Gaussian functions centred on each atom. Each atom contributes with a contracted ‘C44G*’ basis consisting of $(4, 4, 1) (s, p, d)$ Gaussian orbitals, obtained as described in Ref. \cite{12}.

Silicon nanocrystal models consisted of spherical clusters of 87 Si atoms (with about 1.3 nm core diameter). The calculations were performed using real-space boundary conditions, thus eliminating spurious cluster-cluster interactions and the need for neutralising background charge. The electron affinity $[I(−/0)]$ and ionisation energy $[I(0/+)]$ were calculated by direct comparison of the total energies of the clusters in different charge states $[E(C^q)]$,

$$I(−/0) = E(C^0) − E(C^-),$$

and

$$I(0+/+) = E(C^+) − E(C^0),$$

where $C^q$ represents the energy of the relaxed cluster in charge state $q$. The origin of the energy scale is pinned to the vacuum level. In bulk silicon, $I(0/+) \; \text{corresponds to the work function.}$

The calculated ionisation potential of some silanes and small silicon clusters for which experimental data is available, along with the work function and electron affinity of bulk silicon, are given in Table 1. The ionisation energies are in excellent agreement with experiment. However, as expected, the silicon electron affinity is overestimated, reflecting the bandgap underestimation typical of LDA calculations. Still, the systematic error introduced by this approximation should not vary appreciably amongst the calculations presented.

\begin{table}[h]
\centering
\begin{tabular}{lllll}
\hline
Property & system & calc. & Exp. & Ref. \\
\hline
$I_v(0/+)$ & SiH$_4$ & 12.33 & 12.36 & [13] \\
$I_v(0/+)$ & Si$_2$H$_6$ & 10.76 & 10.53 & [14] \\
$I_v(0/+)\;\text{Si}_4$ & 8.13 & 8.2±0.1 & [15] \\
$I_v(0/+)\;\text{Si}_7$ & 8.18 & 7.87.90 & [15, 16] \\
$I_v(0/+)$ & bulk Si$^a$ & 5.32 & 5.15±0.08 & [17] \\
$I_v(−/0)$ & bulk Si$^a$ & 4.64 & 4.05–4.29 & [18, 19] \\
\hline
\end{tabular}
\caption{Calculated vertical ionisation energies ($I_v$) of small silanes and silicon clusters, and work function and electron affinity of bulk silicon. The Ref. column refers to the experimental data. All the values are in eV.}
\end{table}

\footnote{\textit{a} obtained using total energies from a Si$_{1000}$ supercell calculation. Alignment of the energy scale origin with the vacuum level was performed using a (100)Si surface.}

3. Undoped Si-NCs

The 87-atom Si-NC core can be passivated by hydrogen radicals, reconstituting the four-fold coordination of all surface Si atoms. The resulting cluster shows a clean gap of 2.98 eV between the highest occupied and lowest unoccupied single-particle Kohn-Sham energy levels (HOKS and LUKS). Hydroxyl terminations replacing for the hydrogen terminations change the extension of the highest occupied and lowest unoccupied levels, which have now a partial contribution from the oxygen 2p orbitals, increasing the electron affinity and reducing the Kohn-Sham bandgap to 1.22 eV (Fig. 1).
Figure 1. Kohn-Sham one-electron energy levels (eV) of (a) Si$_{87}$H$_{76}$ cluster, (b) Si$_{87}$(OH)$_{76}$ cluster, (c) {Si$_{86}$PH$_{76}$}$^+$ cluster, with the substitutional P$^+$ at the centre, and (d) {Si$_{86}$P(OH)$_{76}$}$^+$ cluster, also with the substitutional P$^+$ at the centre. Filled and empty squares indicate respectively occupied and unoccupied levels.

4. Substitutional Phosphorus
In bulk silicon, P is a shallow donor. However, in nanocrystals the P donor can be regarded as a hydrogen-like atom in a “dielectric box”, and the confinement leads to a high electron binding energy[20]. For the P-doped nanocrystals studied [Si$_{86}$PH$_{76}$ and Si$_{86}$P(OH)$_{76}$], the HOKS state is partially localised on the central P atom, and the envelope of the wavefunction tail, extended through the nanocrystal, is anti-bonding with respect to the Si-Si bonds, resembling the conduction band states of the bulk crystal. The HOKS state of the OH-covered [Si$_{86}$P(OH)$_{76}$] cluster, shows a contribution from the oxygen 2$p$ states. Figure 1 highlights the similarity between the undoped Si$_{87}$H$_{76}$ and Si$_{87}$(OH)$_{76}$ nanocrystals and the isoelectronic crystals where the central Si atom was replaced by P$^+$.

4.1. Formation energy
The interaction between substitutional phosphorus and the surface leads to a site dependence of the defect formation energy in the cluster. This effect, reported in hydrogen-terminated clusters[7], is much enhanced by the hydroxyl surface (Figure 2). In hydroxylated NCs, P shows a marked preference for the outer Si shell, where it is closer to the surface while preserving four Si neighbours (positions C or D of Figure 2-b). This effect is observed both for neutral and positively charged doped clusters, with quantitative differences: while the formation energy of P$^+$ at the position E ($d = 5.4$ Å) is 2.1 eV lower than at the centre, in the neutral cluster (Figure 2) it is 1.3 eV lower.

Apparently there is no correlation between the Si-Si bondlengths at site S and the formation energy of P substituting for Si at that position. Hence, strain effects are not the dominant factor. We believe that the attraction between the electropositive P atom and the electronegative oxygen shell is responsible for this effect. This is consistent with the larger formation energy differences in the positive charge state.

4.2. Ionisation level
The ionisation energy [$I(0/+)$] and electron affinity [$I(-/0)$] are useful quantities to predict the direction of charge transfer between doped and undoped crystals. Usually, phosphorus-doped NCs are intended to behave as electron donors. Thus, we define the quantity

$$E(0/+)^{P-\text{bulk}} = I(0/+)^P - I(-/0)^{\text{bulk}},$$
Figure 2. Relative formation energy \( (E_r) \) of a four-fold coordinated substitutional P as a function of the distance to the centre \( (d) \) (left) both in H-terminated and OH-terminated clusters, and schematic representation of the corresponding positions in a H-terminated cluster (right). The relative energies were calculated in neutral clusters.

Figure 3. Difference between the ionisation energy of the phosphorus-doped nanocrystal and the electron affinity of the pristine nanocrystal \[ E(0/+)_{\text{P-bulk}} = I(0/+)_P - I(-/0)_{\text{bulk}} \], as a function of the distance to the centre, for nanocrystals with H- and OH-covered surfaces.

which corresponds to the energy necessary to transfer an electron from the \( n \)-doped nanocrystal to the undoped crystal, and should ideally be very small or positive.

The calculated electron affinity of undoped \( \text{Si}_{87}\text{H}_{76} \) and \( \text{Si}_{87}(\text{OH})_{76} \) clusters are respectively 2.13 eV and 1.76 eV. The ionisation energy of phosphorus-doped crystals (with P at the central position) is also about 1.7 eV higher in OH-terminated clusters than in H-terminated clusters with the same number of Si atoms (Figure 3). This is the largest contribution to the difference between the \( E(0/+)_{\text{P-bulk}} \) for the hydrogen and hydroxyl-covered nanocrystals. Since the shifts of the Kohn-Sham levels with P substitution is similar in both types of clusters, further research is needed to clarify the origin of the strong binding of the unpaired electron in the \( \text{Si}_{86}\text{P(OH)}_{76} \) cluster.

We now analyse the electron transfer energies \( E(0/+)_{\text{P-bulk}} \) (Figure 3). First, we note that the ionisation energy of phosphorus is much larger than in bulk, as found by previous calculations in hydrogenated clusters[7]. In the \( \text{Si}_{86}\text{PH}_{76} \) clusters, it is approximately constant for \( d < 6 \) Å. In the \( \text{Si}_{86}\text{P(OH)}_{76} \) cluster, \( E(0/+)_{\text{P-bulk}} \) is much larger and decreases at a faster rate with the proximity of the surface.
5. Direct interaction between P and surface atoms
Four-fold coordinated P atoms replacing for Si prefer surface sites where they are bound to one surface hydrogen, rather than to the hydroxyl. This is found by comparing the energy of P⁺ at different surface sites in a cluster with a mixed surface (Si₈₆P⁺H₇₅OH). A configuration where P⁺ bonds to two hydrogen atoms [NC – Si₂P(H)₂] is favoured by 0.55 eV relative to a similar surface site where one of the neighbours is a hydroxyl oxygen.

5.1. Phosphorus-related surface defects
At the surface (positions E and F), P can form tricoordinated defects by releasing one or two surface radicals. The resulting clusters have ionisation energies very close to those of undoped nanocrystals. Si-NCs with a P replacing for atom E and with no hydrogen neighbour [Pₑ(0H)] or a P replacing for atom F and one hydrogen neighbour [Pᶠ(1H)], both with coordination three, have gaps of 2.80 eV and 2.94 eV between the HO and LH Kohn-Sham single-electron levels (respectively), close to the 2.98 eV gap of the pristine cluster, and their ionisation energies are only 0.20 eV and 0.04 eV lower than that of the pristine cluster, respectively. Thus, the donor activity is suppressed by the formation of this type of defects. Similar results are found on the hydroxylated clusters.

The relative stability of tricoordinated defects and tetracoordinated substitutional phosphorus, at the surface or at the NC core, depends on the chemical potential of hydrogen, \( \mu_H \) (\( \mu_{OH} \) in the case of the OH-terminated clusters), which expresses its availability in thermodynamic equilibrium. In the Si-rich limit, the chemical potential of silicon equals its energy in a bulk silicon reservoir, obtained from a calculation with periodic boundary conditions.\(^1\) To determine \( \mu_H \) in this limit (\( \mu_{Si}^H \)), we assume that the source of hydrogen is SiH₄, a typical precursor used for Si-NC growth from the gas phase. The other extreme for \( \mu_{Si} \) and \( \mu_H \), the hydrogen-rich limit, is defined by the conditions \( \mu_{H}^H = \frac{1}{2}E(H_2) \) and \( \mu_{Si}^H = E(SiH_4) - 4\mu_{H}^H \). Similarly, the range of values for the chemical potential of the hydroxyl radical, \( \mu_{OH} \), is defined in the Si-rich limit by its energy in silanol (SiH₃OH), and in the O-rich limit by the energies of molecular hydrogen and oxygen \( [\mu_{OH}^H_{O_2} = \frac{1}{2}E(H_2) + \frac{1}{2}E(O_2)] \).

The formation energies of the phosphorus containing defects,

\[
E_f(D) = E[C(D)] - \sum n_i \mu_i,
\]

where \( C(D) \) is a cluster containing the defect \( D \), and \( n_i \) are the number of atoms of species \( i \) that it contains, can be calculated as a function of the hydrogen (or hydroxyl) chemical potential. For simplicity, we have set the chemical potential of phosphorus to its energy at the centre of the cluster. Figure 4 contrasts the results obtained for the clusters with hydrogen and hydroxyl-covered surfaces.

In the Si₈₆PH₇₆ clusters, the tricoordinated defects are the most stable form of P in the whole range accessible to \( \mu_H \). At the Si-rich limit, the binding energy of hydrogen to Pₑ is about 1.2 eV. On the other hand the estimated limits for the OH chemical potential, used to calculate the formation energies in Si₈₆P(OH)₇₆ clusters, define a wider energy range. Further, in the Si-rich and O-poor limit, the formation energies of tri- and tetracoordinated defects are comparable. However, in the mid-range region, tetra-coordinated defects are most favourable.

6. Conclusion
The chemical composition of the Si-NC surfaces, specifically its coverage by hydrogen or hydroxyl groups, affects the dopant-surface interaction, and consequently the properties of dopant-related

\(^1\) The energy scales of the two calculations were aligned with the aid of an auxiliary calculation performed for a clean [001] silicon surface, where the electrostatic potential of the vacuum was set to zero.
Figure 4. Formation energies of neutral tri- and tetracoordinated P defects in H-covered (left) and OH-covered (right) Si-NCs, as a function of the chemical potentials. $P_S(nH)$ labels a P placed at site $S$ and attached to $n$ hydrogen radicals. The chemical potential of phosphorus is set to be its energy at the centre of the cluster. Estimated limits for the chemical potentials are indicated with arrows.

defects. In the case of P-doped small nanocrystals (87 atoms), we find that hydroxylation suppresses the formation of tricoordinated surface defects. However, it enhances the segregation of P to an outer shell close to the surface, but not directly linked to H or OH. Further, the energy necessary to transfer an electron from a P-doped to an undoped NC [$E(0/+)^{P\text{-bulk}}$] is higher in OH-terminated crystals than in H-terminated crystals.

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