Electronic properties, doping and defects in chlorinated silicon nanocrystals

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Silicon nanocrystals with diameters between 1 and 3 nm and surfaces passivated by chlorine or a mixture of chlorine and hydrogen were modeled using density functional theory, and their properties compared with those of fully hydrogenated nanocrystals. It is found that fully and partially chlorinated nanocrystals are stable, and have higher electron affinity, higher ionization energy and lower optical absorption energy threshold. As the hydrogenated silicon nanocrystals, chlorinated silicon nanocrystals doped with phosphorus or boron require a high activation energy to transfer an electron or hole, respectively, to undoped silicon nanocrystals. The electronic levels of surface dangling bonds are similar for both types of surface passivation, although in the chlorinated silicon nanocrystals some fall off the narrower gap.

I. INTRODUCTION

The manipulation of the silicon surface and its ability to interact with molecules and radicals is gaining importance in view of the use of silicon nanostructures in hybrid inorganic-organic colloids and other functional materials. With a large surface-to-volume ratio, freestanding silicon nanocrystals (NCs) are ideal to explore the surface functionality. They can be obtained by ultrasonic dispersion of porous silicon, liquid phase synthesis by reduction of SiCl$_4$, or plasma processes. Nonthermal plasma synthesis is an efficient method for production of particles of mono-disperse sizes and lists, amongst other advantages, suppressed particle coagulation and selective heating of particles through energetic surface reactions. Additionally, it offers the possibility of dopant (P,B) incorporation during growth.

Although silane is usually chosen as a precursor for plasma synthesis, SiCl$_4$ has also been suggested as a cheaper and safer alternative. Nanocrystals grown from a SiCl$_4$/H$_2$/Ar mixture are terminated with a mixture of chlorine and hydrogen, with variable fractions depending on the plasma composition and reactor pressure.

The fraction of surface Cl on silicon nanocrystals grown by this or other methods can also be increased by Cl$_2$ plasma etching, treatment with a solution of PC$_3$ on chlorobenzene or with di-, tri-, and tetrachlorosilane gases, procedures already in use for industrial processing of silicon single crystal substrates. This leads to the formation of mono-, di- and trichloride terminations at low temperatures (< 400°C). Monochloride is the most stable, remaining at higher temperature. The adsorption of chlorine and SiCl$_4$ on flat silicon surfaces has been extensively studied by theoretical methods. The adsorption energy of Cl$_2$ on a reconstructed Si(100) surface was found to be 5.4 eV, giving a Si-Cl bond energy of about 4 eV. On Si(111) surfaces, the Si-Cl bond energy is similar, the calculated values ranging between 3.5 and 4.2 eV. In both cases, the barrier for chlorine diffusion is about 1 eV, and desorption takes place in the SiCl$_2$ form.

Further, it was found that with increasing chlorine supply the structure of the chlorinated Si(111) surface suddenly changes, with a transition from a monochloride phase to a polychloride phase. The adsorption of chlorine induces Cl-related Cl-Si bonding states below the top of the valence band.

The reactive Si-Cl surface bonds are convenient for surface functionalization with alkene and amine groups. Although Si-Cl bonds are stronger than Si-H bonds, the Cl atoms, with a higher affinity for electrons, can more easily receive an electron from the highest occupied molecular orbital (HOMO) of the other reactant during the interaction. This additional electron is partially localized on the shallowest $p$ orbital of the Cl radical, resulting in Cl$^-$ being released. Forming Cl$^-$ in the transition state is energetically more favorable than breaking Si-H bonds, leading to lower activation energy barriers for grafting in Si-Cl bonds, even for partial Cl coverages.

Additionally, the presence of chlorine changes the optical and electronic properties of the material, opening exciting possibilities for surface-driven electronic structure engineering. Previous electronic structure calculations have found that chlorine-covered nanocrystals have a lower gap between occupied and unoccupied electron energy levels and higher electron affinity than hydrogen-covered nanocrystals. Thus, it is possible that par-
tial or full surface chlorination can be used to control the position of the electronic levels for specific applications.

Given the interest on Cl-terminated nanocrystals, both for subsequent surface conversion or for electronic structure engineering, theoretical information on the stability, electronic and optical properties of silicon nanocrystals is of great interest. Therefore, we have carried out a detailed theoretical study to compare the properties of Cl-terminated silicon nanocrystals with 1-3 nm of diameter with H-terminated nanocrystals in the same size range. The first-principles methodology will be described in Section I. The structure and energetics of perfect nanocrystals will be considered in Section II, and their electronic and optical properties will be given in Section III. Section IV is dedicated to doped and defective Cl- and H-terminated clusters. Finally, Section V discusses the relevance of the results.

II. METHODOLOGY

The electronic structure of the nanocrystals was analyzed using first-principles calculations based on density functional theory, with a pseudopotential approach, as implemented in the Almpro code. The local density approximation was used for the exchange and correlation energy. Core electrons were accounted for by using the pseudopotentials of Hartwigsen et al.

Kohn-Sham orbitals were expanded on a localized basis set consisting of atom-centered Cartesian Gaussian orbitals with angular momentum up to \( l = 2 \), as described in Ref. The core silicon atoms, we used a contracted basis set with 13 functions per atom (44G*), including a polarization function with \( l = 2 \), optimized for bulk silicon. A basis of the same size, optimized for SiH₄, was used for hydrogen. For chlorine, an uncontracted basis set with four \( l = 0 \) and twelve \( l = 1 \) functions per atom was used. Convergence tests for silane, tetrachlorosilane and Si₈₇H₇₀/Si₈₇Cl₇₀ nanocrystals show that these bases offer an excellent compromise between accuracy and computational effort, specially for large nanocrystal diameters, where the electronic structure becomes increasingly bulk-like. For the worst case, the SiH₄ and SiCl₄ molecules, Si-H and Si-Cl bond lengths (Table I) are converged respectively within 0.006 and 0.015 Å, bond energies are converged within 0.1 and 0.5 eV, respectively, and the Kohn-Sham gaps are converged with 0.22 and 0.09 eV, respectively. They are also in good agreement with previous LDA calculations.

Total energy calculations were performed using finite real space boundary conditions. The optical absorption cross section was calculated using periodic boundary conditions, ensuring a minimum distance of at least 10 Å between replicas of the system. In this case, the charge density was expanded in a plane wave basis set with an energy cutoff of 350 Ry.

The equilibrium geometry of the nanocrystals was found by a relaxation of all the atomic coordinates using a conjugate gradient algorithm.

The optical absorption cross-section was calculated in the long-wavelength dipole approximation using the Kohn-Sham eigenvalues \( E^n \) and eigenvectors \( |\psi^k\rangle \). The matrix elements of \( r \) are evaluated using the momentum operator plus the commutator of the non-local part of the pseudopotential. The Brillouin Zone sampling was restricted to the \( \Gamma \) point. The electronic temperature used as parameter in the Fermi-Dirac distribution was 0.1 eV/\( k_B \), where \( k_B \) is the Boltzmann constant, and the Gaussian broadening used was 0.05 eV.

III. STRUCTURE AND ENERGETICS

A. Structure

The nanocrystals used in this study were obtained by cutting an approximately spherical core out of a perfect silicon crystal and passivating the surface dangling bonds with Cl or H atoms. The cutoff diameter can be estimated as \( d = [3n/(4\pi)]^{1/3}u_0 \), where \( n \) is the number of

| TABLE I: Bond length, bond enthalpy, Kohn-Sham gap (\( \Delta E_{KS} = E_{LUKS} - E_{ROKS} \)) and vertical excitation energy of the SiH₄ and SiCl₄ molecules. |
|-----------------|-----------------|-------------------|-----------------|
| property        | \( l_{Si-X} (\text{Å}) \) | \( \Delta H_b \) (eV) | \( \Delta E_{KS} \) | \( \Delta E^n \) |
| SiH₄ This work  | 1.49            | 3.8               | 7.93            |
| Prev. calc.     | 1.50           | 3.5               | 7.93            |
| Exp.            | 1.48           | 3.3, 3.2          |
| SiCl₄ This work | 2.03            | 4.3               | 6.37, 6.67      |
| Prev. calc.     | 2.02           | 4.0               |

| TABLE II: Atomic composition, diameter and symmetry of the SiₙXₘ nanocrystals studied, where \( X \in \{\text{H,Cl}\} \). |
|-----------------|-----------------|-----------------|-----------------|
| \( n \)         | \( m \)         | \( d \) (nm)     | sym.            |
| 35              | 36              | 1.1             | \( T_d \)       |
| 87              | 76              | 1.5             | \( T_d \)       |
| 244             | 144             | 2.1             | \( T_d \)       |
| 275             | 172             | 2.2             | \( T_d \)       |
| 286             | 170             | 2.2             | \( D_{3d} \)    |
| 377             | 196             | 2.4             | \( T_d \)       |
| 513             | 252             | 2.7             | \( T_d \)       |
| 717             | 300             | 3.0             | \( T_d \)       |
silicon atoms and \( a_0 \) is the calculated lattice parameter of bulk silicon (5.39 Å). The surface silicon atoms were four-fold coordinated and had mono- or di-hydride/chloride termination. The number of Si and Cl or H atoms in each nanocrystal is given in Table III. All the nanocrystals were centered at an atomic site, with exception of the Si_{256}A_{170} nanocrystals, which were centered at a bond-center.

After atomic relaxation, all silicon atoms remain four-fold coordinated, and the lengths and angles of the Si-Si bonds are close to those of the bulk crystal, specially those at largest distances from the surface [Fig. 1(a),d] and g]. Both Cl- and H-terminated nanocrystals maintain a marked crystalline character, characterized by a discrete radial pair distribution function relative to the nanocrystal center. However, there are quantitative differences between Cl- and H-terminated nanocrystals. As highlighted in Fig. 1 the bondlength distribution is much broader for the chlorinated nanocrystals. For example, for \( d = 1.5 \text{ nm} \), the average Si-Si bond length of the Cl- and H-terminated nanocrystals deviates only \(-0.01\) and \(+0.02\) Å, respectively, from the calculated bulk Si-Si bond length (2.34 Å), but the standard deviation is four times larger for the latter (Table III). Curiously, the bond angles are closer to the bulk value for the chlorinated nanocrystal, since the effective radius of the Cl atom is closer to that of the silicon atom.

The Si-H surface bonds are elongated about 0.2 Å with respect to their length in the SiH_{4} molecule (1.49 Å, to be compared with the experimental value 1.48 Å[34]). However, the Si-Cl bond lengths are very close to those of SiCl_{4} (2.03 Å, to be compared with the experimental value of 2.02 Å[35]).

We now analyze the structure of nanocrystals with a mixed Cl/H surface. The fraction \( x \) of Cl atoms was varied between 0 and 1 \((x \in [0.25, 0.50, 0.75])\), where \( x \) is the ratio between the number of Cl atoms and the total number of Cl and H atoms. For each \( x \), the bond lengths and angles were averaged over 24 randomly generated samples (Table III). We notice that for the three intermediate \( x \) fractions the distribution of Si-Si bondlengths is more narrow than for \( x = 1 \) (Cl-covered nanocrystal), whereas the bond angle distribution is more narrow than for \( x = 0 \) (H-covered nanocrystal).

### B. Formation and reaction enthalpies

It is important to know how the passivation with Cl affects the stability of the nanocrystals. Although highly metastable structures can be prepared out of equilibrium, for example in non-thermal plasmas, the enthalpy of formation is an useful to characterize the stability in equilibrium and estimate reaction energies. It is therefore useful to evaluate the enthalpy of formation of the nanocrystals with Cl-covered surface or with mixed Cl and H surface passivation.

We calculated the formation enthalpies at \( T = 0 \), defined as the enthalpy change relative to the standard phases of Si (crystalline Si), Cl (molecular Cl_{2}) and H (molecular H_{2})

\[
H_f = E_{NC}(n, m_{Cl}, m_{H}) - nE_{Si} - \frac{1}{2}m_{Cl}E(Cl_{2}) - \frac{1}{2}m_{H}E(H_{2})
\]

where \( E_{NC}(n, m_{Cl}, m_{H}) \) is the calculated total energy of \( Si_{n}Cl_{m}H_{m+n} \), and \( E(Si) \), \( E(Cl_{2}) \) and \( E(H_{2}) \) are the total energy per atom of crystalline silicon and the total energies of the Cl_{2} and H_{2} molecules, respectively, calculated using the same approximations. When the formation reaction is exothermic, \( H_f \) is negative.

We note that the total energies of small molecules, in particular H_{2}, are not accurately calculated using the LDA approximation. Thus, our calculated formation enthalpies of SiCl_{4} and SiH_{4} are underestimated: we obtain \(-7.1\) and \(-0.2\) eV, respectively, whereas the experimental values are \(-6.6\) and \(-0.4\) eV[36]. However, this error often cancels out when calculating reaction energies. For example, the enthalpy change for the hydrogen replacement reaction

\[
SiH_{4} + Cl_{2} \rightarrow SiH_{3}Cl + HCl,
\]

which is \(-2.83\) eV in our calculation, is only underestimated by \(0.06\) eV (relative to the value obtained from the experimental heats of formation[35]). Thus, the calculated formation enthalpies can still be used to draw qualitative conclusions.

| \( x \) | 0    | 0.25 | 0.50 | 0.75 | 1    |
|-------|------|------|------|------|------|
| \( \Delta \bar{\alpha} \) | 103.2| 106.0| 108.2| 109.3| 109.4| 109.5|
| \( \Delta \bar{\sigma} \) | 20.4 | 15.9 | 11.2 | 7.5  | 4.0  |

### TABLE III: Average Si-Si, Si-Cl and Si-H bond lengths

|       | Si-Si | Si-Cl | Si-H |
|-------|-------|-------|------|
| \( x \) | \( \Delta \bar{\alpha} \) | \( \Delta \bar{\sigma} \) | \( \Delta \bar{\sigma} \) |
| 0    | 0.39  | 0.30  | 0.36  |
| 0.25 | 0.39  | 0.30  | 0.36  |
| 0.50 | 0.39  | 0.30  | 0.36  |
| 0.75 | 0.39  | 0.30  | 0.36  |
| 1    | 0.39  | 0.30  | 0.36  |

The enthalpy of formation of the clusters with mixed Cl/H surface follows very closely a linear interpolation of the endpoints \( x = 0 \) and \( x = 1 \). In analogy with the...
alloys, we can define a mixing enthalpy characterizing the deviation from linearity:

\[ \Delta H_{\text{mix}} = E_{\text{NC}}(n, m_{\text{Cl}}, m_{\text{H}}) - [E_{\text{NC}}(n, m_{\text{Cl}} + m_{\text{H}}, 0) - E_{\text{NC}}(n, 0, m_{\text{Cl}} + m_{\text{H}})] \]  

for \( d = 1.5 \text{ nm} \) nanocrystals. Two opposite situations were considered. Starting with \( \text{Si}_{m} \text{Cl}_{n} \text{H}_{75} \), we first created an even distribution of Cl by placing each additional Cl atom in one of the surface sites (position \( r \)) minimizing the objective function

\[ f(r) = \sum_{i=1}^{m_{\text{Cl}}-1} |r - r_i|^{-1}. \]  

This results in a sequence of clusters where Cl replacing for H takes place at the position further away from all the other Cl atoms. The enthalpy changes for this sequence of replacements are compared with those obtained for a concentrated Cl distribution, where each Cl atom is placed as close as possible to the atoms of the same species (thus maximizing \( f(r) \)). The results [Fig 2c] show that there is no clear energetic preference for the first process, although the distribution of the enthalpies of replacement is smoother and narrower. Moreover, the enthalpies of replacement stay approximately constant up to 50% coverage, showing only a slight increase for higher \( x \). So, there is in principle no reason why complete Cl coverage would not be attainable.
IV. ELECTRONIC AND OPTICAL PROPERTIES

A. Analysis of the Kohn-Sham states

Let us start by analyzing the electronic structure of the SiCl$_4$ and SiH$_4$ molecules, as represented by the Kohn-Sham eigenstates and eigenvalues. Although these quantities have only an auxiliary role in DFT, their analysis is useful to understand the bonding and the contribution of Cl and H atoms to the ground state and excited states. The highest occupied state of the SiCl$_4$ molecule is the 2$^t_1$ state, followed closely by the 2$^e$ and 8$^a_1$ states. The HOKS is completely localized on the Cl atoms (formed by Cl 3$p$ states). The 2$^e$ and 8$^a_1$ states also have a localization of less than 10% on the Si atom. In contrast, the HOKS of SiH$_4$, which is the 2$t_2$ state, is a bonding state 41% localized in the Si atom. The lowest unoccupied state of the SiCl$_4$ molecule is the 8$a_1$ state, followed by 1.7 eV above by the 9$t_2$ state, whereas the LUKS of SiH$_4$ is 3$I_2$. Both are partially localized on Si: 54% in the case of the SiCl$_4$ LUKS, 65% in the case of the SiH$_4$ LUKS.

As the number of Si atoms increases, the highest occupied Kohn-Sham (HOKS) state and the LUKS start to resemble the bulk silicon valence and conduction band states, but in the case of the Cl-covered clusters the Cl 3$p$ character is maintained. Figure 3 depicts the charge density associated with the HOKS (triplet) and LUKS states for $d = 1.5$ nm. The localization of those gap-edge states on the surface atoms is greater for the Cl-covered cluster, specially for the HOKS state (the fractional HOKS localizations on Cl/H are respectively 40 and 9% for the Cl- and H-covered NCs). The contribution of the Cl 3$p$ atomic orbitals to the HOKS state is evident in the shape of the charge density isosurface near the surface of the nanocrystal, which resembles the SiCl$_4$ 2$t_1$ state. Similarly, near the surface the LUKS state bears some resemblance to the SiCl$_4$ 8$a_1$ state.

The calculated HOKS-LUKS gap ($E_{KS}$) of the SiH$_4$ and SiCl$_4$ molecules is respectively 7.93 and 6.96 eV (Table I). Although these are not far from the experimental absorption energy thresholds, which are respectively 8.99 eV[40] and 8.84 eV[41] there are several reasons why they cannot be compared directly to experiment. Firstly, the HOKS and LUKS states of SiCl$_4$ are 2$t_1$ and 8$a_1$, respectively, and the HOKS$\rightarrow$LUKS optical transition is forbidden by symmetry; the lowest al-
showed transition, $2t_1 \rightarrow 9t_2$, corresponds to an eigenvalue energy difference of 8.1 eV. Moreover, the Kohn-Sham states change considerably in the excited state, and so do Coulomb, exchange and correlation interactions. Moreover, the threshold energy of the absorption spectra of both molecules is a Rydberg transition ($4s \rightarrow 8t_2$) \cite{10,11}. These excitonic effects leading to Rydberg states are not described by the ground state DFT.

To our knowledge, Rydberg transitions have not been resolved for undoped silicon nanocrystals.

For silicon nanocrystals with diameters between 1 and 3 nm, the lowest excitation energy, obtained by calculating the difference between the total energies of each nanocrystal in the ground state and in the first excited state (at the ground state geometry), $E_{\text{LDA}} = E_1^0 - E_0^0$, differs little from $E_{\text{KS}}$ (Fig. 4). This means that, upon excitation, the change in the electrostatic interaction energy (resulting from the interaction between electron, hole, and image charges) is partially canceled by the change in the exchange and correlation energy.

The excitation energy ($E_x$) of hydrogenated nanocrystals has been previously calculated at different levels of theory. As illustrated in Fig. 4 our results are in good agreement with previous calculations with empirical potentials, and differ less than 1 eV from GW gaps. The reason why the LDA HOKS-LUKS bandgap is a good approximation for the excitation energy is clarified by Delerue et al., who have proved that the differences between the corrections to the self-energy in bulk and in the nanocrystal ($\delta \Sigma E$), are nearly canceled out by the Coulomb interaction between electron and hole ($E_C$). As a result, $E_x \simeq E_{\text{KS}} + \delta \Sigma b$, where $\delta \Sigma b$ is the bulk self-energy correction, which is about 0.6-0.7 eV for the LDA approximation. In this work, we will assume that this correction is independent of the nanocrystal surface, thus justifying the comparison between Cl- and H-covered nanocrystals using the values directly obtained from first-principles.

The minimum excitation energy is lower for the Cl-covered nanocrystal than for the H-covered nanocrystal. This follows the lower effective confinement volume for the HOKS and LUKS states in the Cl-covered nanocrystals. The difference is greater for the smaller diameters, amounting to about 1 eV for $d \sim 1.5$ nm. With increasing $d$, the gap of the Cl-covered clusters decreases almost linearly in this size range, whereas that of the H-covered nanocrystals it varies approximately with $d^{-1.2}$. The average gap of nanocrystals with mixed Cl- and H-coverage varies monotonically between those of the Cl- and H-covered clusters of the same size (Fig. 5). The variation in the gap distribution for each set of samples with the same $d$ and $x$ is not negligible, and is represented in Fig. 5 by the error bars.

FIG. 4: Excitation energy (*) and Kohn-Sham bandgap (○) as a function of the nanocrystal diameter obtained from the present work. Data from previous calculations are shown for comparison: lowest excitation energy excitations calculated by solving the Bethe-Salpeter equation (GW-BSE) from Ref.42, or obtained by time-dependent LDA (TDLDA), also from Ref.42, calculated using empirical pseudopotentials without inclusion of the Coulomb interaction between electron and hole (EP) or including this contribution (EP2), from Ref.43. Dotted lines are a guide to the eye.

B. Optical spectra

We have calculated the optical absorption cross section directly using the Kohn-Sham eigenstates and eigenvalues, as described in Sec. II. Previous theoretical work has shown that optical spectra can, in a good approximation, be obtained from the Kohn-Sham eigenvalues, since only minor charge rearrangements occur between ground and the low excited states.\cite{14} As expected, the absorption threshold energy is lower for the Cl-covered cluster (Fig. 5). However, the energies close to $E_{\text{KS}}$ have very small or vanishing oscillator strengths. The threshold is steeper for the H-covered nanocrystal and for the nanocrystal with mixed surface, were the symmetry is broken, than for the Cl-covered nanocrystals. Overall, the absorption band in the 2-6 eV range is broader for the Cl-covered nanocrystal.

C. Ionization energy and electron affinity

The ionization energy was obtained from the total energies of neutral and charged clusters,

$$I(q/q + 1) = E(q + 1) - E(q),$$

where $q$ is the charge. The results are shown in Fig. 5. The electron affinity of the chlorinated nanocrystals is higher by 2-3 eV, for the whole range of $d$ considered, reflecting the higher affinity for electrons of Cl. The ionization energy is also higher, but only by about 1 eV.
FIG. 5: Kohn-Sham bandgap (a) and calculated absorption spectra (b) of d = 2.2 nm silicon nanocrystals for different fractions of Cl coverage (x = mCl/(mCl + mH)). The eigenvalue gaps for fractional x were obtained by averaging over 24 samples, and the errorbars represent the standard deviation of the results. The absorption spectra for x = 0.5 was obtained by averaging over 10 samples.

V. DEFECTS

A. Dopants

Further, we compare the ionization energy/electron affinity of doped nanocrystals with that of the pristine (undoped) nanocrystals. This comparison is relevant when doping nanocrystal composites where only a small fraction of nanocrystals encloses one or more dopant atoms. In that case, the ideal is that a nanocrystal doped with a shallow donor (for example P) has ionization energy I(0+/+) very close to the electron affinity I(−/−) of the undoped nanocrystal. Ideally, IP(0+/+) − IUD(−/−), where the subscripts label the doped and undoped nanocrystals should be comparable to kT, where T is the temperature and k Boltzmann constant. The reverse is true for shallow acceptors. However, this does not happen either for Cl- or H-covered nanocrystals with d between 2 and 3 nm (Fig. 7). This is due to the carrier confinement and appearance of image charges, which were already extensively discussed for H-covered nanocrystals.[45–49]

B. Dangling bonds

The position of the I(q/q + 1) levels of surface dangling bonds (DBs) relative to the gap edge states of the pristine nanocrystals has also been compared for both types of surface. We considered only dangling bonds on di-chloride or di-hydride surface silicon atoms i.e., those that in the pristine nanocrystal were attached to two surface terminators. In d = 1.5 nm nanocrystals, monohydride DBs, although in average higher in energy by 0.9 eV, have similar properties. For each NC size, there are several nonequivalent surface Si atoms with di-chloride (or di-hydride) terminations where dangling bonds can form. The geometry and energy of each of the respective defects was optimized independently.

First, we note that the (−/−) and (0+/+) level positions do not display a clear trend with the nanocrystal size. The DB levels are very dependent on the particular defect geometry, specially on the Cl-covered nanocrystals (Fig. 5). The main difference between Cl- and H-covered nanocrystals is that, as the gap of the former is smaller, some of the DB levels fall outside the gap. That does not happen for the H-covered nanocrystals.
FIG. 7: Ionization energy [I(0/+)] and electron affinity [I(−/0)] of doped and undoped (a) Cl-covered nanocrystals and (b) H-covered nanocrystals, as a function of the diameter. Shaded areas represent energies lower than the electron affinity or higher than the ionization energy of the undoped nanocrystal. The axis were inverted for easier visualization.

VI. DISCUSSION

Silicon NCs with chlorinated or mixed surface have two main potential uses: as an intermediate material for further surface functionalization and modification, and as an electronic or optoelectronic material. The energies and electronic properties obtained in this study may be useful to design or tune both types of applications.

We have show that the formation enthalpy of the chlorinated Si-NCs is more negative than that of the hydrogenated Si-NCs, relative to the standard states of Cl and H. However, this does not mean that the former will in general be more stable against reaction. In fact, chlorinated Si-NCs have very high electron affinity, and can easily trap electrons to the LUMO state, which is partially localized on the surface Cl orbitals (Fig. 3). This leaves Cl more susceptible to removal and substitution by a foreign radical. It is interesting to note that although mixed Cl and H surfaces have a negative mixing enthalpy, there is no strong repulsion between nearest-neighbor Cl atoms, specially for small coverage ratios. Thus, if the nanocrystals are kept neutral, there is in principle the possibility of engineering next-neighbor surface replace-
may be useful to design heterojunctions with doped Cl-terminated Si-NCs as one of the components. As in the hydrogenated Si-NCs, dangling bonds will act as exciton recombination centers.

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