Ground states of group-IV nanostructures: Magic structures of diamond and silicon nanocrystals

Xiaobao Yang* and Yu-Jun Zhao
Department of Physics, South China University of Technology, Guangzhou 510640, People’s Republic of China

Hu Xu
Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, China

Boris I. Yakobson†
Department of Mechanical Engineering and Materials Science, Department of Chemistry, The Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, Houston, Texas 77005, USA
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We have developed an effective model to investigate the energetic stability of hydrogenated group-IV nanostructures, followed by validations from density-functional theory calculations. The Hamiltonian of $X_n H_m$ ($X = C, Si, Ge,$ and Sn) is expressed analytically by the atom numbers ($m, n$) and the magic numbers of diamond nanocrystals and silicon nanocrystals are determined. It is found that surface reconstructions would alter the morphology of silicon nanocrystals significantly and consequently induce dramatic modulation on their electronic properties.

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I. INTRODUCTION

Semiconductor nanocrystals (NCs) have been greatly attractive and intensively investigated. These nanomaterials have extended the physics of reduced dimensions and offered the opportunity for fundamental study of the regime between nanostructure and bulk states, which have also brought such wide applications as nanoscale electronic and optical devices, fluorescent biological labels, quantum computation media, etc.

Various hydrogenated group-IV [C, Si, Ge, and Sn] nanocrystals with $sp^3$ hybridizations have been synthesized and isolated, in which size-dependent optical gaps have been observed. To demonstrate the quantum confinement, theoretical studies have focused on the optical properties of nanocrystals and employed various methods for accurate calculations of the adsorption spectrum. However, surface reconstruction is predicted to be energetically favourable, which would dramatically reduce the optical gaps and decrease excitonic lifetimes. Meanwhile, the spatial charge distributions of the highest occupied and the lowest unoccupied states are also crucial in the design of the optical nanodevice.

Properties of nanomaterials mostly depend on their structures, however, it is challenging to determine the stable nanostructures from numerous possible candidates due to two main obstacles: (i) the accurate calculation of the total energy is necessary but often computationally expensive, and (ii) many isomeric structures should be considered and the number of these structures increases sharply as the size increases. To reduce the time cost, recent studies calculated the energies using classical potential in Hansel-Vogel (HV) formalism, and searched the magic structures of silicon nanowires using genetic algorithms. The energy decomposition approach is also efficient for stability investigations, where the total energy is separated into contributions from the bulk, surfaces, and the edges between the facets. It is shown that the ground state of thinnest silicon nanowire is of a five-fold rather than a single-crystal type, which is in agreement with experimental observations.

In this paper, we investigate hydrogenated group-IV nanocrystals by both model analysis and first-principles approaches. We propose an effective model and give an analytical expression of the Hamiltonian for $X_n H_m$ ($X = C, Si, Ge,$ and Sn) with the numbers of atoms ($m, n$), as is confirmed by density-functional theory (DFT) calculations. Magic numbers of diamond nanocrystals obtained in our searches are consistent with the experimental results. We also predict stable Si NCs with unique electronic properties.

II. MODEL ANALYSIS

In this section, we study the stability of hydrogenated group-IV nanocrystals $X_n H_m$, according to the effective model of Hamiltonian. We find that there is an analytical dependence of total energies on the numbers of atoms ($m, n$), which greatly enhances the searching efficiency of stable nanostructures. We obtain possible stable structures with the stochastic technique and determine the ground-state structures by the simplex method.

A. The effective Hamiltonian model

In our model, we assume the Hamiltonian of $X_n H_m$ ($X = C, Si, Ge,$ and Sn) to be

$$\mathcal{H} = \sum_{i=1}^{m} (H_{int}^i + H_0^i) - m\mu_X - n\mu_H$$

where $H_{int}^i$ and $H_0^i$ are the contributions from interactions and self energies, and $\mu_X(\mu_H)$ is the chemical potential for X(H) atom. The sum runs over all the group-IV atoms and we have $H_0^i = \mu_X + p_i\mu_H$, where $p_i$ is the number of H atoms in the saturated group of the $i$th X atom and $\mu_X(\mu_H)$ is the isolated atomic energy for the X(H) atom. $H_{int}^i$ includes the energy contributions from the bonded X-atom pair ($-E_{X,X}$)
corresponds to the local minimum and stable structures of hydro-
spond to corners, edges, and faces. We will obtain the ground
 experimental data.

π_0 and the saturated group of the \text{i-th} X atom (−E_{XX_0}). As
shown in the inset of Fig. 1, every X atom has four nearest
neighbors and every X-X bond is shared by two X atoms. This
leads the energy contribution corresponding to the \text{i-th}
X atom to be −2E_{EX,x} for \text{p}_i = 0, and −1.5E_{EX,x} − E_{XH}
for \text{p}_i = 1, analogically. Thus, \( \mathcal{H}_{tot} = (−2 − 0.5\text{p}_i)E_{EX,x} −
E_{XX_0}. \) We assume that the interaction between X and H
atoms is localized and thus \( E_{XX_0} = \text{p}_1 E_{X-H}, \) \( \text{p}_1 = 0,1,2,3. \)

With \( n = \sum_{i=1}^{m} \text{p}_i, \) we found that Eq. (1) can be written
as \( \mathcal{H} = am + bn, \) where \( a = (−2E_{EX,x} − \mu_x + \mu_{X_0}) \) and
\( b = (E_{X-H} + 0.5E_{EX,x} − \mu_h + \mu_{H_0}), \) where \( \mu_x \) and \( \mu_h \) are
the environment-related parameters, while \( E_{X,H}(E_{X-H}) \) and
\( \mu_{X_0}(\mu_{H_0}) \) can be derived from first-principles calculations or
experimental data.

B. Determination of ground-state structures
by the simplex method

Instead of scanning the parameter space \((a, b),\) \(23\) the simplex
method \(24−26\) is used to efficiently determine the combinations
of lowest energy from a set of possible integer combinations
\((m,n),\) which indicates that the stable configurations corre-
spond to corners, edges, and faces. \(26\) We will obtain the ground
states if we construct enough restricting inequalities and solve
the corresponding linear equations. \(26\) In our case, we have
\( m \geq 1 \) and \( n \leq 2m + 2. \) The key task is to determine the lower
limit of \( n \) for a certain \( m, \) for which it is difficult to find out the
expected inequalities. We search the least \( n \) as follows: \(27\) (i)
start from an arbitrary configuration of \( X_mH_n \) \( (n \leq 2m + 2), \)
allowing X atoms on the surface to walk randomly in the crystal
lattice and saturate the configuration with H atoms where
necessary, and (ii) accept the new configuration when the
H-atom number is nonincreasing, otherwise the new geometry
will be accepted with the probability of \( 1/dn, \) where \( dn \) is the
increment of the H-atom number. \( n \) converges into the
minimum after hundreds of iterations.

III. FIRST-PRINCIPLES CALCULATIONS

In this section, we investigate hydrogenated group-IV
nanocrystals \( X_mH_n \) with first-principles approaches. We first
verify our model by the dependence of \( E_{tot} \) on the numbers of
atoms \((m,n),\) together with the linear relationship of cohesive
energy on the ratio \((n/m). \) According to the phase diagram
of chemical potential, we determine the stable structures of
diamond NCs, in excellent agreement with the experimental
observations. For Si NCS, we find that surface reconstructions
would enhance the stability and also induce significant
modulation on the electronic properties, such as the gap values
and charge distributions of the highest-occupied molecular
orbitals (HOMOs) and lowest-unoccupied molecular orbitals
(LUMOs).

A. Model verification

To verify the reliability of our model, we investigate the
energetic stability of group-IV nanocrystals (with the
example of diamond NCS and Si NCS), using the DFT method
implemented in the Vienna Ab initio Simulation Package
(VASP). \(28,29 \) We use Vanderbilt ultrasoft pseudopotentials \(30 \)
and the exchange correlation with the generalized gradient

Figure 1 shows the upper and lower limit of \( n \) as a function
of \( m, \) it is not a standard simplex because both \( m \) and \( n \) will
be increasing with an increasing nanocrystal size of \( X_mH_n. \)
However, we will obtain a convex quadrangle \( A_BCD \) if a
restriction of \( m \leq 8 \) is considered. The convex \( A_1(1,4) \) and
\( B_6(6,12) \) correspond to stable configurations, while \( C_8(8,16) \)
and \( D_8(8,18) \) do not since they are induced by the artificial
restriction of \( m \leq 8. \) Thus, \( XH_4 \) and \( X_4H_2 \) will be stable
configurations for group-IV nanocrystals. Analogically, we
will obtain a new convex quadrangle (in red and yellow) and
find another stable configuration of \( X_{10}H_{16} \) in place of \( X_4H_{12} \)
if we consider a restriction of \( m \leq 12. \) In addition, we find that
\( X_{14}H_{20}, X_{16}H_{24}, \) and \( X_{22}H_{28} \) are also stable configurations.
It should be noted that, except for \( XH_4, \) all other nanocrystals
are metastable states since they are local-convex ascribed to
the size confinement. As is known, the size of nanocrystals
increases with increasing reaction time as more material is
added to the surfaces.

In general, the total energies \( (E_{tot}) \) obtained by DFT do not
involve the environment-related chemical potentials and corre-
spond to the Hamiltonian in Eq. (1) with \( \mu_x = \mu_h = 0. \) Thus,
we have \( E_{tot} = (a + b)H_0, \) where \( a = (−2E_{EX,x} + \mu_x) \) and
\( b = (E_{X-H} + 0.5E_{EX,x} + \mu_{H_0}). \) According to our model, we
conclude that: \( i) \) \( E_{tot} \) can be estimated in the analytical
expression of \((m.n),\) which indicates the fast calculation of
total energies; \( ii) \) only a few possible candidates of \( X_mH_n \)
should be considered, as isomorphic structures with the same
composition will possess the same \( E_{tot}; \) and \( iii) \) magic
numbers of \( X_mH_n \) correspond to the candidates with the most
or least \( n \) for a certain \( m, \) which have been found by our
iterations. In the searching process of magic numbers, we
obtained different stable structures with the same composition,
because the new configuration is accepted when the H atom
number is nonincreasing. Interestingly, there are few isomeric
structures for candidates with magic numbers and the structure
is unique for \( X_6H_{12}, X_{10}H_{16}, \) and \( X_{14}H_{20}. \)
approximation given by Perdew and Wang.\textsuperscript{31} We set the plane-wave cutoff energy to be 350 eV and the convergence of the force on each atom to be less than 0.01 eV/Å. A 1 \times 1 \times 1 mesh of \textbf{k} space is used and the vacuum distance is 9 Å, which is enough to make the systems isolated.

As shown in Fig. 2 (inset), the dots of \((m,n, E_{\text{tot}})\) for diamond NCs and Si NCs satisfy the plane equations respectively, which confirms the model result of \(E_{\text{tot}} = a m + b n\). We define the cohesive energy \(E_{\text{coh}}(m)\) per X atom in the nanocrystals \(X_n H_m\) as \(E_{\text{coh}} = (m \mu_X + n \mu_H - E_{\text{tot}})/m\). According to our model, we have: \(E_{\text{coh}} = 2E_{X-H} - (0.5E_X - E_{\text{bond}})\alpha\), where \(\alpha\) is the ratio \((n/m)\). As predicted, the cohesive energy decreases with the decrease of \(\alpha\) following a linear relationship (shown in Fig. 2) approaching the value of bulk material \((-\mu_{\text{diamond bulk}} = 7.65 \text{ eV} \text{ and } -\mu_{\text{Si bulk}} = 4.67 \text{ eV})\) when \(\alpha\) reaches zero.\textsuperscript{32}

**B. Stable structures of diamond NCs**

In the following, we investigate the stable structures of diamond NCs (C\(_n\)H\(_m\)). We calculated \(E_{\text{tot}}\) of C\(_n\)H\(_m\) with \(m \leq 12\) by DFT and obtained the formation energies as a function of hydrogen chemical potential by \(E_f = (E_{\text{tot}} - m \mu_X - n \mu_H - n \mu_{\text{dimer}})/m\). As shown in the inset of Fig. 3, we find that there is a critical point \(\mu_0\) (about \(-2.6\) eV, our model indicates \(\mu_0 = 0.5E_{C-C} - E_{C-H} \approx -2.63 \text{ eV}\)) of chemical potential, at which the formation energies are the same for all these nanocrystals. Below the critical point C\(_{10}\)H\(_6\) is the most stable, while CH\(_4\) is the most stable when \(\mu_H\) is above the critical point. As predicted, CH\(_4\) and C\(_{10}\)H\(_6\) are stable states when the number of carbon atoms \(m \leq 12\). It should be noted that there is certain difference in \(E_{\text{tot}}\) of isomeric structures obtained from the DFT, while our model indicates \(E_{\text{tot}}\) would be the same. However, the corresponding \(E_f\) is similar for isomeric structures, especially for \(\mu_H\) far away from the critical point. We can consider only one structure for each composition to enhance the efficiency, as is predicted in our model.

**FIG. 2.** (Color online) Cohesive energies of diamond NCs and Si NCs as a function of \(\alpha\). Inset shows the dependence of \(E_{\text{tot}}\) on \((m, n)\). The dots are obtained from the first-principles calculations.

**FIG. 3.** (Color online) Formation energies as a function of the number of carbon atoms for diamond NCs with \(\mu_H = -4 \text{ eV}\). Inset shows the chemical phase diagram for C\(_n\)H\(_m\) with \(m \leq 12\). Light and dark balls represent H and C atoms, respectively.

Figure 3 shows the formation energies for various C\(_n\)H\(_m\) with the chemical potential of hydrogen \(\mu_H = -4 \text{ eV}\). The hollow circles are from our model prediction, which is in excellent agreement with the ones from the DFT calculations (marked with solid triangles). For a certain \(m\), the formation energy decreases as the hydrogen atom number \(n\) decreases. The stable structures can be found at the local minimum of the formation energies, such as C\(_{10}\)H\(_6\), C\(_{14}\)H\(_{20}\), C\(_{18}\)H\(_{24}\), and C\(_{22}\)H\(_{28}\), which are consistent with our model analysis and experimental observations.\textsuperscript{7,8} We can also conclude that, for the chemical potential \(\mu_H > \mu_0\), the formation energy will

**FIG. 4.** (Color online) Formation energies as a function of the number of silicon atoms for Si NCs with and without the dimer reconstructions. Inset shows the possible dimer reconstructions and their effect on the number of hydrogen atoms. Light and dark balls represent H and Si atoms, and the size of dark balls corresponds to Si atoms on different layer.
the matrix. We search the least H number \( n \) for Si NCs (Si\(_m\)H\(_n\)) with a certain \( m \) through a similar procedure. With \( E_{\text{tot}} \) from the DFT, we obtained \( E_f \) of Si NCs with and without reconstructions with \( \mu_H = -4 \) eV. The dimer reconstruction decreases \( E_f \) and changes the stable structures. For example, Si\(_{10}\)H\(_{16}\) might not be the stable structure as \( E_f \) is higher than that of Si\(_8\)H\(_{12}\), which can be obtained from Si\(_8\)H\(_{16}\) with two dimer reconstructions. Besides, Si\(_{12}\)H\(_{16}\), Si\(_{15}\)H\(_{18}\), Si\(_{20}\)H\(_{18}\), and Si\(_{12}\)H\(_{20}\) are new stable structures. The reconstructions also have significant effect on the symmetry of Si NCs. Stable Si NCs without reconstructions tend to be octahedron enclosed by (111) facet (e.g., Si\(_{15}\)H\(_{26}\)). However, the reconstructed Si\(_{20}\)H\(_{18}\) has the symmetry of C\(_3\)v and Si\(_{12}\)H\(_{20}\) is approximately spherical.

Silicon NCs has been an ideal system of demonstrating quantum confinement, as the gap values are inversely proportional to the dot diameter. The gap value of Si\(_{20}\)H\(_{28}\) (the stable structure for Si NCs without surface reconstructions) is 3.80 eV, and both HOMO and LUMO orbits are concentrated in the central area (shown in Fig. 5). However, surface reconstruction dramatically decreases the gaps and the decrement of value depends on the number of Si atoms. The gap value of Si\(_{20}\)H\(_{18}\) (2.84 eV) is a local minimum for Si\(_m\)H\(_n\) with \( m \lesssim 26 \), while it is 3.19 eV for Si\(_{12}\)H\(_{20}\) with larger size. It is noted that HOMO and LUMO orbits are mainly distributed inside while LUMO orbits are concentrated near the surface for Si\(_{20}\)H\(_{18}\) and Si\(_{25}\)H\(_{20}\). For LUMO orbits, there is dimere-like distribution for Si\(_{20}\)H\(_{18}\), while the distribution is localized for Si\(_{12}\)H\(_{20}\). These nanostructures with spatial separation of orbital distributions might be useful in Si-based laser devices, as they would avoid electron-hole recombination and increase the lifetime of exciton carriers.

### IV. SUMMARY

In summary, we have proposed an effective method for the analytical expression of the Hamiltonian of H-terminated group-IV nanostructures, and provided an efficient technique of searching stable structures of \( X_mH_n \) (\( X = \text{C, Si, Ge, and Sn} \)). We showed that the isomeric structures are nearly energetically degenerated and thus the computational cost can be greatly reduced, which is an important complement to the popular DFT calculations for stability determination. The ground-state structure of Si NCs are surface reconstructed, where the highest occupied states are confined in the core and the lowest unoccupied states are distributed on the surface.

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GROUND STATES OF GROUP-IV NANOSTRUCTURES:...

27For simplicity, we did not consider any reconstruction.
34It can be comprehensible that the max decrement of the hydrogen number is independent of the order of Si atoms, and the rank of the matrix is an intrinsic parameter that conserves in the elementary transformations.