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Authors: Nishio, Kengo; Ozaki, Taisuke; Morishita, Tetsuya; Shinoda, Wataru; Mikami, Masuhiro

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Electronic and optical properties of polyicosahedral Si nanostructures: A first-principles study

Kengo Nishio,1,8 Takesuke Ozaki,1,9 Tetsuya Morishita,1 Wataru Shinoda,1 and Masahiro Mikami1
1Research Institute for Computational Sciences (RICS), National Institute of Advanced Industrial Science and Technology (AIST), Central 2, Umezono 1-1-1, Tsukuba, Ibaraki 305-8568, Japan
2Research Center for Integrated Science (RCIS), Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292 Japan

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In a previous molecular dynamics study, we predicted a polyicosahedral Si nanostructure which has a Si20 fullerene cage per icosahedral Si100 nanodot. The unique cage structure is distinct from the crystalline diamond Si nanostructure. Encapsulating a guest atom into the Si20 cage allows us to tune the electronic and optical properties. Here, we report on a systematic first-principles study of the effect of the sodium and iodine doping on the physical properties of the hydrogen-terminated polyicosahedral Si nanostructures. Our calculations reveal the strongly guest-dependent and size-dependent physical properties of the polyicosahedral Si nanostructures: (1) the semiconducting guest-free polyicosahedral nanowire becomes metallic by the sodium and iodine doping, (2) the quantum confinement effect is observed in the icosahedral and polyicosahedral nanodots, and (3) the radiative recombination rate comparable to the luminescent amorphous Si nanostructures is expected from some of the Na- and I-doped polyicosahedral nanostructures. From these results, we assert that the polyicosahedral Si nanostructures are promising candidates for the building blocks of the future nanoscale optoelectronic devices.

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I. INTRODUCTION

Low-dimensional Si nanostructures (NSs), such as Si nanodots (Si NDs) and Si nanowires (Si NWs), have attracted much attention because of the potential uses in the future nanoscale devices. The physical properties of Si NSs dramatically depend on the size and arrangement of Si atoms. For example, Si NSs of different sizes emit different colors of light, and the radiative recombination rate of amorphous Si NSs is higher than that of crystalline diamond Si (cd-Si) NSs.1,2 The stable atomic arrangement also depends on the size of Si NSs, and, interestingly enough, the atomic arrangements not seen in bulk Si could be found in Si NSs due to the large surface-to-volume ratio.3–10 Therefore, enormous efforts have been devoted to explore novel Si NSs.

The stability of Si fullerenes has been studied since the discovery of carbon fullerenes. Although both Si and carbon are members of the group IV of the Periodic Table, single-shell Si fullerenes, such as Si20 and Si60, are found to be unstable.3,11 This is because the nature of bonding is very different between Si and carbon. Carbon atoms can be joined together by sp2 bonding to form fullerene structures without dangling bonds. On the other hand, Si atoms prefer sp3 bonding so that Si fullerenes inevitably have dangling bonds which make Si fullerenes unstable. There are several efforts to stabilize Si fullerenes by encapsulating atoms into Si fullerenes.12–21

The existence of icosahedral Si (i-Si) NDs (Si100, Si280, Si600, . . .) has been suggested by a series of studies.6,8 Recent first-principles calculations have shown that pristine icosahedral Si (i-Si) NDs are energetically more stable than pristine cd-Si NDs for diameters of less than 2.77 nm.5 Our molecular dynamics (MD) simulations using the Tersoff potential22 have demonstrated that an icosahedral Si280 ND is spontaneously formed by freezing a droplet.8 The i-Si NDs can be regarded as multishell Si fullerenes. For example, the icosahedral Si100 ND is a Si20@Si80@Si180 triple-shell Si fullerene, in which the Si80 fullerene is stabilized by encapsulating a Si20 fullerene and the Si180 fullerene is stabilized by encapsulating a Si20@Si80 double-shell fullerene. Unlike carbon fullerenes, Si atoms in the Si fullerenes are arranged in rugged shells because all the atoms are joined by sp3 bonding. Each Si atom is bonded to three atoms within the same shell and to an atom within an adjacent shell. Thus, all the Si atoms except for some atoms in the outermost shell are four coordinated.

Several possible structure models have also been proposed for the Si NW.5,7,23–27 Recently, we have predicted the existence of polyicosahedral Si (pi-Si) NWs (Si150, Si260, Si900, . . .).7 Our MD simulations have demonstrated that the polyicosahedral Si150 NW composed of linked icosahedral Si100 ND is spontaneously formed by freezing liquid Si inside a nanopore, and that the pi-Si NW is stable even in a vacuum up to about 77% of the melting temperature of bulk cd-Si. Furthermore, our structural energy calculations have revealed that the pi-Si NW is the lowest-energy form of one-dimensional Si known so far, at least for diameters of less than 6.02 nm.

The frameworks of Si having fullerene cages, such as Si32, Si34, and Si28 cages, are known as Si clathrates. Three types of Si clathrate, types I, II and III, have been synthesized in the bulk (three-dimensional) systems.28–29 Various kinds of guest atoms can be encapsulated into the fullerene cages of the bulk Si clathrates. For example, Na+, Ba+, and I-doped Si clathrates have been synthesized.28–31 The nature of the electronic band structure depends on the guest atoms. The first-principles calculations have shown that the guest-free type-I Si clathrate (Si34) is a semiconductor.32 On the other hand, Na3Ba3@Si46, I@Si46 are metals.33–35 The stabilities of Si clathrate NWs cut out bulk Si clathrates, the


the hydrogen-terminated or nitrogen atoms in experiment. In our study, we focus on bonds of Si NSs are usually terminated by hydrogen, oxygen, and optical properties of the pi-Si NS. The surface dangling of the effect of sodium and iodine doping on the electronic present paper, we carry out a systematic first-principles study together, has a Si20 cage per i-Si ND, and therefore it can be regarded as a novel low-dimensional Si clathrate. Note that the 1-PINS is a i-Si ND, the 2-PINS is a pi-Si ND constructed by linking two icosaahedra together, and the \( \infty \)-PINS is a pi-Si NW. These pi-Si NSs cannot be made by cutting out bulk Si clathrates.

The unique cage structure of the pi-Si NS is distinct from the cd-Si NS. Encapsulating a guest atom into the Si20 cage allows us to tune the electronic and optical properties. In the present paper, we carry out a systematic first-principles study of the effect of sodium and iodine doping on the electronic and optical properties of the pi-Si NS. The surface dangling bonds of Si NSs are usually terminated by hydrogen, oxygen, or nitrogen atoms in experiment. In our study, we focus on the hydrogen-terminated (H-terminated) pi-Si NSs: the icosaahedral \( \text{Si}_{100}\text{H}_{50} \) ND (1-PINS), the polyicosaahedral \( \text{Si}_{175}\text{H}_{90} \) ND (2-PINS), and the polyicosaahedral \( \text{Si}_{150}\text{H}_{30} \) NW (\( \infty \)-PINS). We also compare the electronic structure of the guest-free pi-Si NW with those of the pentagonal Si (pent-Si), NW (\( \text{Si}_{30}\text{H}_{10} \) NW), and cd-Si NW (\( \text{Si}_{45}\text{H}_{20} \) NW).5,7

II. MODEL AND METHOD

A. Electronic structure calculation

The electronic structure of Si NSs is calculated by the density functional theory (DFT) within the local density approximation (LDA).42,43 Norm-conserving pseudopotentials are used in a separable form with multiple projectors to replace the deep core potential into a shallow potential.44,45 The wave functions are expressed by the linear combination of atomic orbitals centered on atomic sites. The atomic basis functions are generated by solving atomic Kohn-Sham equations using confinement pseudopotentials.46,47 The primitive pseudoatomic basis sets Si6.5-s2p2d1/Na8.0-s2p1/l and I8.0-s1p1d1 are used for Si, Na, and I atoms, respectively, where the abbreviation, for example, Si6.5-s2p2d1, represents the employment of two primitive s orbitals, two primitive p orbitals, and one primitive d orbital of a Si atom which are generated with a confinement radius of 6.5 bohr. The contracted pseudoatomic basis set, H5.5-s52, is used for H atoms, where s52 represents that two s orbitals are generated by contracting five primitive s orbitals of a H atom. The contraction coefficients are optimized to minimize the total energy of the \( \text{Si}_{30}\text{H}_{20} \) cluster. The contracted bases improve the accuracy of the calculation without increasing the computational cost. The real space grid techniques are used with the cutoff energy of about 200 Ry, when calculating Hamiltonian matrix elements and solving the Poisson equation with a fast Fourier transformation.48 The \( \Gamma \) point, five \( k \)-point, and three \( k \)-point samplings are used for the Bril-louin zone sampling in the case of the polyicosaahedral \( \text{Si}_{150}\text{H}_{60} \) NW, pentagonal \( \text{Si}_{30}\text{H}_{10} \) NW, and crystalline diamond \( \text{Si}_{45}\text{H}_{20} \) NW, respectively. The size of the simulation box is set so that the wave functions do not overlap with their images.

### TABLE I.

<table>
<thead>
<tr>
<th>( L ) (nm)</th>
<th>( d ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(<em>{150}\text{H}</em>{60} ) NW</td>
<td>1.706</td>
</tr>
<tr>
<td>Na(<em>{3})@Si(</em>{150}\text{H}_{60} ) NW</td>
<td>1.710</td>
</tr>
<tr>
<td>I(<em>{2})@Si(</em>{150}\text{H}_{60} ) NW</td>
<td>1.705</td>
</tr>
<tr>
<td>Na(<em>{1})@Si(</em>{150}\text{H}_{60} ) NW</td>
<td>1.711</td>
</tr>
<tr>
<td>Si(<em>{45}\text{H}</em>{10} ) NW</td>
<td>0.3819</td>
</tr>
<tr>
<td>Si(<em>{45}\text{H}</em>{20} ) NW</td>
<td>0.52669</td>
</tr>
</tbody>
</table>

All the calculations are carried out using the OpenMX code.49 In order to check our methods, we have calculated the electronic band structures of bulk type-I Si clathrates, \( \text{Si}_{46}, \text{Na}_{8}@\text{Si}_{46}, \) and \( \text{I}_{8}@\text{Si}_{46}, \) and confirmed that our calculations reproduce the literature well.33–35

B. Geometry optimization

The pristine icosaahedral \( \text{Si}_{100} \) ND (\( \text{Si}_{30}@\text{Si}_{60} \) double-shell fullerene) consists of 20 slightly distorted crystalline tetrahedra \( \text{Si}_{3}, \)6 The tetrahedron has four (111) facets, and the adjacent tetrahedra are joined by forming covalent bonds between Si atoms in facing (111) facets. All the Si atoms in the \( \text{Si}_{100} \) ND are joined by tetrahedral bonding. The pristine polyicosaahedral \( \text{Si}_{175} \) ND is constructed by linking two \( \text{Si}_{100} \) NDs together by sharing five crystalline tetrahedra. Thus, the \( \text{Si}_{175} \) ND contains two \( \text{Si}_{30} \) cages. The pristine polyicosaahedral \( \text{Si}_{150} \) NW is constructed by linking \( \text{Si}_{100} \) NDs periodically together and has a \( \text{Si}_{30} \) cage per \( \text{Si}_{100} \) ND.7

First, we place the pristine pi-Si NSs in simulation boxes so that the fivefold symmetry axis coincides with the z axis and optimize the geometries by a steepest decent method using the empirical Tersoff model.22 Second, we terminate surface dangling bonds of the pristine Si NSs by hydrogen atoms. The H-terminated Si NSs, the icosaahedral \( \text{Si}_{100}\text{H}_{60} \) ND, the polyicosaahedral \( \text{Si}_{175}\text{H}_{90} \) ND, and the polyicosaahedral \( \text{Si}_{150}\text{H}_{30} \) NW, are relaxed by a direct inversion in the iterative subspace method50 using the OpenMX until the force on each atom becomes 0.0001 hartree/bohr or less. Third, we place a Na or an I atom on the gravity center of each \( \text{Si}_{30} \) cage. The doped Si NSs are then relaxed again. The optimized length of a unit cell of a pi-Si NW in the z direction (the wire direction) is determined by comparing total energies calculated for different lengths. We summarize the optimized lengths of unit cells in Table I.

For comparison, we optimize the structure of the H-terminated pentagonal \( \text{Si}_{30}\text{H}_{20} \) NW.5,7 The pent-Si NW is composed of five crystalline triangular prisms which are cut out cd-Si. The prism is oriented toward the (110) direction and has two (111) and one H-terminated (100) facets with dimerization. The adjacent prisms are joined by forming covalent bonds between Si atoms in facing (111) facets, and each prism exposes the (100) facet. We also optimize the
The electronic structures of the 1-PINS, where $N_l$ decreases from $\infty$, 2, to 1.52. The size-dependent band gap energy of the polyicosahedral Si NSs is explained by the quantum confinement effect. As the system size increases, the DFT calculation soon becomes practically impossible due to high computational costs. For calculating the band gap energies of...
longer $N_l$-PINSs ($N_l > 2$), the method based on an effective mass approximation (EMA) is useful. It is known that although the EMA is not a good approximation for the smallest nanostructures, it properly describes the electronic structures of larger nanostructures. Thus, the DFT and EMA methods could be complementary to each other to calculate the band gap energy in the wide size range. Using the EMA with the infinite well potential, the band gap energy of the $N_l$-PINS is given as

$$E_{\text{gap}}^{\text{EMA}}(N_l) = E_g(\infty) + \frac{\pi^2 \hbar^2}{2LN_c^2} \left( \frac{1}{m_c^e} + \frac{1}{m_v^e} \right),$$

(1)

where $E_g(\infty)$ is the band gap energy of the polyicosahedral Si$_{150}$H$_{60}$ NW, 1.20 eV, $\hbar$ is the Planck constant divided by $2\pi$, and $L$ is the optimized length of the unit cell of the pi-Si NW in the direction of the wire axis. There are two i-Si NDs in a unit cell so that $LN_c/2$ represents the length of the $N_l$-PINS. The effective masses of conduction and valence bands [at C1−(Γ) and V1+ (Γ) states] of the pi-Si NW are determined from Fig. 3(a) as $m_c^e = 0.40 m_e$ and $m_v^e = 1.71 m_e$, respectively, where $m_e$ is the mass of electron. Figure 4 shows the size dependence of band gap energy. Although the EMA overestimates the band gap energy of the 1-PINS, it reproduces that of the 2-PINS well. Therefore, the band gap energies of longer $N_l$-PINSs ($N_l > 2$) should be properly estimated by Eq. (1).

One might expect that the pi-Si NW emits light efficiently because it has a direct band gap. Within the electronic dipole approximation, the radiative recombination rate $P_{\mu\mu'}$ between the level $\mu$ in the conduction band (c) and level $\mu'$ in the valence band (v) is expressed as

$$P_{\mu\mu'} = \frac{1}{\tau_{\mu\mu'}} = \frac{4n_0 c [E_{\mu\mu'} - E_c]}{3m_c^e \hbar c^2} \left| \langle \Psi_{\mu} | \beta | \Psi_{\mu'} \rangle \right|^2,$$

(2)

where $\tau_{\mu\mu'}$ is the radiative recombination time, $n_0$ is the refraction index (for which we set $n_0 = 1$), $\alpha$ is the fine-structure constant, and $c$ is the velocity of light. The momentum operator is denoted by $\hat{p}$, and $\Psi_{\mu}$ and $\Psi_{\mu'}$ represents the electronic wave functions of the $\mu$ and $\mu'$ states, respectively, while $E_{\mu\mu'}$ and $E_{\mu'}$ are the corresponding energy levels. The lowest unoccupied molecular orbital (LUMO) [C1−(Γ)] and highest occupied molecular orbital (HOMO) [V1+ (Γ)] of the pi-Si NW belong to the $A_{1g}$ and $E_{1g}$ representations in the point group $D_{3h}$, respectively, while $\hat{p}_x$ ($\hat{p}_y$ and $\hat{p}_z$) belong to the $E_{1u}$ and $A_{2u}$ representations, respectively. Since the product $A_{1g} \times E_{1g}$ does not contain the $E_{1u}$ and $A_{2u}$ representations, the momentum matrix element $\langle \Psi_{\text{LUMO}} | \beta | \Psi_{\text{HOMO}} \rangle$ is zero, and the optical dipole transition is prohibited. Therefore, the pi-Si NW does not emit light efficiently, even though it is a direct-band-gap semiconductor.

We have also confirmed that the optical dipole transition between the LUMO and HOMO states is prohibited in the i-Si ND and the pi-Si ND due to the selection rule. Thus, $N_l$-PINSs are not suitable for light emitting devices as they are. However, as we shall show later, the radiative recombination rates of the i-Si ND, pi-Si ND, and pi-Si NW can be enhanced by encapsulating Na or I atoms into their Si$_{20}$ cages.

**B. Comparison with other Si nanowires**

The pristine pi-Si NW is the most stable one-dimensional Si known so far, while the pristine pent-Si NW is the second most stable. The pi-Si NW exposes the (111) facets only which has the lowest surface energy, and the highest stability is explained by the surface energy minimization. The relative
ELECTRONIC AND OPTICAL PROPERTIES OF…

FIG. 5. The formation energy $\Omega$ of H-terminated Si NWs as a function of hydrogen chemical potential $\Delta \mu_H$. The solid, dotted, and dashed lines are results for the polyicosahedral Si$_{150}$H$_{60}$ NW, pentagonal Si$_{30}$H$_{10}$ NW, and crystalline diamond Si$_{45}$H$_{20}$ NW, respectively. The thin horizontal line is the result for the pristine polyicosahedral Si$_{150}$ NW calculated using the Tersoff potential (Ref. 7). The vertical dashed lines indicate transition energies.

The electronic band structures of the pi-Si, pent-Si, and cd-Si NWs depicted in Fig. 6 reveal that all the Si NWs are direct-gap semiconductors, while the bulk cd-Si is an indirect-band-gap semiconductor. However, the optical dipole transition between the LUMO and HOMO states is prohibited in the pent-Si and cd-Si NWs due to the selection rule as well as the pi-Si NW. The band gap energy strongly depends on the wire structure as is summarized in Table II. The cd-Si NW has the largest band gap energy, 1.76 eV. The second is the pi-Si NW, 1.20 eV. The smallest is the pent-Si NW, 0.96 eV. All the band gap energies are larger than the

TABLE II. The band gap energy $E_g$ and the conduction and valence band effective mass $m^*$ and $m_e$ of the polyicosahedral Si$_{150}$H$_{60}$ NW, the pentagonal Si$_{30}$H$_{10}$ NW, and the crystalline diamond Si$_{45}$H$_{20}$ NW.

<table>
<thead>
<tr>
<th>NW</th>
<th>$E_g$ (eV)</th>
<th>$m^*_e/m_e$</th>
<th>$m^*_c/m_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pi-Si NW</td>
<td>1.20</td>
<td>0.40</td>
<td>1.71</td>
</tr>
<tr>
<td>pent-Si NW</td>
<td>0.96</td>
<td>0.13</td>
<td>0.19</td>
</tr>
<tr>
<td>cd-Si NW</td>
<td>1.76</td>
<td>0.27</td>
<td>0.91</td>
</tr>
</tbody>
</table>

The electronic band structures of the pi-Si, pent-Si, and cd-Si NWs depicted in Fig. 6 reveal that all the Si NWs are direct-band-gap semiconductors, while the bulk cd-Si is an indirect-band-gap semiconductor. However, the optical dipole transition between the LUMO and HOMO states is prohibited in the pent-Si and cd-Si NWs due to the selection rule as well as the pi-Si NW. The band gap energy strongly depends on the wire structure as is summarized in Table II. The cd-Si NW has the largest band gap energy, 1.76 eV. The second is the pi-Si NW, 1.20 eV. The smallest is the pent-Si NW, 0.96 eV. All the band gap energies are larger than the

$\Omega = E + n_H e_0 - n_{Si} \mu_{Si} - n_H \mu_H$, where $E$ is the total energy of the Si NW, $e_0$ is the zero-point energy arising from a Si-H vibrational mode, $\mu_{Si}$ is the chemical potential of bulk cd-Si, and $n_{Si}$ and $n_H$ are the numbers of Si and H atoms, respectively. If we measure the $\mu_H$ relative to the $\mu_H^*$ at which the formation energy of a SiH$_4$ molecule is equal to zero, Eq. (3) becomes

$\Omega(\Delta \mu_H) = E - n_H (\Delta \mu_H + E_{SiH_4} - \mu_{Si})/4 - n_{Si} \mu_{Si}$, where $\Delta \mu_H = \mu_H - \mu_H^*$, and $E_{SiH_4}$ is the total energy of a SiH$_4$ molecule. The larger value of $\Delta \mu_H$ means that the Si NW is placed in the hydrogen richer environment. As a reference, we note that the most stable phase of the H-terminated Si (001) bulk surface changes from the $2 \times 1$ monohydride structure to the $3 \times 1$ monohydride plus dihydride structure when $\Delta \mu_H$ exceeds $-0.24$ eV, and then the most stable phase changes to the $1 \times 1$ dihydride structure when $\Delta \mu_H$ exceeds $-0.09$ eV. The formation energies per Si atom of the polyicosahedral Si$_{150}$H$_{60}$ NW, the pentagonal Si$_{30}$H$_{10}$ NW, and the crystalline diamond Si$_{45}$H$_{20}$ NW are shown in Fig. 5. We also show the energy of the pristine polyicosahedral Si$_{150}$ NW calculated using the Tersoff potential (Ref. 7) in Fig. 5. Note that the diameters of the pi-Si, pent-Si, and cd-Si NWs are similar to each other, 1.47, 1.39, and 1.45 nm, respectively (Table I). Figure 5 reveals that the most stable structure changes according to the hydrogen chemical potential. The pristine pi-Si NW is the most stable for $\Delta \mu_H < -0.89$ eV. The transition from the pristine pi-Si NW to the H-terminated pent-Si NW occurs when $\mu_H$ exceeds $-0.89$ eV, and the H-terminated pent-Si NW is the most stable until $\Delta \mu_H$ exceeds $-0.77$ eV. The transition from the H-terminated pent-Si NW to the H-terminated pi-Si NW occurs at $\mu_H = -0.77$ eV, and the H-terminated pi-Si NW is the most stable in the range $-0.77 < \Delta \mu_H < -0.13$ eV. For $-0.13$ eV < $\Delta \mu_H$, the cd-Si NW is the most stable. This trend is explained by means of the ratio of H atoms to Si atoms. The H/Si ratios of the polyicosahedral Si$_{150}$ NW, the pentagonal Si$_{30}$H$_{10}$ NW, the polyicosahedral Si$_{150}$H$_{60}$ NW, and crystalline diamond Si$_{45}$H$_{20}$ NW are 0.00, 0.33, 0.40, and 0.44, respectively. The structure with a higher H/Si ratio becomes more stable as $\Delta \mu_H$ increases, and the most stable structure changes. Although the pi-Si NW and pent-Si NW have not been identified experimentally yet, our results suggest that the hydrogen chemical potential could be a key for synthesizing these Si NWs.
bulk cd-Si (0.51 eV in our theoretical framework). The effective masses of the Si NWs at the valence band maximum and conduction band minimum are also summarized in Table II. The effective masses of the pent-Si NW are considerably small compared to those of the pi-Si NW and cd-Si NW, indicating that carriers in the pent-Si NW might have large mobilities for the diffusive transport.

IV. DOPED POLYICOSAHEDRAL SILICON NANOSTRUCTURES

A. Electronic structure of Na-doped systems

By calculating the encapsulation energy, we find that encapsulating Na atoms into the Si cages of the pi-Si NSs is possible (Appendix C). The electronic structure of the Na@Si100H60 ND is shown in Fig. 1(b). By comparing the wave functions (not shown), we have confirmed that the electronic states labeled by IiNa and h1Na originate in the i and h states of the Si100H60 ND, respectively. Due to the greater electropositivity of sodium, one valence electron is transferred from the Na atom to the host Si100H60 ND so that the Na state near the Fermi level is negligibly small. The effects of the orbital coupling between the i-ND and the Na atom are explained as follows. In our calculations, the 2p, 3x, and 4s orbitals of a Na atom are used as basis functions. The s and p states belong to the A and T representations in the point group Ih, respectively. Therefore, the states of the Si100H60 ND, which belongs to the A state (1l state) and T states, couple with the sodium s and p states, respectively, while the other states (h1, h2, and h3 states) do not. Actually, the sodium s states hybridize with the 11 state of the i-ND, and the Na state shifts downward in energy due to the bonding hybridization. Although the i states of the i-ND couples with the sodium p state, the hybridization effect is negligibly small. As a result, the level spacing between the 12Na (LUMO) and 11Na (HOMO) states (0.56 eV) is enlarged compared with the spacing between the L2 and 11 states (0.23 eV). Interestingly, the optical dipole transition between the L2Na and 11Na states of the Na@Si100H60 ND is possible with a radiative recombination rate of 1.0 × 10^6 s^{-1}, which is comparable to the rates of luminescent amorphous Si NDs.

The electronic structure of the Na2@Si175H90 ND is shown in Fig. 2(b). The electronic states labeled by L1Na and H1Na originate in the Li and Hi states of the Si175H90 ND, respectively. The L1Na state is filled with two valence electrons from the two Na atoms. The band gap energy, the level spacing between the L2Na and L1Na states, is 0.37 eV. The LUMO-HOMO optical dipole transition is possible (P_{L2Na-L1Na} = 1.0 × 10^6 s^{-1}). Since the wave functions of the L2 and L1 states of the i-Si ND have the φ_{i,l}^\pm component (Appendix A), these states hybridize with the sodium s states. Due to the bonding hybridization, the L2Na and L1Na states shift downward in energy. As in the case of the Na@Si100H60 ND, the hybridization effect of the sodium p state near the Fermi level is negligibly small.

The electronic structure of the Na2@Si150H60 NW is shown in Fig. 3(b). The C1Na, V1Na, and V2Na bands of the Na2@Si150H60 NW originate in the C1, V1, and V2 bands of the Si150H60 NW, respectively. The guest-free pi-Si NW is a semiconductor, while the Na-doped pi-Si NW is a metal because the ClNa band is half filled with valence electrons from Na atoms. From Table V, it is considered that the wave functions φ_{i,l}(A1) are mixed in the C1 band of the pi-Si NW, and the ratio of the φ_{i,l}^+ component decreases as the state changes from C1l(T), C1l(X), to C1l(T). Thus, the C1 band, particularly near the C1l(T) state, hybridizes strongly with sodium s states. As a result, the bandwidth of the ClNa band is enlarged. As in the case of the Na@Si100H60 ND, the hybridization effect of the sodium p state near the Fermi level is negligibly small.

One-dimensional structures with partially filled metallic bands often undergo the Peierls distortion when they are relaxed using a larger unit cell, accompanying a metal-semiconductor transition in which the bands split into the lower-energy filled bands and the higher-energy empty bands. The Peierls instability is determined by the competition between the decrease in electronic energy and the increase in distortion energy. The thinner structure is more unstable against the Peierls distortion. The Na-doped pi-Si NW might undergo the Peierls transition, since the ClNa band of the Na2@Si150H60 NW is half filled. In order to check the Peierls instability, we optimized the geometry of the Na-doped pi-Si NW using a double-size unit cell, the Na2@Si150H60 NW, which is prepared by replicating the Na2@Si50H60 NW. Note that the geometry optimization is carried out using a length of the unit cell in the z direction, 2 × 17.10 Å. By analyzing the band structure of the optimized Na2@Si300H120 NW (not shown), we have confirmed that the Na2@Si300H120 NW is a metal and the effect of Peierls distortion is negligibly small.

Figure 7 compares the electronic band structures of partially Na-doped pi-Si NWs, Na@Si300H120 NWs. The geometry of the Na@Si300H120 NW is prepared by replicating the optimized Na2@Si150H60 NW and removing (4–x) Na atoms. The electronic structures are calculated without geometry optimization because we have confirmed that there is no significant difference in the electronic structure near the Fermi level between the optimized Na2@Si150H60 NW and the initial structure, the optimized Na2@Si150H60 NW with a Na atom placed at the gravity center of each Si50 cage. There are four Si cages per unit cell so that there are five possible doping patterns: [OXXX], [OXXO], [OXXO], [OOXO], and [OOOO], where O and X indicate doped and empty Si20 cages, respectively. The band structure of the [OOOO] NW is obtained by folding the bands of the Na2@Si150H60 NW. Therefore, the number of bands become double. Accordingly, we refer the lower and upper parts of the ClNa band to the ClNa and ClNa bands, respectively. Due to the symmetry reduction which depends on doping pattern, there appear energy gaps in the Cl bands of partially Na-doped pi-Si NWs. The [OXXX], [OXXO], and [OXXO] NWs are metals as in the case of the [OOOO] NW. Interestingly, the [OOXX] NW is a direct-band-gap semiconductor with a 0.24 eV energy gap. The optical dipole transition between the Cl(X) and ClNa(X) states is possible with a recombination rate of 3.2 × 10^6 s^{-1}. 

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FIG. 7. (Color online) The electronic band structures of partially Na-doped pi-Si NWs, Na@Si\textsubscript{150}H\textsubscript{60} NWs. Energy is measured from the Fermi energy $E_F$, $-3.83$, $-3.88$, $-3.93$, $-3.95$, and $-3.97$ eV for |OOOO|, |OOOX|, |OXXO|, |OXOX|, and |OXXX| NWs, respectively. The C\textsubscript{i1} and C\textsubscript{i2} bands are drawn in bold solid and dotted lines, respectively. The unit cell is given below each band. The Si–Si bonds are depicted. The bold (red) bonds represent Si\textsubscript{20} cages. Spheres are guest atoms. Note that Si–H bonds in Fig. 2 are not shown for clarity.

B. Electronic structure of I-doped systems

By calculating the encapsulation energy, we find that encapsulating I atoms into the Si\textsubscript{20} cages of the pi-Si NSs is possible (Appendix C). The electronic structure of the I@Si\textsubscript{150}H\textsubscript{60} ND is shown in Fig. 1(c). By comparing the wave functions, we have confirmed that the electronic states labeled by $l_i$ and $h_i$ originate in the $l_i$ and $h_i$ states of the Si\textsubscript{150}H\textsubscript{60} ND, respectively, and that the Ip state originated in the iodine 5$p$ state. Due to the greater electronegativity of iodine, one valence electron is transferred from the Si@Si\textsubscript{150}H\textsubscript{60} ND to the I atom so that the fourfold-degenerated $h_1$ state of the I@Si\textsubscript{100}H\textsubscript{60} ND is partially empty. In our calculations, the 4$d$, 5$s$, and 5$p$ orbitals of an I atom are used as basis functions. The $s$, $p$, and $d$ states belong to the $A_1$, $T_1$, and $H_2$ representations in the point group $I_h$, respectively. Therefore, the states of the Si@Si\textsubscript{100}H\textsubscript{60} ND, which belongs to the $A_1$ (11 state), $T_1$ (12 state), and $H_2$ (3h state) representations, couple with the iodine $s$, $p$, and $d$ states, respectively. However, the hybridization effect is relatively small.

The electronic structure of the I\textsubscript{2}@Si\textsubscript{175}H\textsubscript{90} ND is shown in Fig. 2(c). The electronic states labeled by $l_i$ and $h_i$ originate in the $l_i$ and $h_i$ states of the Si\textsubscript{175}H\textsubscript{90} ND, respectively. The Ip state originates in the iodine 5$p$ state. Since two valence electrons are transferred from the Si@Si\textsubscript{175}H\textsubscript{90} ND to the two I atoms, the twofold-degenerated $H_1$ state of the I\textsubscript{2}@Si\textsubscript{175}H\textsubscript{90} ND is partially empty. Although the wave functions of the iodine 5$p$ (5$p_x$ and 5$p_y$) state do not couple with the wave functions $\Psi_{1i}^{I[H_1]}$ of the i-Si ND, they couple with the wave functions $\Psi_{2i}^{H_1}$ of the pi-Si ND which is composed of the wave functions $\phi_{2i}^{I[H_1]}$ (Appendix A). The symmetry reduction in the local icosahedral structure is a key to understand the hybridization effect. The structure of the pi-Si ND is strained due to the stress caused by linking i-Si NDs together. Actually, the symmetry of the Si\textsubscript{20} cages is lowered from $I_h$ (i-Si ND) to $C_{5v}$ (pi-Si ND) (Appendix B). Therefore, although the wave functions $\phi_{2i}^{I[H_1]}$ resemble the $\Psi_{2i}^{I[H_1]}$, they are not the basis functions of the $H_{1i}$ representation but those of the $E_1(C_{5v})$ representation. Since the 5$p$ state belongs to the $E_1$ representation in the point group $C_{5v}$, the wave functions $\phi_{2i}^{I[H_1]}$ hybridize with the wave functions of the iodine 5$p$ state. Due to the antibonding hybridization, the $H_3$ state is upshifted and lies above the H2$^\text{H}2$ state in energy. The hybridization effect on the other states near the Fermi level is relatively small.

The electronic structure of the I\textsubscript{2}@Si\textsubscript{150}H\textsubscript{60} NW is shown in Fig. 3(c). The C1$^\text{V1}$, V2$^\text{V2}$, and V$^\text{V1}$ bands of the I\textsubscript{2}@Si\textsubscript{150}H\textsubscript{60} NW originate in the C1, V2, and V1 bands of the Si@Si\textsubscript{150}H\textsubscript{60} NW, respectively. Since the valence electrons transfer from the host Si@Si\textsubscript{150}H\textsubscript{60} NW to the I atoms, the V2$^\text{V1}$ and V$^\text{V1}$ bands are partially empty. Therefore, the I\textsubscript{2}@Si\textsubscript{150}H\textsubscript{60} NW is partially metal. As in the case of the I\textsubscript{2}@Si\textsubscript{175}H\textsubscript{90} ND, due to the strain induced symmetry reduction of the $\phi_{2i}^{I[H_1]}$, the V2$^\text{V2}$ band hybridizes with the iodine 5$p$ state so that the bandwidth of the V2$^\text{V2}$ band is enlarged, and the V2$^\text{V2}$ state lies above the V$^\text{V1}$ state in energy.

Figure 8 compares the electronic band structures of partially I-doped pi-Si NWs, the I@Si\textsubscript{150}H\textsubscript{60} NWs. As in the case of the Na@Si\textsubscript{150}H\textsubscript{60} NWs, the electronic structures are calculated without geometry optimization because we have confirmed that there is no significant difference in the electronic structure near the Fermi level between the optimized I@Si\textsubscript{150}H\textsubscript{60} NW and the initial structure, the optimized Si@Si\textsubscript{150}H\textsubscript{60} NW with an I atom placed at the gravity center of each Si\textsubscript{20} cage. The band structure of the |OOOO| NW is obtained by folding the bands of the I\textsubscript{2}@Si\textsubscript{150}H\textsubscript{60} NW. Thus, the number of bands becomes double. We refer the upper parts of the V\textsuperscript{1$^*$} and V\textsuperscript{2$^*$} bands to the V\textsuperscript{1$^*$} and V\textsuperscript{2$^*$} bands, respectively. The V\textsuperscript{1$^*$} bands of partially I-doped pi-Si NWs are shifted downward in energy as the doping ratio decreases, because the hybridization effect between the V\textsuperscript{2$^*$} band and the iodine 5$p$ state decreases. As a result, the V\textsuperscript{2$^*$} band of the |OXXX| NW lies below the V\textsuperscript{1$^*$} band. All the NWs are metal, but the bands which cross the Fermi energy depend on the doping pattern: |OOOO| (V\textsuperscript{1$^*$} and V\textsuperscript{2$^*$}), |OXXX| (V\textsuperscript{2$^*$}), |OXOX| (V\textsuperscript{1$^*$} and V\textsuperscript{2$^*$}), and |OXXX| (V\textsuperscript{1$^*$}). The optical dipole transition between the C\textsuperscript{V1$^*$} (\(\Gamma\)) and V\textsuperscript{1$^*$} (\(\Gamma\)) states is prohibited in the I\textsubscript{2}@Si\textsubscript{300}H\textsubscript{120} NW because the contribution to the momentum matrix element $\langle \Psi_{C1\textsuperscript{V1}}(\Gamma) | i | \Psi_{V\textsuperscript{1$^*$}}(\Gamma) \rangle$ from the i-th i-Si ND completely cancels with the |(i+1)th| i-Si ND. However, the cancellation becomes incomplete in the partially I-doped pi-Si NWs. Thus, the optical dipole transition becomes possible in the partially I-doped pi-Si NWs, but the radiative recombination rates are relatively low ($<0.1 \times 10^6$ s$^{-1}$).
shown in Fig. 2 levels. The H3NaI and L3NaI states are also downshifted out Si20 cage and an I atom is encapsulated into the other cage. Note that a Na atom is encapsulated into one NW. The electronic and optical properties of guest-free, Na-doped, transition energies of the [OXXX], [OXOX], [OXXX], and [OOXX] NWs are 1.33, 1.20, 1.31, and 1.20 eV, respectively.

C. Electronic structure of NaI-doped systems

The electronic structure of the NaI@Si175H90 ND is shown in Fig. 2(d). The electronic states labeled by LiNaI and HiNaI originate in the Li and Hi states of the Si175H90 ND, respectively. Note that a Na atom is encapsulated into one Si20 cage and an I atom is encapsulated into the other cage. Due to the electropositivity of sodium and the electronegativity of iodine, one valence electron is transferred from the Na atom to the I atom. The HOMO and LUMO states of the Na-doped pi-Si ND originate in the HOMO and LUMO states of the pi-Si ND, respectively. The band gap energy of the Na-doped pi-Si ND (1.09 eV) is smaller than that of the guest-free pi-Si ND (1.60 eV). The other states are also affected by the Na encapsulation. The L3NaI state is upshifted in energy far away from the range we depicted the energy levels. The H3NaI and L3NaI states are also downshifted out of the range. On the other hand, the H6NaI and H8NaI states are upshifted in the range.

The electronic band structure of the NaI@Si175H90 NW is shown in Fig. 3(d). The C1NaI, V1NaI, and V2NaI bands originate in the C1, V1, and V2 bands of the pi-Si NW, respectively. The valence electrons transfer from the Na atoms to the I atoms, and the Na-doped pi-Si NW is a direct-gap semiconductor. The band gap energy of the Na-doped pi-Si NW (1.09 eV) is smaller than that of the guest-free pi-Si NW (2.09 eV). The V2 band hybridizes with the iodine 5p_x state so that the V2NaI is upshifted in energy. However, the hybridization effect is small compared with the I2@Si150H60 NW, and the energy of the V2NaI(Γ) state is almost the same as the V1NaI(Γ) state. As the in the case of partially I-doped pi-Si NWs, the incomplete cancellation in the momentum matrix element occurs. Thus, the optical dipole transition between the C1NaI(Γ) and V2NaI(Γ) states is possible with a radiative recombination rate of $0.5 \times 10^6 \text{s}^{-1}$.

V. SUMMARY

We have reported a systematic first-principles study of the electronic and optical properties of guest-free, Na-doped, I-doped, and Na-doped pi-Si NSs. The band gap energy of the guest-free pi-Si NS increases from 1.20, 1.60, to 2.09 eV as the number of linked i-Si NS decreases, decreases from $\infty$ (polyicosahedral Si150H60 NW), 2 (polyicosahedral Si175H90 ND), to 0 (icosahedral Si100H60 ND) due to the quantum confinement effect. Although the pi-Si NW is a direct-band-gap semiconductor, the optical dipole transition between the LUMO and HOMO states is prohibited in the pi-Si NSs. The analyses of electronic wave functions show that the wave functions of the pi-Si ND and the pi-Si NW can be expressed as linear combination of wave functions which resemble to the wave functions of the i-Si ND. The comparison of the electronic band structure of the pi-Si NW with the similar-size pentagonal Si30H10 NW and crystalline diamond Si45H20 reveals that the band gap energy and the effective masses of the Si NW strongly depend on the arrangement of Si atoms. We have compared the stability of the nanowires as a function of the hydrogen chemical potential and found that the hydrogen chemical potential could be a key for synthesizing the pi-Si NW and the pent-Si NW.

The calculated encapsulation energy suggests that the encapsulation of Na or I atoms into the Si20 cages of pi-Si NSs is possible. In Na-doped pi-Si NSs, the valence electron transfers from the Na atom to the Si framework due to the greater electropositivity of sodium. As a result, the LUMO-HOMO optical dipole transition becomes possible in the NaI@Si100H60 ND and NaI@Si175H90 ND with transition energies of 0.56 and 0.37 eV, respectively. The Na2@Si150H60 NW is a metal (half-filled C1NaI band), while the corresponding guest-free Si150H60 NW is a semiconductor. The Na-doped pi-Si NW is stable against the Peierls distortion. The nature of the electronic band structure of partially Na-doped piSi NWs strongly depends on the doping ratio and doping pattern. The [OXXX], [OXOX], and [OOOX] NWs are metals as in the case of the [OOOO] NW. On the other hand, the [OXXX] NW is a direct-band-gap semiconductor. The LUMO-HOMO optical dipole transition is possible in the [OXXX] NW with a transition energy of 0.24 eV.

In I-doped pi-Si NSs, the valence electron transfers from the Si framework to the I atom due to the greater electronegativity of iodine, which results in the metallic I2@Si150H60 NW (partially empty V1 and V2 bands). The strain in the local icosahedral structures caused by linking icosahedra together enables the hybridization of the V2 band and the iodine 5p_x state. As a result, the bandwidth of the V2 band is enlarged, and the V2(Γ) state lies above the V1(Γ) state in energy. The optical dipole transition between the C1− and V2+ states is possible in partially I-doped pi-Si NWs due to the incomplete cancellation of the momentum matrix element, but the radiative recombinations are relatively low ($<0.1 \times 10^6 \text{s}^{-1}$).

In Na-doped pi-Si NSs, the valence electron transfers from the Na atom to the I atom due to the electropositivity of sodium and the electronegativity of iodine. The band gap energies of the NaI@Si175H90 ND (1.09 eV) and NaI@Si150H60 NW (1.09 eV) are decreased compared with the corresponding guest-free pi-Si ND (1.60 eV) and pi-Si NW (2.06 eV), respectively. The V2 band hybridizes with the iodine 5p_x state so that the V2NaI is upshifted in energy.
However, the hybridization effect is small compared with the I$_2$@Si$_{130}$H$_{60}$ NW, and the energy of the V$_{2Nal}$($\Gamma$) state is almost the same as the V$_{1Nal}^+(\Gamma)$ state. The optical dipole transition between the C$_{1Nal}^-(\Gamma)$ and V$_{2Nal}^+(\Gamma)$ states is possible with a transition energy of 1.09 eV.

Our results demonstrate that the electronic and optical properties of the pi-Si NSs can be tuned by doping appropriate guest atoms and controlling the size. The tunability is suitable for the building blocks of the future nanoscale Si-based optoelectronic devices. The pi-Si NS has not been identified experimentally yet, but the synthesis of the pi-Si NS would open up new avenues for science and technology. We hope that our results will stimulate further studies for synthesizing the pi-Si NS.

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APPENDIX A: ELECTRONIC WAVE FUNCTIONS

By comparing electron wave functions of the i-Si ND (1-PINS) to those of the pi-Si ND (2-PINS) and pi-Si NW (\infty-PINS), we find that the wave function \Psi^i_{Nf} of the \infty-PINS is well expressed as linear combinations of wave functions \phi^i_{Nf} which resemble to the wave function \Psi^i_{Lf} of the i-Si ND, where \mu and \nu are the indices of electronic state. Our findings described below will help us understand the effects of encapsulating Na and I atoms into the Si$_{20}$ cages.

First, we discuss the wave functions of the i-Si ND. The l1, l2, h1, h2, and h3 states of the i-Si ND belong to the Ag symmetry is lowered from $C_{5v}$, respectively. The wave functions of the degenerated states 

\begin{equation}
\Psi^i_{\infty}(r) = \sum_i \phi^i_{\infty}(\hat{r}_i(r - r_i)),
\end{equation}

where \hat{r}_i is the operator of the reflection about a plane which is perpendicular to the fivefold symmetry axis (z axis) and passes through the origin. The $r_i$ and $r_i$ are the positions of the gravity centers of the upper and lower Si$_{20}$ cages, respectively. Similarly, the LUMO wave function $\Psi^i_{\infty}$ of the pi-Si NW is a bonding orbital of wave functions $\phi^i_{\infty}$ and is expressed as

\begin{equation}
\Psi^i_{\infty}(r) = \sum_i \phi^i_{\infty}(\hat{r}_i(r - r_i)),
\end{equation}

where $r_i$ is the position of the gravity center of the $i$th Si$_{20}$ cage.

The wave functions of HOMO of the pi-Si ND (H1 state) and pi-Si NW [V1$^+(\Gamma)$ state] are expressed with linear combinations of wave functions which resemble the HOMO wave functions of the i-Si ND (h1 state) as well. However, the situation is rather complicated because the h1 state belongs to the fourfold-degenerated $G$ representation while the H1 and V1$^+(\Gamma)$ states are twofold degenerated. As is summarized in Table III, the wave functions of the $G$ state are classified into $\{\Psi^i_{G[E1]}\}$ and $\{\Psi^i_{G[E2]}\}$. We find from Fig. 10 that the HOMO wave functions $\Psi^i_{H1,a}$ of the pi-Si ND are antibonding orbitals of wave functions $\phi^i_{G[E2,1]}$ and are expressed as

\begin{equation}
\Psi^i_{H1,a}(r) = \phi^i_{G[E2,1]}(r - r_a) - \phi^i_{G[E2,2]}(\hat{r}_a(r - r)).
\end{equation}

Note that the wave functions $\phi^i_{G[E2,1]}$ have nothing to do with the H1 state of the pi-Si ND. Similarly, the HOMO wave functions $\Psi^{V1^+(\Gamma),a}$ of the pi-Si NW are antibonding orbitals of wave functions $\phi^i_{G[E2,1]}$ and are expressed as

\begin{equation}
\Psi^{V1^+(\Gamma),a}(r) = \sum_{i} (-1)^i \phi^i_{G[E2,1]}(\hat{r}_a(r - r_i)).
\end{equation}

Note that we implicitly assume in Eq. (1) that the LUMO and HOMO wave functions of the \infty-PINS are expressed as linear combinations of wave functions which resemble the LUMO and HOMO wave functions of the i-Si ND, respectively.

Table III. The classification of wave functions of the icosahedral Si$_{100}$H$_{60}$ ND.

<table>
<thead>
<tr>
<th>State</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>l2</td>
<td>${\Psi^i_{l1}(E1)}$, ${\Psi^i_{l1}(E1)}$</td>
</tr>
<tr>
<td>l1</td>
<td>${\Psi^i_{l2}(E1)}$, ${\Psi^i_{l2}(E1)}$</td>
</tr>
<tr>
<td>h1</td>
<td>${\Psi^i_{G[E1]}}$, ${\Psi^i_{G[E1]}}$</td>
</tr>
<tr>
<td>h2</td>
<td>${\Psi^i_{h1}(E1)}$, ${\Psi^i_{h1}(E1)}$</td>
</tr>
</tbody>
</table>

using XCRYSDEN. We find from Fig. 9 that the LUMO wave function $\Psi^i_{21}$ of the pi-Si ND is a bonding orbital of wave functions $\phi^i_{\infty}$, which resemble the LUMO wave function $\Psi^i_{\infty}$ of the i-Si ND, and is expressed as

\begin{equation}
\Psi_{21}(r) = \phi_{\infty}(r - r_a) + \phi_{\infty}(\hat{r}_a(r - r)),
\end{equation}

where $r_a$ is the position of the gravity center of the $i$th Si$_{20}$ cage.

The wave functions of HOMO of the pi-Si ND (H1 state) and pi-Si NW [V1$^+(\Gamma)$ state] are expressed with linear combinations of wave functions which resemble the HOMO wave functions of the i-Si ND (h1 state) as well. However, the situation is rather complicated because the h1 state belongs to the fourfold-degenerated $G$ representation while the H1 and V1$^+(\Gamma)$ states are twofold degenerated. As is summarized in Table III, the wave functions of the $G$ state are classified into $\{\Psi_{G[E1]}\}$ and $\{\Psi_{G[E2]}\}$. We find from Fig. 10 that the HOMO wave functions $\Psi_{H1,a}$ of the pi-Si ND are antibonding orbitals of wave functions $\phi_{G[E2,1]}$ and are expressed as

\begin{equation}
\Psi_{H1,a}(r) = \phi_{G[E2,1]}(r - r_a) - \phi_{G[E2,2]}(\hat{r}_a(r - r)).
\end{equation}

Note that the wave functions $\phi_{G[E2,1]}$ have nothing to do with the H1 state of the pi-Si ND. Similarly, the HOMO wave functions $\Psi^{V1^+(\Gamma),a}$ of the pi-Si NW are antibonding orbitals of wave functions $\phi_{G[E2,1]}$ and are expressed as

\begin{equation}
\Psi^{V1^+(\Gamma),a}(r) = \sum_{i} (-1)^i \phi_{G[E2,1]}(\hat{r}_a(r - r_i)).
\end{equation}

Note that we implicitly assume in Eq. (1) that the LUMO and HOMO wave functions of the \infty-PINS are expressed as linear combinations of wave functions which resemble the LUMO and HOMO wave functions of the i-Si ND, respectively.
The wave functions $\psi_{2}^{A_{2}}(\mathbf{r})$ and $\psi_{2}^{B_{1}A_{1}}(\mathbf{r})$ are mixed in the wave function of the L2 state of the pi-Si ND. Actually, we have confirmed that the wave function $\psi_{2}^{L_{2}}$ is well expressed as

$$\psi_{2}^{L_{2}}(\mathbf{r}) = \phi_{2}^{A_{2}+B_{1}A_{1}}(\mathbf{r} - \mathbf{r}_{a}) - \phi_{2}^{A_{1}}(\mathbf{r} - \mathbf{r}_{b})$$

(A8)

where

$$\phi_{2}^{A_{2}+B_{1}A_{1}}(\mathbf{r}) = \frac{1}{\sqrt{2}} \phi_{2}^{A_{2}}(\mathbf{r}) + \frac{1}{\sqrt{2}} \phi_{2}^{B_{1}A_{1}}(\mathbf{r})$$

(A9)

Similarly, the wave function of the C1(X) state of the pi-Si NW is well expressed as

$$\psi_{C_{1}(X)}^{C_{1}}(\mathbf{r}) = \sum_{i} (-1)^{\text{floor}(i/2)} \phi_{2}^{A_{2}+B_{1}A_{1}}(\mathbf{r} - \mathbf{r}_{i})$$

(A10)

Note that the floor $(x)$ is the largest integer less than or equal to $x$. 

FIG. 9. (Color) The isosurface $(\pm 0.01$ electrons/$a_{0}^{3/2}$) and contour maps of the LUMO wave functions: (a) the l1 state of the icosahedral Si100H60 ND, (b) the L1 state of the polyicosahedral Si175H90 ND, and (c) the C1−(Γ) state of the polyicosahedral Si150H60 NW, where $a_0$ is the Bohr radius. The color plane divides the structure into two parts and contains the fivefold symmetry axis.

FIG. 10. (Color) The isosurface $(\pm 0.01$ electrons/$a_{0}^{3/2}$) and contour maps of the HOMO wave functions: (a) the h1 [Gg(E2)] state of the icosahedral Si100H60 ND, (b) the H1 state of the polyicosahedral Si175H90 ND, and (c) the V1+(Γ) state of the polyicosahedral Si150H60 NW, where $a_0$ is the Bohr radius. The color plane divides the structure into two parts and contains the fivefold symmetry axis.
we consider two half spheroids joined at the equator, where

\[ \psi_2^{L2}(r) = \phi_2^{L2}(r-r_a) + \phi_2^{L2}(r-r_b) \]

\[ \psi_2^{H1}(r) = \phi_2^{H1}(r-r_a) + \phi_2^{H1}(r-r_b) \]

\[ \psi_2^{L1}(r) = \phi_2^{L1}(r-r_a) + \phi_2^{L1}(r-r_b) \]

Our results including the other states are summarized in Tables IV and V.

### APPENDIX B: Si20 CAGE STRUCTURE

The Si20 cage of the i-Si ND is an equilateral dodecahedron with \( I_5 \) symmetry. The Si20 cages of the pi-Si ND and the pi-Si NW would be strained due to the stress caused by linking i-Si NDs together. As we have shown in Sec. IV B, the strain in the Si20 cage, or the symmetry breakdown, is a key to understand how I atoms affect the electronic structure of pi-Si NSs. In order to characterize the Si20 cage structure, we consider two half spheroids joined at the equator,

\[ f(r, a, c_+, c_-) = \begin{cases} \frac{x^2 + y^2 + z^2}{a^2 + c_2} & \text{if } z > 0 \\ \frac{x^2 + y^2 + z^2}{a^2 + c_2} & \text{if } z < 0 \end{cases} = 1, \quad (B1) \]

near whose surface the Si atoms are located. We search for a set of parameters \((a, c_+, c_-)\) which minimize the error,

\[ E_r = \frac{1}{20} \sum_{i=1}^{20} [f(r_i, a, c_+, c_-) - 1]^2, \quad (B2) \]

where \( r_i \) is the position of the \( i \)th Si atom measured from the gravity center of the Si20 cage. Note that, for an equilateral dodecahedral Si20 cage, \( a = c_+ = c_- \) and \( E_r = 0 \).

### APPENDIX C: ENCAPSULATION ENERGY

Sodium and iodine atoms can be encapsulated into the Si20 and Si20 cages of the bulk type-I Si clathrate (Si100)28,30 On the other hand, it is unclear whether these atoms can be encapsulated into the Si20 cages of pi-Si NSs or not. For discussing the feasibility of encapsulation, we calculated the energy per atom of encapsulating Na and I atoms into the cages of host H defined as

\[ E_{enc} = E(Na, I, @H) - xE(Na) - yE(I) - E(H), \quad (C1) \]

where \( E(X) \) is the total energy of X molecule and \( x \) and \( y \) are the numbers of Na and I atoms in the unit cell, respectively. The encapsulation energies are summarized in Table VII. In calculating the total energies of isolated Na and I atoms, the spin-polarization effects are taken into account within the local spin-density approximation.\42,43\ and the counterpoise correction is applied to minimize the basis set superposition error. As a reference, we also calculated the encapsulation energies for bulk Na8@Si100 and I8@Si100. Our results show that the encapsulation energy of a Na atom decreases with increasing the number of linked icosahedra: Na@Si100.
ND (0.91 eV), Na$_2$@Si$_{175}$H$_{80}$ ND (0.71 eV), and Na$_2$@Si$_{150}$H$_{60}$ NW (0.52 eV). This means that the encapsulation of Na atoms is energetically more feasible for longer p-Si NSs. Although the positive values indicate that the encapsulation of Na atoms is energetically less favorable, we expect that the encapsulation is possible because the values are comparable to the bulk Na$_8$@Si$_{146}$ (0.84 eV), which has been synthesized experimentally. Note that the positive values are consistent with the $E_{\text{enc}}$ of the Na@Si$_{20}$H$_{20}$ cluster.\textsuperscript{49}

All the encapsulation energies for I-doped and NaI-doped p-Si NSs are negative values, indicating that the encapsulation is energetically favorable. Note that $E_{\text{enc}}(\text{NaI@H}) < (E_{\text{enc}}(\text{Na$_2$@H}) + (E_{\text{enc}}(\text{I$_2$@H}))/2$ is explained by the ionic bond between Na and I atoms.

\begin{table}
\centering
\caption{The encapsulation energy $E_{\text{enc}}$ (eV).}
\begin{tabular}{lll}
\hline
Bulk Na$_8$@Si$_{146}$ & 0.84 & bulk I$_8$@Si$_{146}$ & $\sim$1.73 \\
Na$_2$@Si$_{100}$H$_{60}$ ND & 0.91 & I$_2$@Si$_{100}$H$_{60}$ ND & $\sim$0.89 \\
Na$_2$@Si$_{175}$H$_{80}$ ND & 0.71 & I$_2$@Si$_{175}$H$_{80}$ ND & $\sim$1.09 \\
Na$_2$@Si$_{150}$H$_{60}$ NW & 0.52 & I$_2$@Si$_{150}$H$_{60}$ NW & $\sim$1.17 \\
\hline
\end{tabular}
\end{table}
51 Each i-Si ND is rotated 180° about the wire axis against its adja-
cent i-Si NDs.
52 Note that LDA underestimates the energy of unoccupied states.
Actually, in our theoretical framework, the band gap energy of
the bulk cd-Si is 0.51 eV, which is smaller than experimental
value of 1.17 eV by 0.66 eV.
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