

## Effect of surface reconstruction on the structural prototypes of ultrasmall ultrabright Si<sub>29</sub> nanoparticles

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We propose, using density functional, configuration interaction, and quantum Monte Carlo calculations, structural prototypes of ultrasmall ultrabright particles prepared by dispersion from bulk. We constructed near spherical structures (Td point group symmetry) that contain 29 Si atoms, five of which constitute a tetrahedral core and the remaining 24 constitute a hydrogen terminated reconstructed Si surface. The surface is a highly wrinkled or puckered system of hexagons and pentagons (as in a filled fullerene). We calculated, for several surface reconstruction models, the coordinates of atoms, the absorption spectrum, the absorption edge, polarizability, and the electron diffraction pattern. The Si<sub>29</sub>H<sub>24</sub> (six reconstructed surface dimers) gives a size of 0.9 nm, an absorption spectrum and bandgap (3.5±0.3 eV), in fair agreement with measurement. The structure yields a polarizability of 830 a.u. with an effective “dielectric” constant of ~6.0. The calculated electron diffraction of single particles shows residual crystalline coherent scattering for large but not small scattering angles. © 2001 American Institute of Physics. [DOI: 10.1063/1.1356447]

Bulk crystalline silicon has been recently dispersed into ultrasmall luminescent Si nanoparticles with electronic and optical properties.<sup>1–4</sup> The particles are ultrabright blue luminescent such that emission from single particles is readily detectable.<sup>1</sup> The emission from aggregates of the particles exhibit highly nonlinear stimulated emission,<sup>2</sup> collimated blue beam emission,<sup>3</sup> and exhibit second harmonic generation.<sup>4</sup> The particle’s capacitance is small enough such that single electron charging energy or the quantum confinement electronic energies are much larger than the thermal agitation energy at room temperature or higher.<sup>5</sup> Direct transmission electron microscopy imaging shows that the particles are ~1 nm in diameter with spherical shape. Auger electron and infrared spectroscopy show that they are hydrogen terminated with reconstructed surface. The particles may, however, be prepared with an oxygen termination.<sup>6</sup>

In this letter, we explore, using a combination of the density functional generalized approximation, single excitation configuration interaction, and quantum Monte Carlo computation,<sup>7–10</sup> some structural prototypes and properties of near spherical ultrasmall Si particles scaled down from bulk. We determine the coordinates of the atoms, absorption spectrum, absorption edge, and polarizability for several surface reconstruction models. One interesting structure contains 29 atoms, five of which constitute a single tetrahedral core and the remaining 24 constitute a hydrogen terminated reconstructed Si surface (Si<sub>29</sub>H<sub>24</sub>, with six reconstructed surface dimers). The surface is a highly wrinkled or puckered system of hexagon and pentagon rings. The relaxed prototype gives a diameter of 0.9 nm, an absorption spectrum and absorption edge (3.5±0.3 eV), giving the best agreement with measurement. The structure yields a polarizability of

830 a.u. with an effective dielectric constant of ~6.0 (12% accuracy), a drop by a factor of 2 from bulk. The calculated electron diffraction shows residual crystalline coherent scattering for large but not small scattering angles.

The computational search started from a spherical piece of a crystalline bulk Si which, for a size of ~1 nm, contains 29 atoms (magic number for the Td point group symmetry). We examined several surface models with hydrogen saturation and reconstruction of the dangling bonds. The absorption edge is known to increase with hydrogen saturation because dangling bonds produce extra states in the gap. We examined three surface structures. All dangling bonds were first terminated by hydrogen resulting in the Si<sub>29</sub>H<sub>36</sub> system as shown in Fig. 1(a). By eliminating 12 H atoms, we arrived at a structure of Si<sub>29</sub>H<sub>24</sub> [shown in Fig. 1(b)] with six recon-

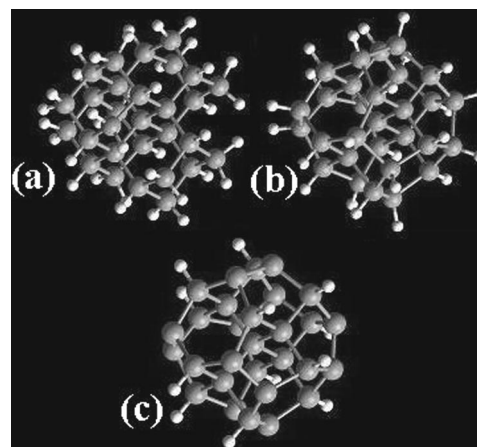


FIG. 1. Configuration structures of a particle that contains 29 atoms (magic number for the Td symmetry and spherical shape). Silicon atoms (gray), and hydrogen atoms (white). (a) All dangling bonds are saturated with hydrogen. (b) Twenty-four of the 36 dangling bonds are terminated by hydrogen with six reconstructed surface Si dimers. (c) Twelve of the 36 dangling bonds are terminated by hydrogen with 12 reconstructed surface Si dimers.

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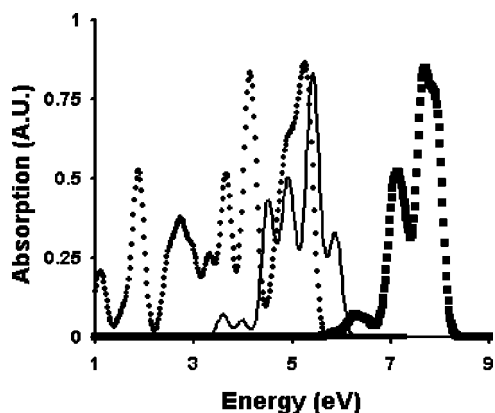


FIG. 2. The calculated absorption spectrum of the structures given in Fig. 1, with a Gaussian broadening of 0.12 eV.  $\text{Si}_{29}\text{H}_{36}$  (no surface reconstruction) (dotted), and  $\text{Si}_{29}\text{H}_{24}$  (solid) and  $\text{Si}_{29}\text{H}_{12}$  (solid square).

structed surface H–Si–Si–H dimers in a manner similar to the well-known Si(001) surface  $2\times 1$  reconstruction.<sup>8</sup> Reconstructed Si–Si bonds have recently been proposed as a source of optical activity in ultrasmall particles.<sup>11,12</sup> Eliminating 24 H atoms, we arrived at a structure of  $\text{Si}_{29}\text{H}_{12}$  [shown in Fig. 1(c)] with 12 reconstructed surface dimers. The resulting structures were then relaxed using the density function theory (DFT) with the PW91 exchange-correlation functional.<sup>7</sup> The coordinates of the atoms in the relaxed  $\text{Si}_{29}\text{H}_{24}$  particle ( $x, y, z$ ) in angstroms (Td point group symmetry) are as follows. There are twelve atoms with positions at  $(-2.72\ 321\ 736\ 7, -2.72\ 321\ 736\ 7, -0.019\ 165\ 260\ 3)$  and their permutations. Another 12 atoms are at  $(-3.932\ 353\ 408\ 4, 0.0885\ 964\ 176\ 3, -0.885\ 964\ 176\ 3)$  and the permutations. Four atoms are at  $(-1.393\ 665\ 252\ 7, -1.393\ 665\ 252\ 7, -1.393\ 665\ 252\ 7)$  and their permutations. Finally, the center atoms is located at  $(0.000\ 000\ 000\ 0, 0.000\ 000\ 000\ 0, 0.000\ 000\ 000\ 0)$ . The surface atoms form four hexagonal rings. Three atoms from a surface hexagonal ring with three of the internal tetrahedral unit (one is the center atom) form a hexagonal ring. There is a total of eight of such hexagons; those slice the particle as deep as the center, creating deep ridges. There is also a total of eight pentagon rings, each is formed by four surface atoms and one of the tetrahedral internal atoms (excluding the center atom). The participation of the internal atoms in ring formation makes the particle highly wrinkled or puckered.

We next calculated the optical absorption spectrum. We employed the configuration interaction singles (CIS) method<sup>9</sup> which constructs the wave functions with correct spatial and spin symmetries and which accommodates, to the first order, a part of the excitonic effects. Although the relative amplitudes and positions of the peaks are usually well reproduced in the CIS approach, the whole spectrum is shifted towards higher energies due to the incomplete treatment of the electron correlation effects. We used quantum Monte Carlo calculations<sup>10</sup> of the first two transitions ( $T1 \rightarrow T2$ ) which correspond to the edge of the absorption spectrum to correct for an overall shift of the spectrum. The calculated spectra were then treated with a Gaussian broadening of 0.12 eV, which qualitatively takes into account the temperature and any experimental size averaging effects. The resulting spectra for the three cases are shown in Figs. 2(a)–

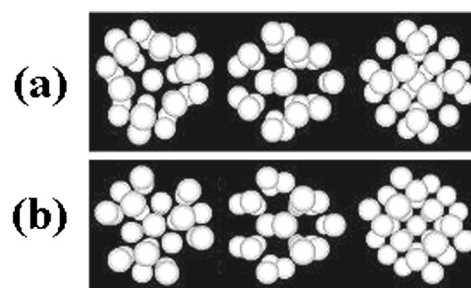


FIG. 3. Structural prototype of (a)  $\text{Si}_{29}\text{H}_{24}$  and of (b)  $\text{Si}_{29}\text{H}_{36}$  for three orientations, viewed along axes 111, 011, and 100 (from left to right).

2(c). The figures show that the spectra have pronounced molecular (discrete) patterns. The absorption edge of the  $\text{Si}_{29}\text{H}_{36}$  particle is  $\sim 4.8$  eV and the spectrum consists of three peaks at 5.5, 6.3, and 7 eV. The absorption edge of  $\text{Si}_{29}\text{H}_{24}$  is  $\sim 3.5$  eV, and the spectrum consists of three bands centered at  $\sim 3.7, 4.8,$  and  $5.5$  eV. The absorption spectrum of  $\text{Si}_{29}\text{H}_{12}$  is quite complex with very low absorption edge (about 0.1 eV).

We now examine the dielectric properties of the prototype structures. We calculate the polarizability, a uniquely defined property. We used two independent approaches (DFT and Hartree–Fock) and with increasing accuracy of the basis set from 6-31G\* to 6311-G\*\*. The calculated polarizability of  $\text{Si}_{29}\text{H}_{24}$  is 830 a.u. with an accuracy of about 12%. A general definition of a dielectric constant in semiconductor nanoparticles is not possible since the energy levels are discrete (as demonstrated in Fig. 1). However, to get a feel, we estimated an effective dielectric constant. From the coordinates of the atoms in the prototype, and assuming that the distance between the center and the outermost Si atom is an effective interior radius ( $\sim 4.2$  Å), hence, defining an appropriate “cluster interior volume,” we get an effective dielectric constant of  $\sim 6.0$  with 20% accuracy. Similar procedures give a polarizability of 970 a.u. for the  $\text{Si}_{29}\text{H}_{12}$  surface model, and 807 a.u. for the  $\text{Si}_{29}\text{H}_{36}$  surface model.

It is interesting to calculate electron diffraction from single particles. Figure 3 gives structural prototype of  $\text{Si}_{29}\text{H}_{24}$  and  $\text{Si}_{29}\text{H}_{36}$  for three orientations, along axes 111, 110, and 100. We use a standard electron-atom potential. Figure 4 gives the results. The diffraction pattern with no surface reconstruction ( $\text{Si}_{29}\text{H}_{36}$ ) for three orientations along the 111, 110, and 100 directions show coherent electron diffraction. The figure also shows the corresponding results for  $\text{Si}_{29}\text{H}_{24}$ . There is a strong loss of the crystalline pattern at small scattering angles. Since the small angle scattering is dominated by the response from the outer part of the particle, then this loss of the coherent dot pattern reflects the strong reconstruction on the surface of the particle. On the other hand, we can still see the coherent dot pattern for large scattering angle. A large angle scattering is dominated by the core of the particle. This is interesting since the core consists of only one tetrahedral unit.

Absorption measurements in the UV/visible/near-infrared were carried out using a spectrophotometer. The procedure for the synthesis of the particles and characterizations were described elsewhere.<sup>1–6,13</sup> The absorption of a pure solvent sample was recorded under the same beam conditions. Figure 5 gives the measured absorption with the nor-

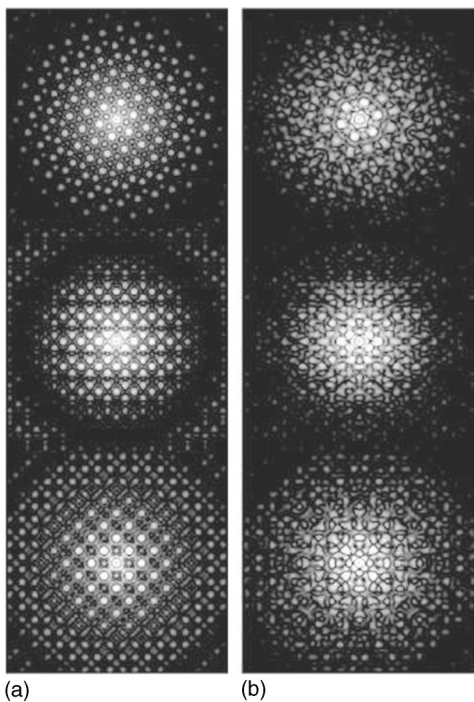


FIG. 4. Calculated electron diffraction patterns for three orientations, along 111, 110, and 100 from top to bottom. (a) No surface reconstruction ( $\text{Si}_{29}\text{H}_{36}$ ). (b) With surface reconstruction ( $\text{Si}_{29}\text{H}_{24}$ ).

malized calculated spectra for  $\text{Si}_{29}\text{H}_{24}$ . The overall spectrum and relative band strengths of the  $\text{Si}_{29}\text{H}_{24}$  prototype present a fair agreement with the measured band spectrum, however, the details of the structure may differ (at  $\sim 5$ , and 3.6 eV for example). It is interesting to compare the absorption spectrum of the particle with that of bulk. The absorption coefficient

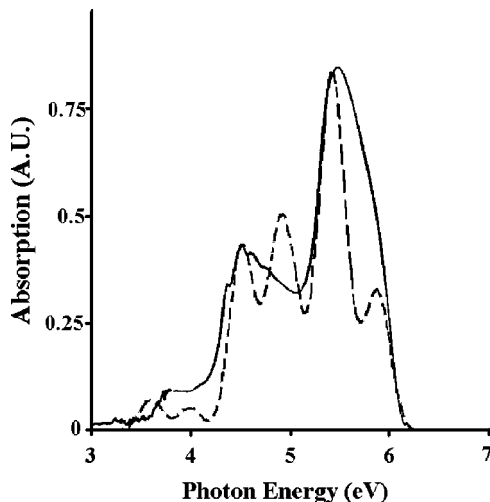


FIG. 5. The calculated absorption spectrum of the prototype structure  $\text{Si}_{29}\text{H}_{24}$  (dotted), along with the experimental spectrum of the particles (solid).

of bulk silicon (not shown) is immediately recognizable by the three band features near 3.5, 4.5 eV, and  $E_1$  and  $E_2$  bands, and the 5.5 eV band.<sup>14</sup> The measured particle spectrum shows generally a three-band structure which may be associated with those of the crystalline resonance signature, however, with different details. Contrary to crystalline silicon, the band at  $\sim 3.5$  (excitonic transition) has become the weakest in the particle spectrum. Second, contrary to crystalline bulk, the 5.5 eV band has become the strongest among the transitions in the particle spectrum. The  $E_2$  band at  $\sim 4.5$ , strongest in bulk, is now the intermediate strength band in the particle spectrum.

In conclusion, we constructed spherical structures that contain 29 atoms with five atoms constituting a tetrahedral core and 25 atoms constituting a hydrogen-terminated reconstructed Si surface. The  $\text{Si}_{29}\text{H}_{24}$  (six reconstructed surface dimers) gives a size of 0.9 nm, an absorption spectrum and band gap ( $3.5 \pm 0.3$  eV) that is in fair agreement with measurement. The structure yields an effective dielectric constant of  $\sim 0.6$ . The simulated electron diffraction of single particles shows residual crystalline coherent scattering for large scattering angles, but not for small angle scattering.

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