

## Using Silicon to Understand Silicon: Doping of Nanostructures

by James R. Chelikowsky

It is often said that silicon is the quintessential building material for electronic devices. However, silicon is more than a building material. It is a very special material that allows us to build computers, and to learn much about the electronic properties of materials, *e.g.*, these computers built with silicon can be used to solve for the electronic properties of silicon itself. To illustrate this situation, an example is given of how computational approaches can be used to understand the behavior of dopants in silicon at the nanoscale.

Silicon is the material of our time. We live in the age of silicon; it is all around us in terms of electronic gadgets and computers. However, it has not always been that way. Before the 1940s, transistors did not exist at all and in the early 1950s, transistors were made of germanium, not silicon. These germanium transistors were not reliable; in particular they were difficult to package and process. This changed by the mid-1950s, when silicon transistors were developed. Within about fifteen years after the invention of the transistor, a silicon chip containing over two thousand transistors was constructed. Today, the Pentium-4 processor made by Intel contains 42 million transistors.<sup>1</sup> By the end of this decade, we should see a processor containing one billion transistors. This is an amazing and unprecedented progression of technology, which has affected all of science. Specifically, an accompanying revolution in our understanding of the theory of materials has accompanied this technological revolution. Silicon technology has provided a material for serving both as a testing ground material and as the basic material for computational tools to study the properties of materials.<sup>2</sup>

One measure of scientific impact is to examine the technical literature. Suppose we examine the number of scientific papers on silicon published since the discovery of the silicon chip. A quick search of the scientific and engineering literature suggests that over a quarter of a million papers have been written over the last 30 years that mention silicon.<sup>1</sup> Many of these papers are not directly related to silicon technology or silicon science, but a good fraction is.

For a theorist interested in electronic materials research, this is a "treasure trove" of information. Specifically, this vast database can be used to test and benchmark theoretical methodology and approximations. This is an imperative

activity as the quantum theory of materials deals with extraordinarily complex materials. In a macroscopic crystal of silicon, one has about  $10^{23}$  electrons and nuclei. In principle, the application of the known laws of quantum mechanics allows

one to predict all physical and chemical properties of such a system. However, given the astronomical number of particles, it is absolutely hopeless to extract physically meaningful results without some dramatic approximations. What approximations will work and how well? An obvious answer to this question is to test methods using the silicon database as a reference. This has been the route used by most condensed matter theorists, at least those interested in the electronic properties of solids (and liquids).

### Pseudopotentials and Density Functional Theory

The first realistic energy band diagrams for electronic materials were constructed using silicon data. These band diagrams provided information on transport, optical, and photoemission spectra. They were constructed using empirical methods based primarily on optical data to solve the one-electron Schrödinger equation.<sup>3</sup>

To solve such an equation, the electronic interactions must be accurately described. One can approximate these electronic interactions by a potential that contains the average interactions of all the chemically active (valence) electrons within the system. In the 1960s, these potentials (called pseudopotentials) were developed and applied to silicon and related materials.<sup>3</sup> Establishing the accuracy of these potentials was a key test and the results were strikingly successful. One may accurately replicate the experimental results with only a few parameters. If this initial test had failed, it would have suggested that a one-electron description of matter was not possible.

In more recent work, electronic potentials were fixed not by experiment, but from first principles. These first principles pseudopotentials often rely on density functional theories, which are exact in principle, but in practice rely on various

approximations such as the local density approximation. A solution to the electronic structure is obtained in this approach from the Kohn-Sham equation<sup>4,5</sup>

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V_{ion}(r) + V_H(r) + V_{xc}(r) \right] \Psi_n(r) = E_n \Psi_n(r) \quad [1]$$

where  $V_{ion}$  is the ion-core pseudopotential,  $V_H$  is the Coulomb or Hartree potential, and  $V_{xc}$  is the effective exchange-correlation potential. The Hartree potential is obtained by solving the Poisson equation

$$\nabla^2 V_H(r) = -4\pi e \rho(r) \quad [2]$$

where  $\rho$  is the charge density given by

$$\rho(r) = -e \sum_{occup} |\Psi_n(r)|^2 \quad [3]$$

The summation is over all occupied states. Within the local density approximation, the  $V_{xc}$  potential is functional of the charge density:  $V_{xc} = V_{xc}[\rho]$ .

Solving the Kohn-Sham problem corresponds to the construction of a self-consistent screening potential ( $V_H$  and  $V_{xc}$ ) based on the charge density. The ion-core pseudopotential is based on an atomic calculation, which is easy to implement.<sup>6,7</sup> For silicon, the ion-core potential corresponds to the nuclear charge plus the screening potential from the core electrons ( $1s^2 2s^2 2p^6$ ). The pseudopotential when so screened yields the same solution as the all electron potential, save for the charge density near the core region.

Once the Kohn-Sham equation is solved, the total electronic energy of the system can be obtained from knowledge of the energy levels and wave functions

$$E_{Total} = \sum_{occup} E_n - \frac{1}{2} \int V_H \rho d^3r + \int (E_{xc} - V_{xc}) \rho d^3r + E_{ion-ion} \quad [4]$$

The sum is over all occupied states. The second term subtracts off the double counting terms. The third term subtracts off the exchange-correlation potential and adds in the correct energy density functional. The last term is the ion-ion core repulsion term.

Silicon played a crucial role in assessing the validity of this approach, which has proved to be reasonably accurate

for electronic materials. Typically, bond lengths may be calculated to within a few percent, although chemically accurate bond energies are more problematic. Initial applications of first principles pseudopotentials constructed within the local density approximation included studies of silicon polymorphs under pressure.<sup>8</sup> This work produced some rather remarkable predictions, *e.g.*, it predicted some high-pressure forms of silicon would be *superconducting*.<sup>9</sup> This prediction was later confirmed by experiment. Also, the first *quantum* molecular dynamics simulations were done on silicon, including the first theoretical studies to examine the electronic and structural properties of liquid silicon and amorphous silicon.<sup>10,11</sup>

### New Algorithms: Silicon Leads the Way

The Kohn-Sham problem, cast within the pseudopotential-density functional formalism, is easy to solve for simple elemental crystals such as silicon. For crystalline materials, the number of degrees of freedom is dramatically reduced by symmetry, *i.e.*, the use of Bloch wave functions.<sup>7</sup> However, for systems with little symmetry, the Kohn-Sham problem remains difficult. Confined systems such as fragments of the bulk crystal, or extended systems such as an amorphous solid or a liquid are examples of such systems. In these systems, the solution of the Kohn-Sham equation involves many degrees of freedom and often scales poorly with the number of electrons in the system. Any solution of this complex problem must be handled by making several numerical and physical approximations.<sup>7</sup> Computing the electronic struc-

ture of a known material such as silicon can test these approximations.

Here we briefly outline a popular algorithm for describing the electronic structure of a localized system. This algorithm solves the Kohn-Sham equation on a grid in real space.<sup>12</sup> This method was first tested against traditional solutions for silicon clusters and quantum dots. The real space approach, as opposed to reciprocal space methods, has become popular and several groups have implemented different variations of this general approach.<sup>13-16</sup>

We illustrate a particular version of real space approaches based on high-order

finite differencing.<sup>12,17</sup> This approach overcomes many of the complications involved with non-periodic systems such as replicating the vacuum, and although the resulting matrices can be larger than with other methods such as plane waves, the matrices are sparse. Also, real space methods are easier to parallelize than methods using plane waves.<sup>17</sup> Even on sequential machines, we find that real space methods can be an order of magnitude faster than plane wave methods.<sup>17</sup>

Real space algorithms avoid the use of fast Fourier transforms (FFTs) by performing all calculations in real physical space instead of Fourier space. A benefit of

avoiding FFTs is that the new approaches have few communications between processors. A key aspect to the success of the finite difference method is the availability of high-order finite difference expansions for the kinetic energy operator. High-order finite difference methods significantly improve convergence of the eigenvalue problem when compared with standard finite difference methods. If one imposes a simple, uniform grid on our system where the points are described in a finite domain by  $(x_i, y_j, z_k)$ , we approximate

$$\frac{\partial^2 \psi(x_i, y_j, z_k)}{\partial x^2} = \sum_{n=-M}^M C_n \psi(x_i + nh, y_j, z_k) + O(h^{2M+2}) \quad [5]$$

where  $h$  is the grid spacing,  $C_n$  are expansion coefficients, and  $M$  is a positive integer. This approximation is accurate to  $O(h^{2M+2})$  given the assumption that  $\psi$  can be accurately approximated by a power series in  $h$ . This is a good assumption if *pseudopotentials* are used. Algorithms are available to compute the coefficients  $C_n$  for arbitrary order in  $h$ .<sup>18</sup>

With the kinetic energy operator expanded as in Eq. 5, one can set up the Kohn-Sham equation over a grid. One may assume a uniform grid, but this is not a necessary requirement.  $\psi(x_i, y_j, z_k)$  is computed on the grid by solving the eigenvalue problem

$$\begin{aligned} & \frac{-\hbar^2}{2m} \left[ \sum_{n_1, n_2, n_3=-M}^M C_{n_1 n_2 n_3} \psi_n(x_i + n_1 h, y_j + n_2 h, z_k + n_3 h) \right] \\ & + [V_{ion}(x_i, y_j, z_k) + V_H(x_i, y_j, z_k) + V_{xc}(x_i, y_j, z_k)] \psi_n(x_i, y_j, z_k) \\ & = E_n \psi_n(x_i, y_j, z_k) \end{aligned} \quad [6]$$

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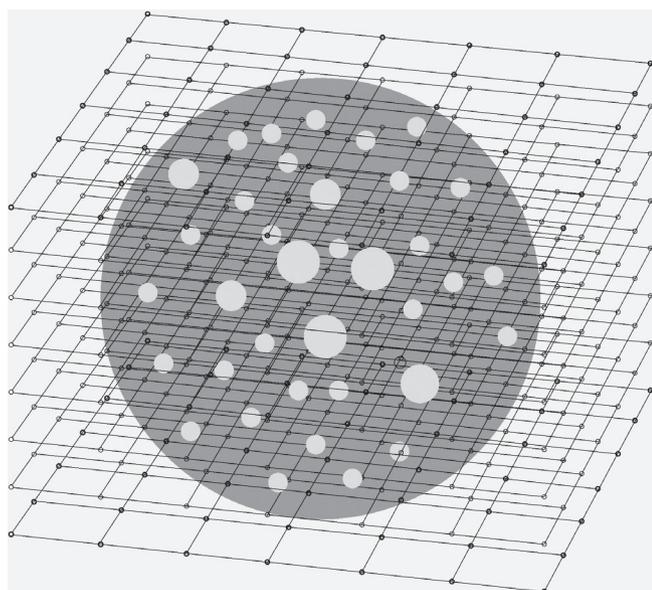


Fig. 1. Real space grid configuration for atoms (light spheres) within a confined domain (gray sphere). Outside the domain, the wave functions vanish.

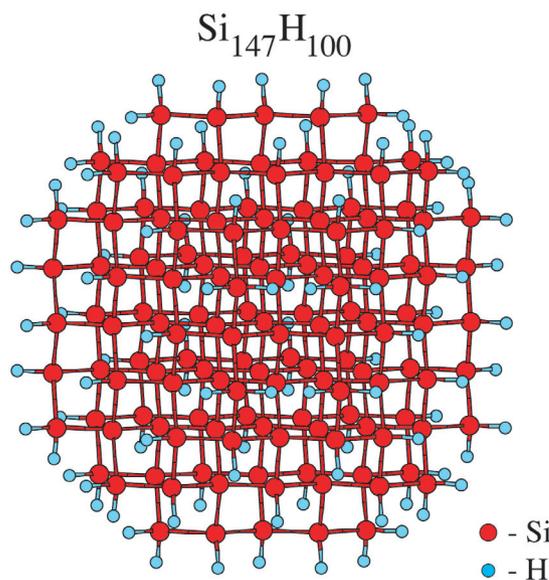


Fig. 2. Small quantum dot of silicon. The surface is passivated with H atoms; the interior structure corresponds to a bulk fragment.

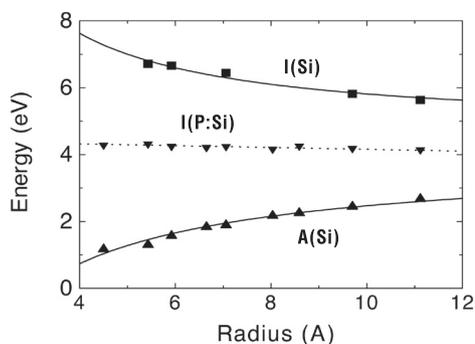


FIG. 3. Ionization energy of undoped Si quantum dot,  $I(\text{Si})$ , ionization energy of a doped dot,  $I(\text{P:Si})$ , and the electron affinity of an undoped dot,  $A(\text{Si})$ .

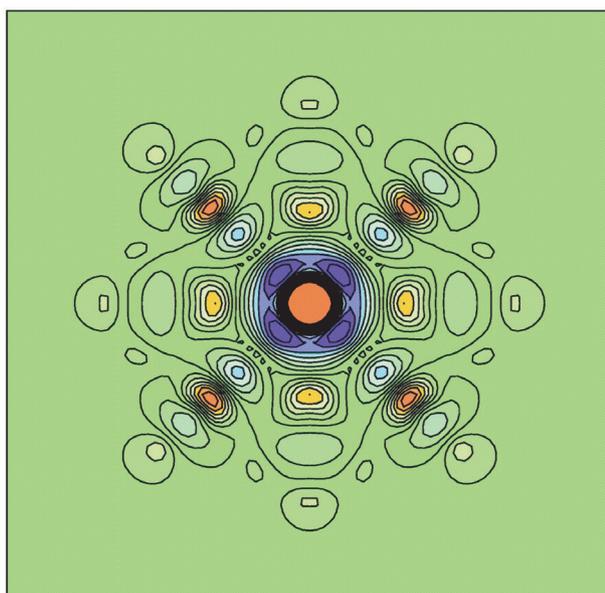


FIG. 4. Colorized contour map of the donor state charge density. The (100) plane shown is illustrated with the P atom in the center of the dot.

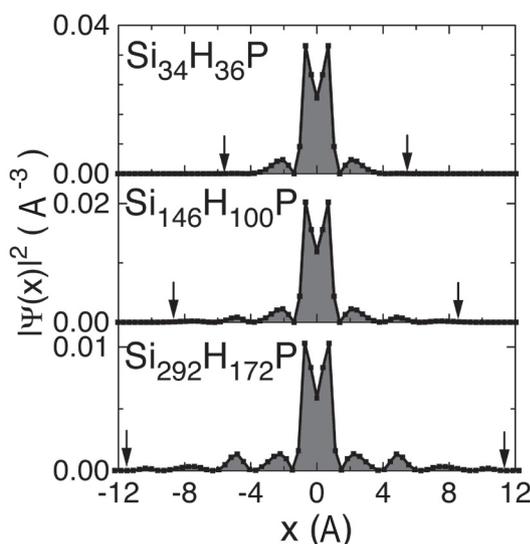


FIG. 5. Charge density of the donor state localized around the P atom. The arrows indicate the physical size of the quantum dot.

A typical uniform grid configuration is illustrated, which examines the electronic structure of a localized system in Fig. 1. In this illustration, a cluster is shown. Outside a given domain the wave functions must vanish.

### Doping in Silicon Quantum Dots

In nanocrystals or quantum dots, where the motion of electrons (or holes) is limited in all three dimensions, one expects that both electronic and optical properties will be affected as well. For example, in bulk semiconductors, shallow donors (or acceptors) are crucial in determining the transport properties required to construct electronic devices.<sup>19</sup> However, these properties are significantly altered in highly confined systems such as quantum dots. Important questions arise as to whether dopants will continue to play a role similar to that in bulk semiconductors and whether new applications such as quantum computation will become possible.

As is typical for electronic materials, these questions have been explored in small fragments of silicon, typically passivated with hydrogen atoms. In Fig. 2, we illustrate such a system containing over a hundred silicon atoms. To examine the role of a dopant atom, one may consider such a dot doped with a single phosphorus atom.<sup>19</sup> In such a system, the binding environment of the phosphorus-silicon bond may be strongly modified, due to quantum confinement, resulting in a large change in the electron ionization energy of the phosphorus donor electron.

We can calculate the electron affinity ( $A$ ) and ionization energies ( $I$ ) by calculating the total energy of the system in different charge states

$$I = E_{\text{Total}}(N-1) - E_{\text{Total}}(N)$$

$$A = E_{\text{Total}}(N) - E_{\text{Total}}(N+1) \quad [7]$$

In a crystal, one can calculate the bonding energy of a donor electron by finding the energy difference in ionizing the phosphorus atom relative to adding an electron to an undoped crystal. The donor energy,  $E_d$ , is given by

$$E_d = A(\text{Si}) - I(\text{P:Si}) \quad [8]$$

where  $I(\text{P:Si})$  represents the ionization energy of the doped crystal and  $A(\text{Si})$  represents the energy of the undoped crystal. For a crystal,  $E_d$  is typically a few millielectronvolts. Owing to quantum confinements, the situation is quite different for a quantum dot.

The ionization and affinity energies as a function of quantum dot radius,  $R$ , are shown in Fig. 3. The ionization energies for undoped hydrogenated Si nanocrystals are also given for comparison. The most striking feature in Fig. 3 is

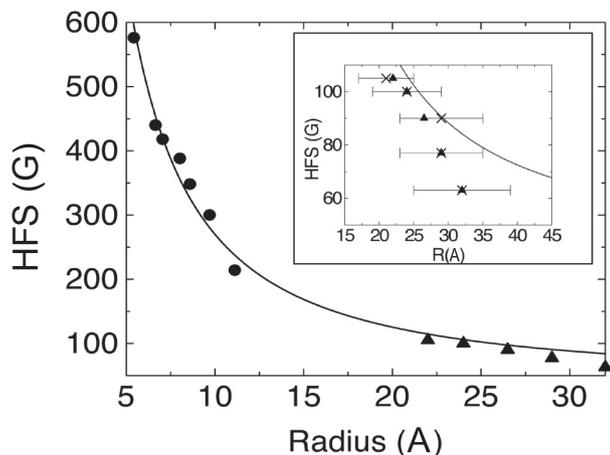


Fig. 6. Calculated (●) and experimental (▲) hyperfine splitting (HFS) vs. the radius,  $R$ , of the quantum dot. The solid line is the best fit to the calculated values. The inset shows experimental data of Ref. 20 together with the fit to results of the calculations.

that the ionization energy for the doped dot shows a very weak dependence on the size of the dot. The size dependence of ionization energy is different from the behavior of the ionization energy in undoped Si quantum dots where this quantity is very large at small radii and gradually decreases, scaling as  $R^{-1.1}$ . Although this dependence of the ionization energy on radius is weaker than  $R^{-2}$  law predicted by effective mass theory, it is, nevertheless, a consequence of spatial confinement of electrons (holes) in quantum dots. The absence of a strong dependence of the ionization energy in a doped dot is largely due to the weak screening present in quantum dots and the physical confinement of the donor electron within the dot. From Fig. 3, it is clear that the donor energy,  $E_d$ , is on the order of several electronvolts, not several millielectronvolts as for the bulk crystal. In this sense, phosphorus is not a shallow donor in nanoscale silicon dots.

Figure 4 illustrates the charge density of the donor states in the Si quantum dot. This plot shows the square of the wave function for the highest occupied state. This plot confirms the localization of the charge around the phosphorus atom. This may be quantified by examining the density plotted along a line through the P atom as shown in Fig. 5.

Given the charge distribution of the dopant electron, one can evaluate the isotropic hyperfine parameter and the corresponding hyperfine splitting (HFS), which is determined by the contact interaction between the electron and defect nuclei.<sup>20</sup> The method by van de Walle and Blöchl allows one to extract the isotropic hyperfine parameter and the resulting HFS from knowledge of the charge density at the nuclear site.<sup>21</sup> The calculated HFS for a P atom positioned in the dot center are given in Fig. 6.

At small sizes, the HFS is very large owing to strong localization of the electron around the impurity. As the radius increases, the value of the splitting decreases. Our calculated results scale

with radius of the dot as  $R^{-1.5}$  (effective mass theory gives  $R^{-3}$ ).<sup>19</sup> In Fig. 6, we also present experimental data.<sup>20</sup> The measured values of the HFS fall on the best fit to calculated results with the limit of the fit constructed to approach the bulk value. Computational limitations prevent direct comparison to the experimental size regime.

No strong dependence was found on the choice of the P site. We examined other sites by replacing one Si atom in each shell with a P atom while retaining the passivating hydrogen atoms. We found that the ionization and binding energies were unchanged to within 5%, independent of the impurity atom position, save for the surface site.

This work illustrates how computational work may be used to describe doping in silicon nanostructures. Other work on these quantum dots includes extensive studies of the optical properties and recent studies on nanowires composed of silicon.

### The Future

Will silicon continue to play such an important role in understanding the electronic properties of materials? I suspect it will. As almost everyone knows, Gordon Moore, a pioneer of silicon technology, predicted in 1965 that the number of transistors per integrated circuit would double every 12 months, expanded to 18 months in 1975. Moore's law has worked for the past three decades and many predict that it will hold for the remainder of this decade and perhaps beyond. As long as Moore's law holds for silicon technology, I see no reason why silicon will not continue to be the testing ground for new theoretical tools for the foreseeable future. ■

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