

Designing Opto-Electronic Nanomaterials Using First Principles Simulations

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ABSTRACT

When the dimensions of a material are reduced to the nanoscale, many of its physical properties change dramatically from those of the bulk material. In semiconductor materials, such as silicon, the enhanced surface to volume ratio at the nanoscale results in an increased influence of the size, shape and surface chemistry on the relative structural stabilities of different silicon nanostructures. Additionally, when the dimensions of the material are reduced below the size of the exciton radius, the electronic and optical properties of the material become increasingly size dependent.

In this paper, we review the results of recent first principles, quantum mechanical simulations of the structural, electronic and optical properties of silicon nanomaterials. We show how these simulations can be used to interpret existing materials synthesis and characterization experiments, and, in particular how to use simulations in combination with experimental measurements to characterize the properties of nanoscale materials that are too small to be directly imaged and measured. We also demonstrate how to use first-principles simulations to design novel nanoscale materials with customized electronic and optical properties.

Keywords: Quantum dots, nanowires, silicon, density functional theory, simulations

1 FIRST PRINCIPLES METHODS

In this paper, we report the results of Density Functional Theory (DFT) and Quantum Monte Carlo (QMC) calculations of the structural, electronic and optical properties of silicon nanomaterials. The DFT calculations were performed using the QBox and PWSCF packages using the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) functionals. The silicon atomic cores are represented by norm conserving pseudopotentials. The wavefunctions describing the valence electrons are expanded in a plane wave basis set with an energy cutoff of 35 Ry. For each of the silicon nanostructures studied here, the initial atomic coordinates are calculated assuming the diamond structure of bulk silicon. The atomic surfactants that passivate the surface of the nanostructures are attached at bond lengths typical of the equivalent molecular species, e.g. hydrogen atoms are attached to surface silicon atoms at the experimental bond length from the SiH₄ molecule. The electronic structure is then calculated within DFT to obtain the groundstate charge density for the system. Using this

charge density, the forces acting on each of the atoms in the system are then calculated. These forces are then used to relax the atomic coordinates to their closet local energy minimum structure. Once the relaxed groundstate geometry has been calculated, the single particle band structure, band gaps, and effective masses are calculated. While DFT calculations are typically able to predict the bond lengths and angles of silicon materials to within 1% of the experimental values, they are well known to underestimate the calculation of the band gaps of the material. For example, DFT calculations using the standard LDA functional predict a band gap of silicon of 0.55 eV, compared to the experimental value of 1.1 eV. Therefore, in addition to performing DFT calculations, we use the structures calculated by DFT as input to more accurate

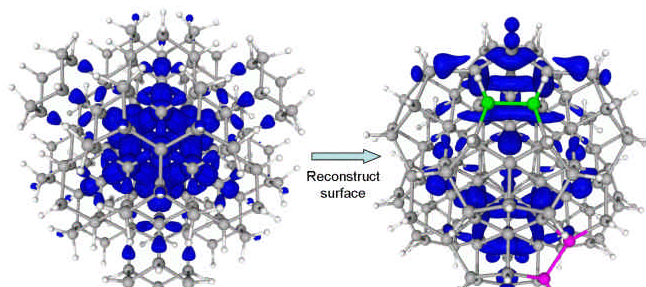


Figure 1 Structures of 2nm hydrogen terminated silicon quantum dots with ideal and reconstructed surfaces

QMC calculations of the total energy. We use the fixed node, Diffusion Monte Carlo (DMC) variant of QMC calculations, implemented within the CASINO QMC package.ⁱ The optical excitation energies of the system are calculated by performing two separate total energy calculations of the nanomaterial in its electronic groundstate and in an excited state. The difference in these two total energies provides is the optical excitation energy of the system. More details of our DFT and QMC approaches can be found in Refs i-v.

2 CALCULATIONS OF STRUCTURAL PROPERTIES

Using the DFT techniques described above, we have studied the structures and structural stabilities of a wide range of nanoscale silicon systems. In particular, we have examined zero dimensional silicon quantum dots^{ii,iii,iv}, or nanoparticles, and one dimension silicon nanowires.^v

Surface Reconstructions of Silicon Quantum Dots

When the dimensions of silicon are reduced to the nanoscale, the surface to volume ratio is dramatically enhanced compared to the bulk material. For example, in a silicon quantum dot, with a 2 nm diameter, half the silicon atoms are on the surface of the dot. Therefore, one anticipates that the structure and chemistry of the nanoparticle surface will exert considerable influence on its properties.

In the last twenty years, the relative stability of hydrogen terminated bulk silicon surfaces has been well documented. To understand how this picture will change at the nanoscale, we studied a series of silicon quantum dots with ideal hydrogen termination and reconstructed silicon surfaces.

Figure 1 shows the calculated atomistic structure of two hydrogen terminated silicon quantum dots with diameters of 2 nm.^{iv} The nanoparticle on the left was constructed by selecting an atom centered, spherical cluster of diamond structure silicon containing 148 silicon atoms. The dangling bonds on the surface were terminated with 120 hydrogen atoms creating a $\text{Si}_{148}\text{H}_{120}$ particle. The nanoparticle on the right was obtained by performing a (2x1) reconstruction of all the neighboring SiH_2 groups on the (001)-type facets of this structure. This reconstruction removes 48 hydrogen atoms creating a $\text{Si}_{148}\text{H}_{72}$ particle. The free energy of formation of each cluster was then calculated as a function of the chemical potential of hydrogen surrounding the cluster. Assuming the nanoparticles are surrounded by an H_2 gas at 1 atmosphere of pressure, these calculations predict that the surface will reconstruct from 120 hydrogen atoms to 72 hydrogen atoms at a temperature of 500K. Below 500K the chemical potential of H_2 is sufficiently high, that it is energetically favorable for as much hydrogen as possible to attach to the surface of the nanoparticle. Above 500K, the increased entropy of the hydrogen gas makes it energetically

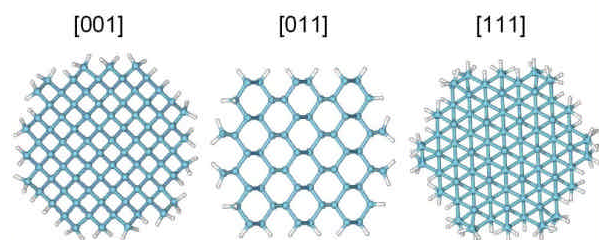


Figure 2 Cross sectional structures of [001], [011], and [111] silicon nanowires

favorable for the surface to reconstruct and hydrogen to leave the surface of the nanoparticle.

Relative Stabilities of Silicon Nanowires

We have also recently used similar DFT calculations to examine the relative stability of hydrogen terminated silicon nanowires.^v Silicon nanowires are typically grown in three specific directions; [100], [110], and [111]. The structure of the surface facets, the amount of hydrogen coverage, and the structural symmetry of the wires all depend on their growth direction.

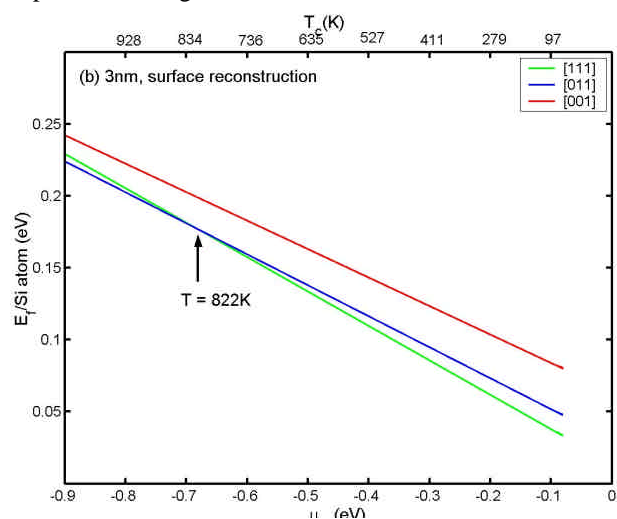


Figure 3 Relative formation energies of silicon nanowires grown in different directions

Figure 2 shows a cross sectional structure of silicon nanowires grown in these 3 directions. Figure 3 shows the results of a DFT calculation of the relative stability of hydrogen terminated, silicon nanowires, with a (2x1) surface reconstruction, grown along each of these directions as a function of the chemical potential of hydrogen in the surrounding gas. It shows that [001] wires have a higher energy of formation for chemical potentials of hydrogen, i.e. under synthesis conditions ranging from 100K to 1000K, [001] wires are never the most thermodynamically stable structure. Depending on the synthesis temperature, Figure 3 shows that DFT calculations predict that [111] wires will be most stable below 822K and [011] wires are the most stable above 822K. While the growth processes of silicon nanowires, for example using the Vapor-Liquid-Solid (VLS) procedure, are extremely complex and are probably controlled by a mixture of thermodynamic and kinetic factors, it is interesting to note that the thermodynamic study in Figure 3 does correctly predict the two growth directions, [011] and [111] that are most commonly observed during this growth process.

3 CALCULATIONS OF OPTICAL PROPERTIES

In addition to predicting the structures and structural stability of silicon nanostructures, first principles

simulations can also be used to predict their optical and electronic properties. Perhaps the most well known effect of reducing the dimensions of a semiconductor to the nanoscale is the quantum confinement effect, by which the optical gap of materials increases as their dimensions are reduced. This arises from the confinement of an exciton (an electron-hole pair) into a volume of space (the nanoparticle) which is smaller than it would ideally like to adopt. For example, the exciton radius in bulk silicon is 5 nm. When the dimensions of a silicon nanoparticle of wire are reduced by 5 nm, excitons in the material are confined by the potential barrier at the surface of the material. This increased confinement increases their kinetic energy and increases the optical gap of the material.

Size Dependence of the Optical Gap of Silicon Quantum Dots

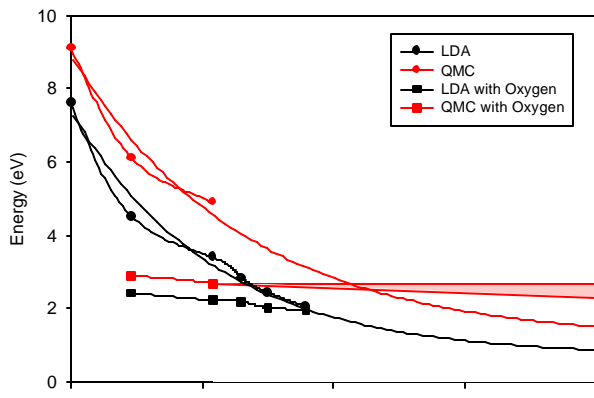


Figure 4 Size dependence of the band gap of hydrogen and silicon terminated quantum dots

Figure 4 shows the results of LDA-DFT and QMC calculations of this quantum confinement effect in hydrogen and oxygen terminated silicon quantum dots.^{ii,iii} It shows that in the absence of oxygen, quantum confinement effects increase the nanoparticle gap from 1 eV to 9 eV when the size is decreased from 4 to 1 nm. When oxygen is added to the surface of the nanoparticles, the excitonic states become localized on oxygen-silicon bonds on the nanoparticle surface. These states act like impurities or surface traps, effectively reducing the gap of the nanoparticle. When oxygen is present, even when the diameter is reduced to 1 nm, the gap never increases above 2.8 eV.

Silicon Quantum Dots Embedded in Silicon Nitride
Quantum confinement effects can also manifest themselves in semiconductor heterostructures, where optical excitons are confined within one semiconductor material that is surrounded by a host matrix. Figure 5 shows a structural model of a silicon nanoparticle surrounded by a Si_3N_4 matrix. In this extremely complex system, the optical properties are controlled by a mixture of quantum confinement effects in the silicon nanoparticle, strain

effects introduced by the lattice mismatch between the silicon nanoparticle and defect states introduced by dangling bonds at the interface between the Si nanoparticle and the host matrix. These defects include Si-N-Si bridge structures (highlighted by ellipses in the Figure 5). In a highly complex structure such as this, it is essential to have accurate first principles models as well as detailed experimental characterization to understand how the optoelectronic properties depend on the structure of the material.

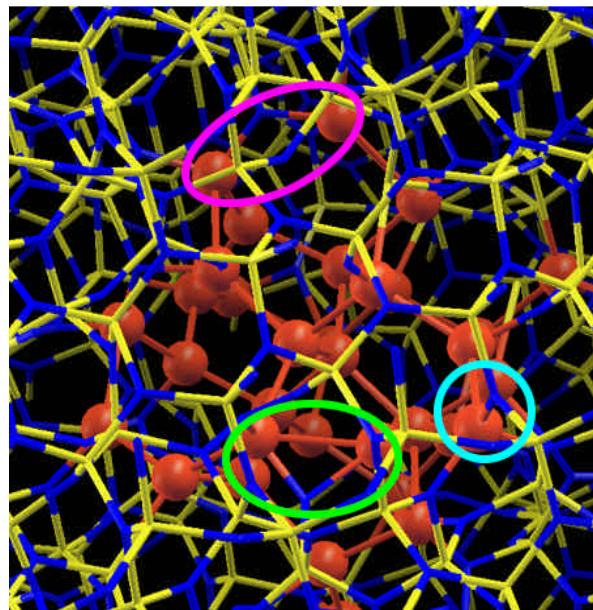


Figure 5. Silicon dot embedded in Si_3N_4

4 ELECTRICAL PROPERTIES

Effective Masses of Silicon Nanowires

DFT calculations can also be used to calculate the electronic band structure of nanoscale semiconductor materials. These bandstructure calculations can be used to extract properties, such as the effective mass of electrons and holes, which indicate how the electronic transport properties of nanomaterials will depend on their size, shape and structure. Our recent calculations of the electron effective masses of the silicon nanowires shown in Figure 2 indicate an extremely interesting result. For nanowires grown in [001] and [111] directions, the effective mass is larger than that of the bulk material, and as the diameter of the wire increases, the effective mass approaches the bulk value. However, for [011] nanowires, the symmetry of the electronic states is such that the electron effective mass is

below the bulk value and virtually independent of nanowire diameter. This reduced effective mass would directly translate into increased electron mobility in devices constructed from [011] nanowires.

5 CONCLUSIONS AND ACKNOWLEDGEMENTS

We have demonstrated that first principles simulations provide a powerful tool for predicted how the structural, optical and electronic properties of nanoscale semiconductor materials depend on their size, shape and chemistry. Due to their reduced dimensions and increased surface to volume ratio, the surface dominates many of the physical properties. These materials provide an exciting opportunity to design novel materials with tailored physical properties.

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