

Calculation of optical properties of Si nanostructures from first principles

S. Hamel* and A. Williamson*, H. Wilson**, F. Gygi**, G. Galli**, E. Ratner*** and D. Wack***
* Lawrence Livermore National Laboratory, **UC Davis, ***KLA Tencor

ABSTRACT

In this paper, we present an analysis of the dielectric properties of silicon slabs and rods as a function of size and shape, based on first principles, Density Functional Theory calculations (DFT). In particular, we discuss the relative influence of quantum confinement and surface effects, and propose a way to monitor changes in the dielectric properties at the nanoscale, based on the local dielectric response functions.

Keywords: dielectric response, DFT, rods, slabs, fin-FET

1 Introduction

For continued scaling of Si transistor performance, dual- or tri-gate FinFET architectures based on Si or Ge are candidates under research and development. When minimum dimensions of crystal Si nanostructures are scaled below 10nm, it is anticipated that quantum confinement effects will begin to influence the dielectric response. This poses a challenge to optical metrology techniques which in current practice assume bulk behavior for Si optical response (eg., piece-wise constant) when modeling the spectral signatures of diffracted or scattered optical beams. One such optical metrology is optical or spectroscopic scatterometry, which monitors the geometric profiles of periodic structures during semiconductor device fabrication by solving the inverse scattering problem. To gauge or avoid measurement bias in these or similar optical measurements, the size- and shape-dependence of Si/Ge optical response should be examined for relevant nanostructures.

However, for systems such as rods, methods based on DFT are only practical for sizes below 5 nm and it is difficult to extend them to the 5 - 25nm size regime of interest to many experiments. In order to couple theory to experiment for this important class of systems, we have developed computational techniques based on the Empirical Pseudopotential Method (EPM) [6]. Here we compare EPM and DFT results for small nanostructures to evaluate the sensitivity of the dielectric response to the hamiltonian.

The nature of dielectric response of nanostructures has been the subject of debate [4], [2], [7], [8]. While

there is agreement that the dielectric response is less than the bulk dielectric response for the same material, there are questions as to what is responsible for the decreased screening. When one considers the Adler-Wiser expression for the dielectric response [3],

$$\epsilon(G, G', \omega) = \delta_{G, G'} + 2 \frac{8\pi e^2}{N\Omega |\mathbf{q} + \mathbf{G}|^2} \times \sum_{v, c, \mathbf{k}} \frac{\langle v, \mathbf{k} | \exp(i[\mathbf{q} + \mathbf{G}] \cdot \mathbf{r}) | c, \mathbf{k} + \mathbf{q} \rangle \times \langle c, \mathbf{k} + \mathbf{q} | \exp(-i[\mathbf{q} + \mathbf{G}'] \cdot \mathbf{r}) | v, \mathbf{k} \rangle}{E(\mathbf{k} + \mathbf{q}) - E(\mathbf{k}) + \hbar\omega} \quad (1)$$

the presence of differences of energy between valence and conduction levels in the denominator makes it clear that unless the numerator compensates the rapid change in the value of the gap with size at the nanoscale, the value of the gap should have a strong impact on the dielectric response. Hence, models for the dielectric constant of quantum dots were proposed based on the bulk dielectric function with an added dependence on the direct gap [6], [7]. Since we consider vertical transitions between the bands, the opening of the gap may not be the most important metric to consider. At least at first, a gradual transfer from X to Gamma for the cbm is observed. This means that the direct gap (E2 peak) is not changing much in energy as the structure is confined and it eventually becomes the band gap. It is thus only when the direct gap changes that the "quantum confinement effects" should be observed.

Others argue that this is a surface effect [4], [5]. They find that the dielectric response is much smaller on the surface of slabs and rapidly goes to the bulk value in the core of the slabs. Hence, they argue, the effective dielectric response is small because of the increasing surface to volume ratio as slabs get smaller. Moreover, Nakamura *et al.* [9] conclude that the decrease in dielectric response for ultrathin slabs is due to the effective reduction of the depolarization field near the surface rather than quantum confinement. This is related to the fact that the induced surface charge penetrates slightly inside the slab. Delerue *et al.*, Nakamura *et al.* and Giustino and Pasquarello use a local quantity for the dielectric response. Compared to the complicated Adler-Wiser expression, a local dielectric response is much simpler yet as far as we know it is

not known how appropriate that approximation is for bulk or nanostructures. Assuming this approximation capture the essential physics and that the presence of less polarizable bonds at the surface is leading to the reduced screening found in the case of ultrathin slabs, one would expect that rods and clusters will show even less screening.

2 The Finite Electric Field Method

Here we outline the Finite Electric Field Method [1]. The dielectric tensor or relative permittivity tensor ϵ relates the electric displacement \mathbf{D} field to the total electric field \mathbf{E} :

$$\mathbf{D}(r) = \int d\mathbf{r}' \epsilon(\mathbf{r}, \mathbf{r}') \mathbf{E}(\mathbf{r}') \quad (2)$$

$$\mathbf{E}(r) = \int d\mathbf{r}' \epsilon^{-1}(\mathbf{r}, \mathbf{r}') \mathbf{D}(\mathbf{r}') \quad (3)$$

For the geometry of a slab, $\mathbf{D} = \epsilon_0 \mathbf{E}_0$ where \mathbf{E}_0 is the electric field applied in the absence of the dielectric. A simple first approximation to ϵ is that it is a constant such as "11" in the case of bulk silicon. Another is that the most important part of the screening comes from the point where the perturbation is applied, i.e. ϵ is a local function of position. As such it can be defined as the ratio between \mathbf{D} and \mathbf{E} . For a slab, using equation 3 and the particular case of a constant applied field \mathbf{E}_0 ,

$$\mathbf{E}(r) = \epsilon_0 \mathbf{E}_0 \int d\mathbf{r}' \epsilon^{-1}(\mathbf{r}, \mathbf{r}') \quad (4)$$

$$\bar{\epsilon}_{ij}(\mathbf{r}) = \epsilon_0 \frac{\mathbf{E}_0 \cdot \mathbf{i}}{\mathbf{E} \cdot \mathbf{j}} = \frac{1}{\int d\mathbf{r}' \epsilon_{ij}^{-1}(\mathbf{r}, \mathbf{r}')} = \frac{\mathbf{D}(\mathbf{r}) \cdot \mathbf{i}}{\mathbf{E}(\mathbf{r}) \cdot \mathbf{j}} \quad (5)$$

where i,j can be x,y,or z directions. \mathbf{D} and \mathbf{E} can be obtained from minus the gradients of the bare and screened potentials resulting from an electronic structure calculation.

3 Computational Details

The calculations were performed within the local density approximation (LDA). For each structure, the atomic coordinates were relaxed to the closest local minimum of the potential energy surface and then the opto-electronic properties were calculated for the relaxed structure. The calculations use norm conserving, Troullier-Martins pseudopotentials and a plane-wave basis with a 15 Ry energy cutoff. This cutoff is sufficient to get a converged dielectric response for the structures considered. The atomic relaxations were performed until the residual force on all atoms was lower than 10^{-3} eV/Å. The PWSCF [10] code was used for the structural relaxations. The dielectric response was evaluated with a in-house post-processing

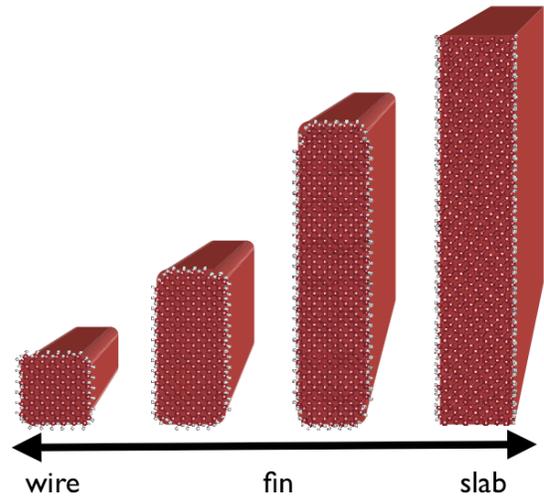


Figure 1: Planar average of the local value of the dielectric response for a 1.5 nm thick slab of hydrogen-terminated crystalline silicon. The peaks correspond to bonds and valleys to silicon atoms. There is a rapid decrease at the surface, corresponding to the outermost atomic layers.

code using the PWSCF electronic densities and potentials. The EPM calculations were done with an in-house code. A cutoff of 15Ry was also found to be necessary in this case to describe accurately the response of the density.

4 Results and Discussion

We use this Finite Electric Field approach and the complementary Adler-Wiser perturbation theory approach to explore the dielectric function of 1D and 2D silicon nanostructures. Slabs and rods are especially interesting nanostructures in that they have both bulk and confined attributes. The silicon fin found in finFETs is an intermediate structure (Figure 1) between rods (with circular cross-sections) and slabs. It is not known if the optical properties of a fin are closer to the slab or the rod.

In the case of slabs, Delerue et al. use a tight-binding approach to this problem while Nakamura *et al.* and Giustino and Pasquarello use DFT. The sensitivity of the dielectric response to the hamiltonian is also not known. We use DFT as well as the parametrized hamiltonian of the Empirical Pseudopotential Method (EPM) to address this issue.

Figure 2 shows the local value of the dielectric response $\bar{\epsilon}(z)$ averaged over the periodic dimensions of the slab. The peaks correspond to bonds (this is where the valence electrons are) while the Si atoms are in the valleys. We find good agreement between EPM and DFT except near the surface. This is an artifact of the parametrization of the hydrogen atoms in EPM.

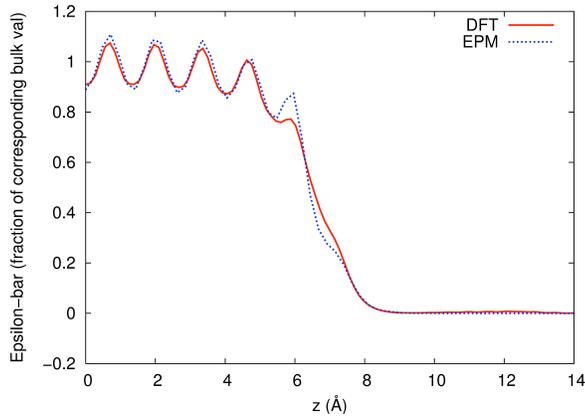


Figure 2: Planar average of the local value of the dielectric response for a 1.5 nm thick slab of hydrogen-terminated crystalline silicon. The peaks correspond to bonds and valleys to silicon atoms. There is a rapid decrease at the surface, corresponding to the outermost atomic layers.

One can verify whether the decrease in $\bar{\epsilon}(z)$ at the surface is related to a skin depth as argued by Nakamura et al. by superposing the dielectric response of slabs of different thickness while using a common surface. This is done in Figure 3 and it nicely shows that the decrease at the surface is independent of the thickness of the slab and can indeed be ascribed to the notion of a skin depth. This shows that at least in this long wavelength regime, the value of the gap does not influence the dielectric response. For the frequency dependent part of the dielectric response, we may expect different conclusions as the exciton peak may be more sensitive to changes in the gap.

For wires, using sizes comparable to the slab calculations, we find a much reduced screening (Figure 4). There is indeed a strong surface effect just as in the slabs with the screening in the wire rapidly (in the space of a few atomic layers) reaching a constant value. But this constant value is much further from the bulk value than for a slab of a comparable thickness. Because of the curvature of the surface in a rod or a fin, in the particular case of a constant electric field, the skin depth is much larger than that of a slab of comparable dimensions. As for the fin geometry, we calculated rods of four different aspect ratio. Our reference rod has a 2 nm circular cross-section and a dielectric constant of 85% that of Bulk Si. For a 2 nm by 4 nm (width by height) elliptical rod, the dielectric constant jumps to 96% that of Bulk Si while for a 2 nm by 8 nm rod we get 97%. This is to be compared to a value of 99% for a 2 nm slab.

Following the trends found in figure 4, we can predict that for fins of 5 nm by 25 nm, the dielectric constant will be that of bulk silicon. The spatial variation and the

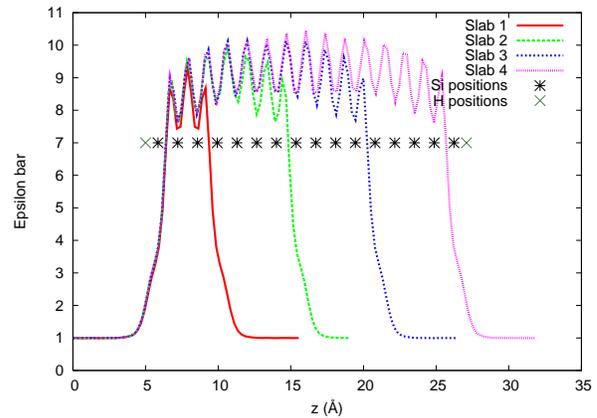


Figure 3: Planar average of the local value of the dielectric response for slabs of increasing thickness. The slabs were aligned on a common surface. The rapid decrease at the surface is independent of the thickness of the slab.

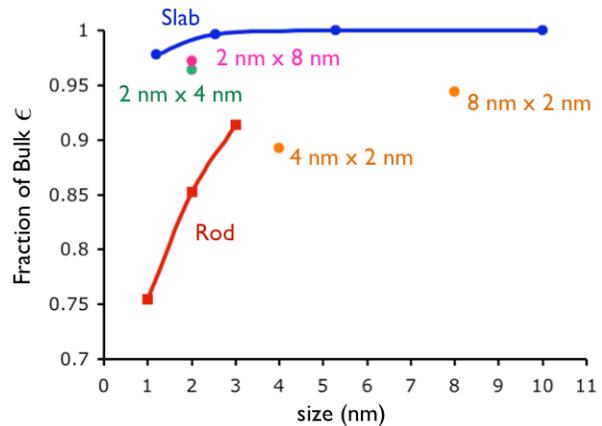


Figure 4: Size dependence of the average value of the dielectric response in the center of different nanostructures. Rods show a much reduced screening compared to slabs of similar thickness. Structures closer to the fin geometry (2 nm x 4 nm) and (2 nm x 8 nm) show an asymptotic convergence to the slab value

size dependence of $\bar{\epsilon}$ can form the basis of a model dielectric function that could be used to address the frequency dependence of the dielectric function i.e. the absorption spectra. This is the object of ongoing work.

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