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ELECTRONIC STRUCTURE OF SILICON QUANTUM FILMS, WIRES AND DOTS: HOW GOOD IS THE EFFECTIVE MASS APPROXIMATION?

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Abstract

Direct diagonalization of the pseudopotential Hamiltonian in a plane-wave basis provides a benchmark against which the traditional effective mass approximation for quantum structures can be tested. Significant discrepancies are noted.

The basic properties of semiconductor quantum structures have been reviewed recently[1-4]. In addition to specialized sophisticated calculations, much of the phenomenology of quantum structures relies heavily on the simple effective mass model[1-4]. In this approach one describes the electronic consequences of *kinetic energy confinement* of parabolic band electrons in some 1D, 2D or 3D-shaped objects[1-4]. While this model has been eminently successful in describing single and multiple quantum *wells* (possessing semiconductor-semiconductor interfaces separating electronically similar materials), much less is known on the performance of the effective-mass model for quantum *films*, *wires* and *boxes* (having semiconductor-vacuum interfaces[5]). A straightforwards test of the predictions of the effective mass approximation (EMA) would entail solving the Schroedinger equation with *microscopic* atomic potentials as used in conventional band structure calculations. In practice, this can be done by constructing a large, "super unit cell" having inside it the quantum structure, surrounded by vacuum. Applying periodic boundary condition to such super cells thus permits the utilization of ordinary band theoretic approaches. Spurious interactions *between* the (periodically arranged) quantum structures are then reduced (to practically zero) by increasing the thickness of the vacuum layers. Thus, in this method ("direct diagonalization") one solves

$$[-\frac{1}{2}\nabla^2 + V(\mathbf{r})]\psi_i(\mathbf{r}) = \epsilon_i\, \psi_i(\mathbf{r}), \tag{1}$$

where $V(\mathbf{r})$ is the *periodic microscopic potential* inside the structure, approaching the vacuum level outside the structure. One need not imply parabolic bands (as in the simple EMA), or restrict the interactions to a given range (as in tight-binding), or

expand ψ_i in a restricted set of bulk Bloch bands (as in the Luttinger model), or neglect surface effects (as in all of the above). The practical difficulty lies, of course, in the needed to solve Eq.(1) for large super cells, containing sometimes hundreds of atoms: The effort to do this scales as the cube power of the number of atoms, making practical solutions intractable. It has been noted[6] however, that this is the case only if one insists on obtaining *all* eigensolutions, starting from the valence band *minimum* (about 13 eV below the VBM). If, on the other hand, one is interested in the physics only near the band edges, it is possible to obtain the exact $\{\epsilon_i, \psi_i\}$ in an effort that is only *linear* with the system's size[6-7] by simply replacing Eq.(1) by:

$$[-\frac{1}{2}\nabla^2 + V(\mathbf{r}) - \epsilon_{ref}]^2 \psi_i(\mathbf{r}) = [\epsilon_i - \epsilon_{ref}]^2 \ \psi_i(\mathbf{r}), \tag{2}$$

where ϵ_{ref} is a constant placed inside the band gap. Equation (2) has exactly the same solutions as Eq(1) except that its energy spectrum is folded. The point is that while Eq.(1) gives *all* eigensolutions, thus requiring mutual orthogonalization, the lowest solution of Eq.(2) is the one closest to ϵ_{ref}. Thus the VBM and CBM states can be calculated directly (by shifting ϵ_{ref}) wasting no time on the lower energy states.

We have solved Eq.(2) for Si quantum films, wires and dots using a carefully parameterized empirical pseudopotential[5-8] for $V(\mathbf{r})$ and saturating the surface dangling bonds by hydrogen atoms. The wavefunctions are expanded in a large set of plane waves. We assume bulk inter-atomic distances. Our main results, compared to the EMA expectations are:

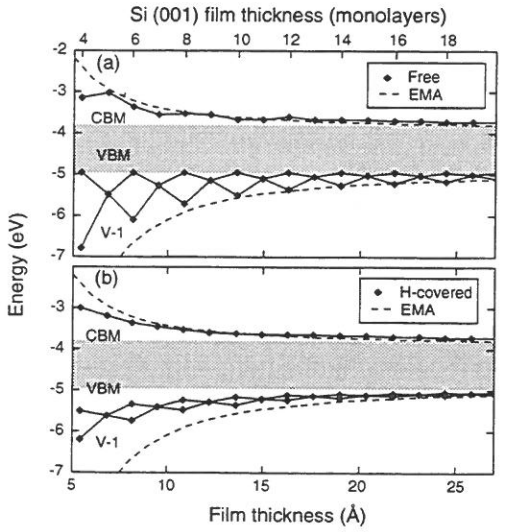

Figure 1. Calculated near-gap energy levels of (001) oriented hydrogen free (part a) and hydrogen covered (part b) Si films. All states shown are bulk-like (i.e., surface states are omitted). Note the oscillations in the highest occupied (VBM) and next-to-highest occupied (V-1) valence bands, absent in the EMA description (dashed line). The shaded area denotes the bulk band gap region. The zero-confinement state having a size independent energy is apparent in part a.

(i) While in the EMA the energy levels vary monotonically with (quantum) size, direct solutions for (001)-oriented quantum films (Fig. 1a) show non-monotonic (even-odd) oscillations in the valence band energies. The amplitude of these oscillations is reduced somewhat when the film's surface is covered by hydrogen (Fig. 1b). No oscillations exist in (110) oriented films (not shown). The EMA fails quantitatively in describing the valence band states (in either cases: clean or H covered surfaces) for film's thickness below ~20Å. The reason is that the EMA fails to recognize the changes in symmetry in going from an even to an odd number of atomic layers: all EMA knows about is the thickness.

(ii) Direct solutions of a hydrogen-free (001) quantum film exhibit a VBM state

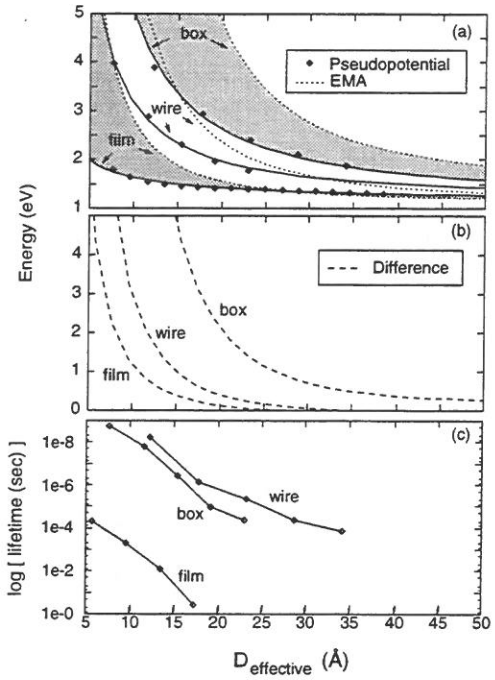

Figure 2. Energy gaps (part a), absolute EMA errors in the band gap (part b) and radiative lifetimes (part c) for H-covered Si films, wires and boxes. The surface orientations are (110) for films, (110)×($\bar{1}$10) for wires, and (110)×($\bar{1}$10)×(001) for boxes. We use D_{eff}=D_{110} for films, D_{eff}=D_{110}=$D_{1\bar{1}0}$ for wires and D_{eff}=3.3685N$^{1/3}$ for boxes, where N is the number of Si atoms and D_{110} is the H surface layer to H surface layer distance in (110) direction. The EMA results in (a) and (b) are taken from T. Takagahara and K. Takeda [Phys. Rev. B **46**, 15578 (1992)] for boxes, from Read at al. [Phys. Rev. Lett. **69**, 1232 (1992); *ibid* **70**, 12050 (1993)] for wires, and from Ref. [5] for films.

whose energy does not change with film thickness (see even-layers in Fig. 1a). This "zero confinement state" (ZCS) is missing in the EMA. In the language of the EMA, the ZCS[5] corresponds to a cosine-type envelope function with a principal quantum number (or momentum) of zero. Both features are forbidden in the EMA. This represents a qualitative failure of the EMA. The ZCS corresponds physically to the case where boundary conditions are satisfied by the Bloch function, not the envelope function. The ZCS energy becomes unpinned under H chemisorption (Fig. 1b) and in (110) films. It is absent in wires and boxes.

(iii) The EMA overestimates significantly the band gap opening due to quantum confinement (Fig. 2a). The *absolute* EMA error (Fig. 2b) increases in the order film → wire → box and reaches ∼2 eV for a 20Å diameter box. However, the *relative* EMA error (the absolute error divided by its corresponding band opening) is about the same for film, wire and box. The size (d) dependence of the band gap $E_g(d) = E_g(bulk) + A/d^n$ obtained in the EMA is (A;n) = (170;2); (497;2), and (1488;2) for Si film, wire and box, respectively. In contrast, fitting the pseudopotential results gives (A;n) = (3.8;0.81); (39;1.28) and (58;1.21) for film, wire and box, respectively.

(iv) We have calculated the radiative lifetime τ_R (Fig. 2c). The τ_R for the box and wire correspond to the average transition between 4 highest VB states and 4 lowest CB states in the system. This average represents finite temperature average of about 300 K. On the other hand, only the VBM and CBM states are used to calculate the τ_R of the film. Recall that τ_R measures the extent to which the interband transition is allowed. As the quantum size decreases, τ_R becomes faster (transitions are "more allowed") due to interband coupling. The transition lifetime is more sensitive to the geometry and surface relaxations than the energy gap due to the fact that the oscillator strength ($\propto 1/\tau_R$) is very close to zero. The decay rate $1/\tau_R$ of the film decreases faster with the increasing size d than the expected scaling of $1/d^6$ given by the EMA results [at (001) direction][11].

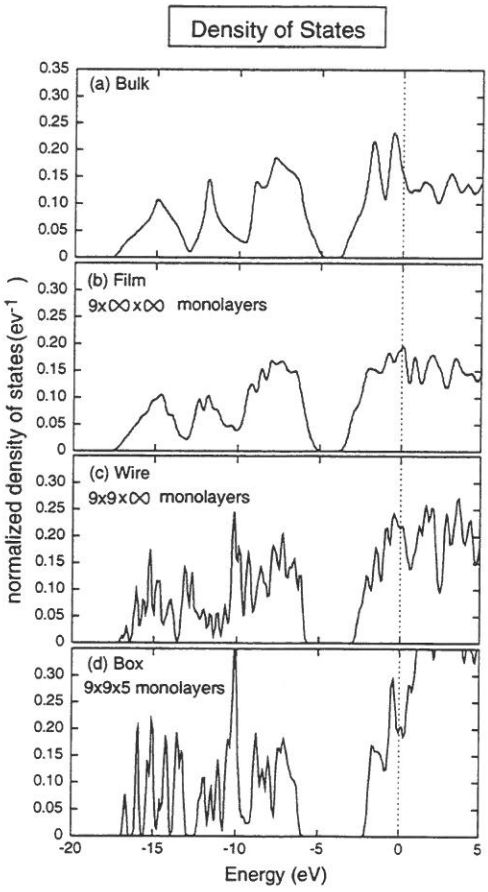

Figure 3. Density of states of H-saturated films, wires and boxes with surface orientations denoted in the caption of Fig. 2. They are normalized so that the integral of the valence electrons equals 1. The results for parts (a) and (b) were computed directly from eigenvalues of Eq(1), while the results for (c) and (d) were obtained with the moments method of Refs [9]-[10]. Gaussian broadening is 0.2 eV.

(v) The density of states of films (Fig. 3b) is rather similar to that of the bulk (Fig. 3a) while wires (Fig. 3c) show sharp features which evolve into molecular-like states in a quantum box (Fig. 3d). The electron affinity (distance from vacuum level to the CBM) decreases in the series film→wire→box.

These observations clarify areas where improvements to the traditional EMA are needed.

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