Prediction of unusual electronic properties of Si quantum films

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Prediction of unusual electronic properties of Si quantum films

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Direct pseudopotential band structure calculations of thin Si(001) films reveal a number of

[redacted]

envelope function, and (iii) the energy of the highest occupied film state remains pinned at a constant value for all even-layered film. We demonstrate a simple alternative to the

[redacted]

Free-standing quantum films are two-dimensional [redacted] the film, (ii) multiband and [redacted] that the bulk bands have a parabolic $\hbar^2(\mathbf{k}-\mathbf{k}_0)^2/2m^*$ dis-

[redacted]

The film's energy eigenvalues ϵ_f vary monotonically with film thickness L as $\epsilon_f \propto 1/L^2$. (b) the film has a *sine-type* envelope function which guarantees that the wave functions vanish at the film's boundaries and (c) the [redacted] of all levels depend on the film's thickness.

Naturally, these predictions could reflect, in part, the underlying approximations of the effective-mass model (EMA). To assess this we will first describe the [redacted] niques, thus obviating the effective-mass approximation. This can be done by defining a "supercell" consisting of N_f layers of the film's material straddled on each side by N_v [redacted]

$$[-\tfrac{1}{2}\nabla^2+V_{\rm film}(\mathbf{r})]\psi_f^{\rm direct}(\mathbf{r})=\epsilon_f^{\rm direct}\psi_f^{\rm direct}(\mathbf{r}), \qquad (1)$$

where ψ is expanded, e.g., in plane waves. The number N_v of vacuum layers is increased until the resulting energy spectrum $\{\epsilon_f^{\rm direct}\}$ becomes independent of N_v. We construct $V_{\rm film}(\mathbf{r})$ by a superposition of screened Si atomic empirical pseudopotentials $V_i(\mathbf{r}-\mathbf{R}_i)$ over the atomic sites $\mathbf{R}_i$. Far outside the film $V_{\rm film}(\mathbf{r})$ approaches the vacuum level, thus establishing the work function. We fit $V_{\rm Si}(\mathbf{r})$ to the bulk Si band structure as well as to the film work function[2] $\Phi=4.9$ eV. Equation (1) is solved by expanding the wave functions in a plane wave basis with a cutoff of 4.5 Ry. The *bulk* energy eigenvalues [in eV, relative to the bulk valence-band maximum (VBM)] at the symmetry points X_{1c}, L_{1c}, L_{3c}, and $\Gamma_{2'c}$ are 1.28 (1.13); 2.18 (2.04); 4.02 (3.9), and 4.11 (4.15), respectively, where the values in parentheses are experimental.[3] Our primary aim is to compare our results with "surfaceless" [redacted] iterating the films potential to self-consistency as we do not wish to propagate surface effects into the interior of the [redacted]

(1) the potential $V_{\rm film}(\mathbf{r})$ includes both the periodic part inside the film and the confining vacuum potential outside [redacted] discarded.

sults.

(1) *Even–odd oscillations*: Figure 1 depicts the directly calculated [Eq. (1)] film eigenvalues at the VBM [not in-] the conduction band minimum (CBM) as a function of the number N_f of Si monolayers. The dashed line depicts the predictions of the EMA. Note the marked even–odd oscil- [redacted] its effects by m^*, it misses this symmetry-mandated effect.

(2) *Cosine-type envelope functions*: Figure 2(a) depicts the directly calculated film wave function for valence band $f=20$ of a 12-layer Si(001) film at the center of the film's [redacted]

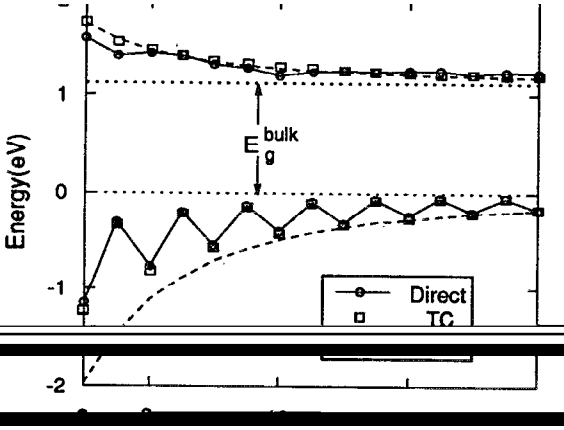

FIG. 1. Size dependence of the highest valence-band and lowest conduction-band states.

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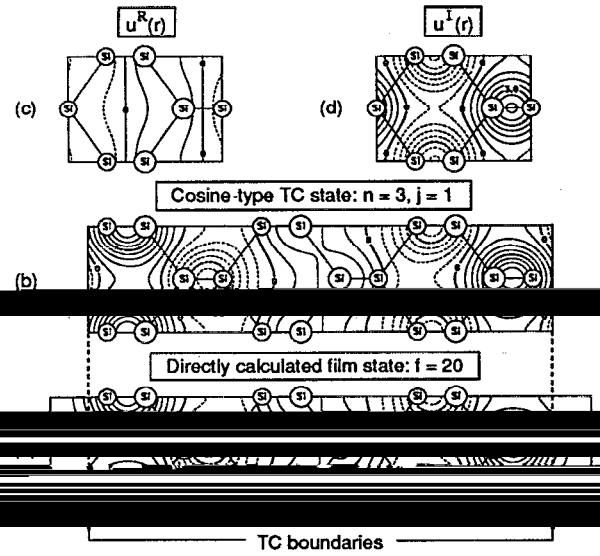

FIG. 2. Wave function for a cosine-type film state. Solid (dashed) lines are positive (negative) contours.

have independently constructed the function

$$\chi_f^{TC}(\mathbf{r}) = \sqrt{2}[u_{n,\mathbf{k}}^R(\mathbf{r})\sin(\mathbf{kr}) + u_{n,\mathbf{k}}^I(\mathbf{r})\cos(\mathbf{kr})], \quad (2)$$

tion $u_{n,\mathbf{k}}(\mathbf{r})$ for the $n=3$ band at $\mathbf{k}=2\pi/a(0,0,2/N_f)$. $\sqrt{2}\,u_{n,\mathbf{k}}^I(\mathbf{r})\cos(\mathbf{kr})$. Since $\chi_f^{TC}(\mathbf{r})$ is nearly identical with the directly calculated wave function shown in Fig. 2(a), this film state has a cosine-type envelope function absent in the EMA formalism.

(3) *Zero confinement state (ZCS)*: Figure 3(a) shows

of this state does not depend on film thickness, in apparent defiance of the concept of quantum confinement. The

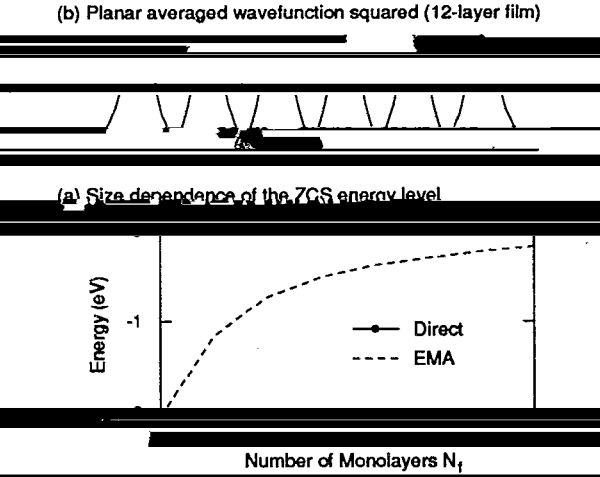

FIG. 3. The zero-confinement state. Solid dots in (b) indicate the positions of atomic planes.

dashed line in Fig. 3(a) shows the thickness dependence expected from EMA. Part (b) of this figure shows the planar-averaged ZCS wave function squared. Note the constant peak heights which imply a constant envelope function.

Figures 1–3 establish significant *qualitative* discrepancies between the "exact" diagonalization approach and the EMA for Si(001) quantum films.

What is wrong with the EMA and how can it be fixed?

pure kinetic energy form

$$\epsilon_{n,\mathbf{k}}^{\mathrm{EMA}} = \epsilon_{n,\mathbf{k}} + \frac{\hbar^2(\mathbf{k}-\mathbf{k}_0)^2}{\quad}, \quad (3)$$

proximated by a product of an envelope function $f_{\mathbf{k}-\mathbf{k}_0}(\mathbf{r})$ and the cellular function $u_{n,\mathbf{k}_0}(\mathbf{r})$ of the band edge state $\psi_{n,\mathbf{k}_0}^{\mathrm{bulk}}(\mathbf{r})$. The external potential is permitted in the EMA to modify the envelope function and its energy $\hbar^2(\mathbf{k}-\mathbf{k}_0)^2/2m^*$, but not $u_{n,\mathbf{k}_0}$ and $\epsilon_{n,\mathbf{k}_0}$. These approxi-

effects of the periodic potential inside the film and the confinement effects of the external potential. Instead, we will use here the "exact" $\{\epsilon_{n\mathbf{k}}^{\mathrm{bulk}}\}$ and $\{\psi_{n\mathbf{k}}^{\mathrm{bulk}}(\mathbf{r})\}$ without ap-

envelope part. Furthermore, we permit variational coupling of n and $\mathbf{k}$ through $V^{\mathrm{film}}(\mathbf{r})$. We will thus construct a

interference between two degenerate Bloch waves with opposing $\mathbf{k}$. For zone center ($\bar{\Gamma}$) film states where $\mathbf{k}=(0,0,k_z)$, this leads to

$$\chi_{n,k_z^*}^{TC}(\mathbf{r}) = \begin{cases} \psi_{n,k_z^*}^{\mathrm{bulk}}(\mathbf{r}) - \psi_{n,-k_z^*}^{\mathrm{bulk}}(\mathbf{r}) & \text{if } 0 < z \leqslant L \\ \end{cases} \quad (4)$$

where k_z^* is quantized k_z such that $\chi_{n,k_z^*}^{TC}(\mathbf{r})$ is zero at $z=0$ and $z=L$. This gives

$$k_z^* = \frac{\pi}{L} j \begin{cases} j=1,2,3,\ldots,j_{\max} & \text{for } n=1 \end{cases} \quad (5)$$

Note that the solution $j=0$ for $n\neq 1$ is allowed, while

$\psi_{n,-k_z^*}(\mathbf{r}) = [\psi_{n,k_z^*}(\mathbf{r})]^*$, Eq. (5) can be written for $0<z$

envelope function is possible in this generalized description. Using the TC basis of Eq. (4), a film eigenstate (f) at the zone center can be expanded as

$$\psi_{f,\bar{\Gamma}}^{\mathrm{direct}}(\mathbf{r}) = \sum_n \sum_{k_z^*} a_{n,f}(k_z^*)\chi_{n,k_z^*}^{TC}(\mathbf{r}). \quad (6)$$

One can now proceed and directly diagonalize the film Hamiltonian of Eq. (1) using the representation of Eq.

sum of the bulk eigenvalues $\epsilon_{n,k_z^*}^{\mathrm{bulk}}$ with coefficients

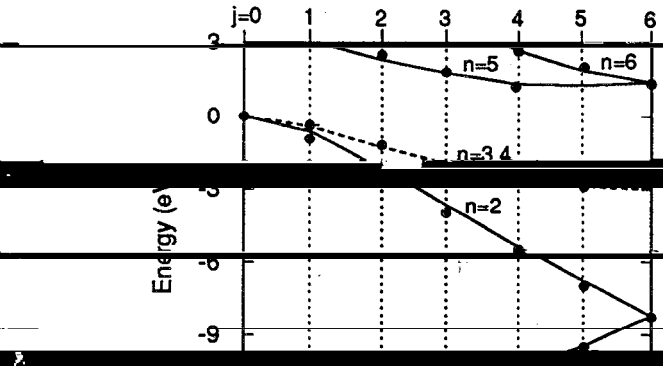

FIG. 4. Mapping of the directly calculated film eigenvalues onto those given by the TC approach.

$|a_{n,f}(k_z^*)|^2$. Our central observation (verified in Fig. 4

and

$$\epsilon_{f,\Gamma}^{\text{direct}} \quad \epsilon_{n,\mathbf{k}}^{\text{bulk}} \qquad (8)$$

Thus, *the TC approach predicts a one-to-one mapping between the film energy eigenvalues* $\epsilon_{f,\Gamma}^{\text{direct}}$ *and those of the*

is precisely the procedure followed empirically in earlier

with those obtained in direct diagonalization. Figure 1 shows such a comparison for valence- and conduction-band eigenvalues, whereas Fig. 2 shows that the TC wave function [Eqs. (4) and (7)] constructed from the bulk

The ZCS of Fig. 3 is a particular case of the cosine envelope function discussed above. Equation (5) shows that for $n \neq 1$ the solution $j=0$ (i.e., $k_z^*=0$) is allowed. Hence a film state for which $u_{n,\mathbf{k}}^R(\mathbf{r}) \approx 0$ with $k_z^*=0$ gives from Eq. (2) $\gamma_{ZCS}^{TC}(\mathbf{r}) \approx u_{n,\mathbf{k}}^I(\mathbf{r})$ having a constant envelope

tion depicted in Fig. 3(b) can be described quantitatively in this fashion.

The TC representation lead to another useful result: To within a good approximation one can guess the (non-surface state) eigenvalues of a film from the bulk disper-

$$\mathbf{k}_{(001)}^* = \frac{2\pi}{a}\left(0,0,\frac{2j}{N_f}\right); \quad 0 \leq j \leq j_{\max} = N_f/2. \qquad (9)$$

Thus, $\epsilon_n^{\text{bulk}}[2\pi/a(0,0,2j/N_f)]$ approximates the zone-center eigenvalues of an N_f-layer (001) film. Similarly,

energy levels of a quantum film and its orientation. Results

intersections miss the directly calculated energies (solid dots) gives the error in the TC approximation. The errors are small; hence, Eqs. (8) and (9) provide a natural classification of (001) film eigenvalues in terms of bulk dispersion relations. When the real $\epsilon_{n,\mathbf{k}}^{\text{bulk}}$ has a parabolic dispersion [Eq. (2)], the EMA result $\epsilon_{n,\mathbf{k}}^{\text{EMA}} = (\pi^2\hbar^2/L^2 m_n^*) j^2$

(7) and (8) provide a simple alternative to the EMA for

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[1] See, J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 14, 556 (1976).