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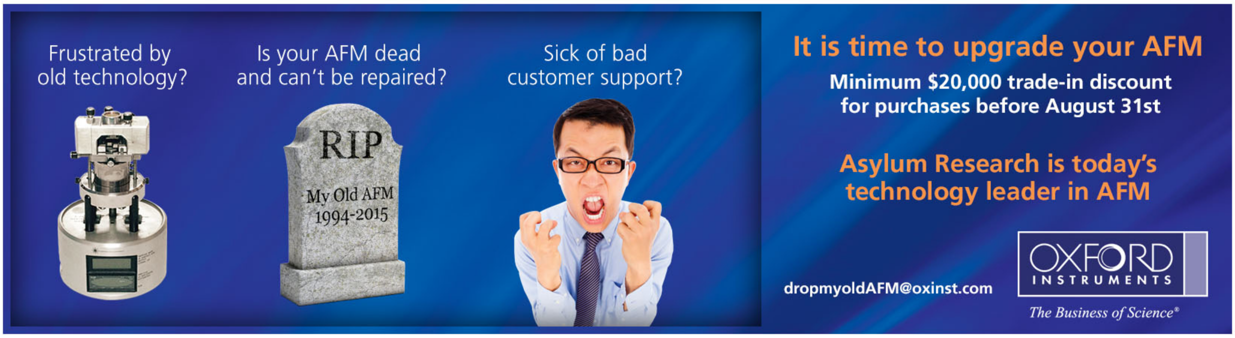

Prediction of unusual electronic properties of Si quantum films

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Direct pseudopotential band structure calculations of thin Si(001) films reveal a number of features that are unexpected on the basis of conventional quantum confinement models: (i) The energies of some valence-band states exhibit oscillations when the number of monolayers in the film changes from even to odd, (ii) certain film wave functions have a cosine (rather than sine) 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 effective-mass model which explains these results.

Free-standing quantum films are two-dimensional (2D)-periodic systems confined in the perpendicular dimension by vacuum. The qualitative features of their electronic structure can be described by the effective-mass particle-in-a-box model.[1] This approach predicts that (a) 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 energies 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 electronic structure of quantum films by direct band structure techniques, 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 layers of vacuum, and imposing periodic boundary conditions. The electronic structure of the film is then addressed by directly diagonalizing

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

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 $V_{\rm Si}(\mathbf{r}-\mathbf{R}_i)$ 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" models such as the EMA. Thus, we deliberately avoided iterating the films potential to self-consistency as we do not wish to propagate surface effects into the interior of the film. Likewise, surface reconstruction is not included. This approach avoids the effective-mass approximation in that (i) the potential $V_{\rm film}(\mathbf{r})$ includes both the periodic part inside the film and the confining vacuum potential outside the film, (ii) multiband and intervalley couplings neglected in the EMA are permitted, (iii) no implication is made that the bulk bands have a parabolic $\hbar^2(\mathbf{k}-\mathbf{k}_0)^2/2m^*$ dispersion. The results obtained from Eq. (1) can then be contrasted with the EMA predictions. Of course, such a comparison requires that surface states, which could appear in the solutions of Eq. (1) but not in the EMA, be discarded.

Such calculations reveal the following unexpected results.

(1) *Even–odd oscillations*: Figure 1 depicts the directly calculated [Eq. (1)] film eigenvalues at the VBM [not including the zero confinement state (ZCS), see below] and 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 oscillations in the direct calculation. These reflect the changing film symmetries with N_f; for N_f=even the symmetry is D_{2h} while for N_f=odd the symmetry is D_{4h}. Since the EMA renormalizes away the periodic potential, replacing 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

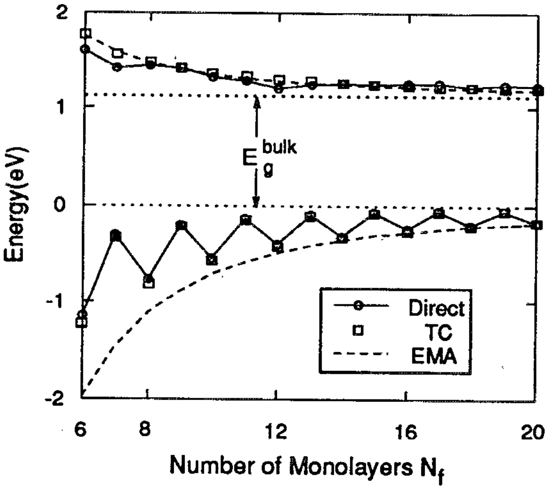


FIG. 1. Size dependence of the highest valence-band and lowest conduction-band states.

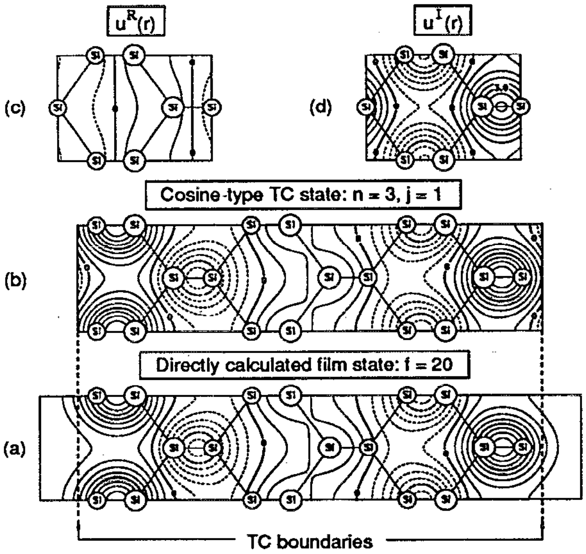


FIG. 2. Wave function for a cosine-type film state. Solid (dashed) lines are positive (negative) contours.

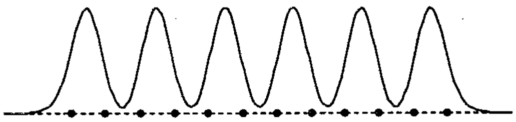
Brillouin zone. To find its underlying envelope function we have independently constructed the function

$$\chi_f^{TC}(\mathbf{r}) = \sqrt{2}[u^R_{n,\mathbf{k}}(\mathbf{r})\sin(\mathbf{kr}) + u^I_{n,\mathbf{k}}(\mathbf{r})\cos(\mathbf{kr})], \qquad (2)$$

where $u^R_{n,\mathbf{k}}(\mathbf{r})$ and $u^I_{n,\mathbf{k}}(\mathbf{r})$, shown in Figs. 2(c) and 2(d), are the real and imaginary parts of the *bulk periodic* function $u_{n,\mathbf{k}}(\mathbf{r})$ for the $n=3$ band at $\mathbf{k}=2\pi/a(0,0,2/N_f)$. Note that ${}^{TC}_{f}(\mathbf{r})$, shown in Fig. 2(b), is essentially $\sqrt{2}\, u^I_{n,\mathbf{k}}(\mathbf{r})\cos(\mathbf{kr})$. 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 the directly calculated highest occupied film eigenvalues as a function of N_f, for even N_f values. Note that the energy of this state does not depend on film thickness, in apparent defiance of the concept of quantum confinement. The 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.

(b) Planar averaged wavefunction squared (12-layer film)



(a) Size dependence of the ZCS energy level

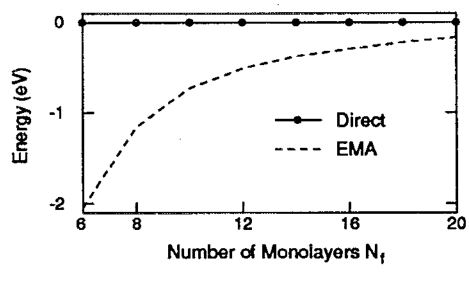


FIG. 3. The zero-confinement state. Solid dots in (b) indicate the positions of atomic planes.

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? The EMA replaces the exact bulk dispersion $\epsilon^{\text{bulk}}_{n,\mathbf{k}}$ by the pure kinetic energy form

$$\epsilon^{\text{EMA}}_{n,\mathbf{k}} = \epsilon_{n,\mathbf{k}_0} + \frac{\hbar^2(\mathbf{k}-\mathbf{k}_0)^2}{2m^*_{n,\mathbf{k}_0}}, \qquad (3)$$

taken with respect to the energy $\epsilon_{n,\mathbf{k}_0}$ of the band edge state $\psi^{\text{bulk}}_{n,\mathbf{k}_0}(\mathbf{r})$. Furthermore, $\psi^{\text{EMA}}_{n,\mathbf{k}}(\mathbf{r}) = f_{\mathbf{k}-\mathbf{k}_0}(\mathbf{r})\mathrm{u}_{n,\mathbf{k}_0}(\mathbf{r})$ is approximated 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 $\psi^{\text{bulk}}_{n,\mathbf{k}_0}(\mathbf{r})$. The external potential is permitted in the EMA to modify the envelope function and its energy $\hbar^2(\mathbf{k}-\mathbf{k}_0)^2/2m^*_{n,\mathbf{k}_0}$, but not $u_{n,\mathbf{k}_0}$ and $\epsilon_{n,\mathbf{k}_0}$. These approximations remove the coupling between the band structure effects of the periodic potential inside the film and the confinement effects of the external potential. Instead, we will use here the "exact" $\{\epsilon^{\text{bulk}}_{n\mathbf{k}}\}$ and $\{\psi^{\text{bulk}}_{n\mathbf{k}}(\mathbf{r})\}$ without approximating them by a $\mathbf{k}$ independent cellular part and an envelope part. Furthermore, we permit variational coupling of n and $\mathbf{k}$ through $V^{\text{film}}(\mathbf{r})$. We will thus construct a truncated crystal (TC) basis set representing a destructive 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

$$\chi^{TC}_{n,k_z^*}(\mathbf{r}) = \begin{cases} \psi^{\text{bulk}}_{n,k_z^*}(\mathbf{r}) - \psi^{\text{bulk}}_{n,-k_z^*}(\mathbf{r}) & \text{if } 0<z\leqslant L \\ 0 \quad \text{if } z\leqslant 0 \text{ or } z>L \end{cases}, \qquad (4)$$

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

$$k_z^* = \frac{\pi}{L} j \begin{cases} j=1,2,3,\ldots,j_{\max} & \text{for } n=1 \\ j=0,1,2,\ldots,j_{\max} & \text{for } n\neq 1 \end{cases}. \qquad (5)$$

Note that the solution $j=0$ for $n\neq 1$ is allowed, while conventional EMA solutions start at $j=1$. Since $\psi^{\text{bulk}}_{n,-k_z^*}(\mathbf{r}) = [\psi^{\text{bulk}}_{n,k_z^*}(\mathbf{r})]^*$, Eq. (5) can be written for $0<z<L$ in the form of Eq. (2). This shows that a cosine 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

$$\psi^{\text{direct}}_{f,\bar{\Gamma}}(\mathbf{r}) = \sum_n \sum_{k_z^*} a_{n,f}(k_z^*)\chi^{TC}_{n,k_z^*}(\mathbf{r}). \qquad (6)$$

One can now proceed and directly diagonalize the film Hamiltonian of Eq. (1) using the representation of Eq. (6). This will produce the exact film eigenvalues given as a sum of the bulk eigenvalues $\epsilon^{\text{bulk}}_{n,k_z^*}$ with coefficients

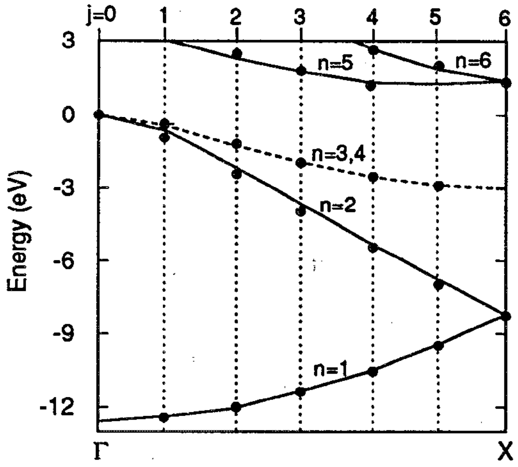


FIG. 4. Mapping of the directly calculated film eigenvalues onto those given by the TC approach.

$|a_{n,f}(k_z^*)|^2$. Our central observation (verified in Fig. 4 below) is that the matrix representation of Eq. (6) is essentially diagonal in the band index n and wave vector k_z^*. The truncated crystal *approximation* thus consists of retaining in Eq. (6) just a single dominant term with $f=(n,j)$, so

$$\psi_{f,\Gamma}^{\text{direct}}(\mathbf{r}) \approx \chi_{n,k_z^*}^{TC}(\mathbf{r}) \tag{7}$$

and

$$\epsilon_{f,\Gamma}^{\text{direct}} \approx \epsilon_{n,k_z^*}^{\text{bulk}}. \tag{8}$$

Thus, *the TC approach predicts a one-to-one mapping between the film energy eigenvalues* $\epsilon_{f,\Gamma}^{\text{direct}}$ *and those of the periodic bulk crystal* $\epsilon_{n,k_z^*}^{\text{bulk}}$ *at some special k points* k_z^*. This is precisely the procedure followed empirically in earlier TC approach,[4] where it was demonstrated that the eigenvalues of finite clusters form a subset of the eigenvalues of the periodic crystal.

To test the TC approximation, we compare its results 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 states $u_{n,\mathbf{k}}^R(\mathbf{r})$ and $u_{n,\mathbf{k}}^I(\mathbf{r})$ agrees closely with that calculated directly. Note that for this state the boundary conditions are satisfied by the nodal planes of $u_{n,\mathbf{k}}^I(\mathbf{r})$ rather than by the envelope function.

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) $\chi_{\text{ZCS}}^{\text{TC}}(\mathbf{r})\approx u_{n,\mathbf{k}}^I(\mathbf{r})$ having a constant envelope function. Indeed, the directly calculated ZCS wave function 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 (nonsurface state) eigenvalues of a film from the bulk dispersion relation at the special $\mathbf{k}_{\hat{e}}^* = (2\pi/L)j\hat{e}$ points where $\hat{e}$ is the film's orientation. For (001) films, for example, $L=N_f a/4$, where a is the cubic lattice constant, so the special $\mathbf{k}$ points are

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

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, $\epsilon_n^{\text{bulk}}[2\pi/a(j/N_f,j/N_f,0)]$ approximates those of a (110)-oriented film. This establishes a simple relation between the energy levels of a quantum film and its orientation. Results for an $N_f=12$ (001) film is shown in Fig. 4. The dotted vertical lines give the quantized TC wave vectors $\mathbf{k}_{(001)}^*$. Their intersections with the bulk bands give the TC predictions for the film energies. The amount by which these 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. (3)], the EMA result $\epsilon_f^{\text{EMA}} \propto (\hbar^2\pi^2/L^2m^*)j$ coincides with the TC result [Eq. (8)]. In summary, Eqs. (7) and (8) provide a simple alternative to the EMA for quantum films.

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