Evanescent states in thin silicon films and their significance

J. U. Kim and Hong H. Lee*
School of Chemical Engineering, Seoul National University, Seoul, 151-742 Korea
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The full-zone $\mathbf{k}\cdot\mathbf{p}$ method is used along with the effective-mass and envelope-function approximations to investigate the photoluminescence (PL) behavior of free-standing thin silicon films. The formulation reveals that blue and red PL bands coexist and that the blue band is due to the transition from a high evanescent state to a heavy-hole state. The square of the transition momentum is such that the blue band decays fast whereas the red decays slowly. The presence of the high evanescent state explains why the blue PL can be observed in relatively thick silicon films.

I. INTRODUCTION

The observation of room-temperature photoluminescence (PL) of porous silicon has attracted a great deal of theoretical and experimental interest since its discovery.[1] The origin of this interesting phenomenon has been suggested to be due to the quantum confinement of photoexcited carriers within nanometer-sized silicon structures.[2,3] More specific suggestions have followed. These are surface effects[4] that are size independent and size effects that are size dependent.[5] Experimental results are also available, indicating that both surface- and size-related bands coexist.[6,7] Theoretical studies[8–11] center on the existence of a direct band gap and the effects of chemisorption on the energy gap.

In this article, we investigate the nature of PL for a free-standing [001] silicon film in which the confinement is in the z direction on the basis of the full-zone $\mathbf{k}\cdot\mathbf{p}$ perturbation scheme with the effective-mass approximation (EMA) and envelope-function approximation (EFA). It is shown that multiple PL bands can exist in the silicon film and that the blue PL band can be found in relatively thick silicon films. This blue band is found to be due to an evanescent state.

II. CONFINEMENT CONDITION

Consider a free-standing [001] silicon film whose thickness is $2q$ in the z direction. There are three doubly degenerate Δ_5 bands, three Δ_1 bands, and five Δ_2 bands in the [001] direction.[12] These bands are given by the following 3×3 and 5×5 matrices:

$$\Delta_5=\begin{bmatrix} E(\Gamma^{l}_{25'})+k_z^2 & Qk_z & 0 \\ Qk_z & E(\Gamma_{15})+k_z^2 & Q'k_z \\ 0 & Q'k_z & E(\Gamma^{u}_{25'})+k_z^2 \end{bmatrix}, \tag{1}$$

$$\Delta_1=\begin{bmatrix} E(\Gamma_{15})+k_z^2 & Tk_z & T'k_z \\ Tk_z & E(\Gamma^{u}_{1})+k_z^2 & 0 \\ T'k_z & 0 & E(\Gamma^{l}_{1})+k_z^2 \end{bmatrix} \tag{2}$$

and

$$\Delta_2=\begin{bmatrix} E(\Gamma^{l}_{25'})+k_z^2 & Pk_z & 0 & -\sqrt{2}Rk_z & P''k_z \\ Pk_z & E(\Gamma^{l}_{2'})+k_z^2 & P'k_z & 0 & 0 \\ 0 & P'k_z & E(\Gamma^{u}_{25'})+k_z^2 & -\sqrt{2}R'k_z & P'''k_z \\ -\sqrt{2}Rk_z & 0 & -\sqrt{2}R'k_z & E(\Gamma_{12})+k_z^2 & 0 \\ P''k_z & 0 & P'''k_z & 0 & E(\Gamma^{u}_{2'})+k_z^2 \end{bmatrix}, \tag{3}$$

where $E(\Gamma_i)$ is the zone-centered energy corresponding to Γ_i and the Q's, T's, P's, and R's are the matrix elements of the momentum. Here, the crystal momentum in the transverse direction is neglected. Atomic units are used throughout.

With the EMA and EFA, Eqs. (1)–(3) can be rewritten as

$$\Delta_i\mathbf{F}^m=E^m\mathbf{F}^m, \tag{4}$$

where the superscript m represents the state, e.g., electron, heavy hole, etc., such that $\mathbf{F}^m$ is the column vector for the envelope functions of the state m and E^m is the corresponding energy level. The column vector for the envelope functions of the heavy hole, $\mathbf{F}^{\rm hh}$, becomes

$$\mathbf{F}^{\rm hh}=\begin{bmatrix} F_1^{\rm hh} \\ F_2^{\rm hh} \\ F_3^{\rm hh} \end{bmatrix}, \tag{5}$$

where

$$F_1^{\rm hh}=A_1^{\rm hh}e^{ikz}+B_1^{\rm hh}e^{-ikz},$$

$$F_2^{\rm hh}=\frac{iQ(E_{25}^u+k^2)}{(E_{15}+k^2)(E_{25}^u+k^2)-Q'^2k^2}F_{1,z}^{\rm hh}\equiv -i\,\eta_2^{\rm hh}F_{1,z}^{\rm hh},$$

$$F_3^{\rm hh}=\frac{QQ'k^2}{(E_{15}+k^2)(E_{25}^u+k^2)-Q'^2k^2}F_1^{\rm hh}\equiv \eta_3^{\rm hh}F^{\rm hh}.$$

Here, the subscript z is for the derivative with respect to z and the E's are defined by

$$E_{15}=E(\Gamma_{15})-E^{\rm hh} \quad \text{and} \quad E_{25}^u=E(\Gamma_{25}^u)-E^{\rm hh}.$$

Since the present $\mathbf{k}\cdot\mathbf{p}$ perturbation scheme enables expansion of the full-zone Bloch function in terms of the Bloch functions associated with $\mathbf{k}=\mathbf{0}$,[13] the wave function of the heavy hole is

$$\Psi^{\rm hh}=F_1^{\rm hh}u_{25'}^l+F_2^{\rm hh}u_{15}+F_3^{\rm hh}u_{25'}^u$$

$$=F_1^{\rm hh}u_{25'}^l-i\,\eta_2^{\rm hh}F_{1,z}^{\rm hh}u_{15}+\eta_3^{\rm hh}F_1^{\rm hh}u_{25'}^u\,. \tag{6}$$

The wave functions of the electron and evanescent states are given in the Appendix. The evanescent states are treated in the same way as the propagation state. There is one evanescent state in the Δ_5 bands between $E(\Gamma_{25'}^l)$ and $E(\Gamma_{15})$ and another in the Δ_2 bands between $E(\Gamma_{25'}^l)$ and $E(X_{1c})$. The large purely imaginary wave vectors are taken as spurious solutions.[14]

For a silicon film surrounded by vacuum, the boundary conditions at the surface may be written as follows:[15]

$$\Psi_{,z}^{\rm hh}+\lambda^{\rm hh}\Psi^{\rm hh}=0 \quad \text{at } z=q, \tag{7a}$$

$$\Psi_{,z}^{\rm hh}-\lambda^{\rm hh}\Psi^{\rm hh}=0 \quad \text{at } z=-q, \tag{7b}$$

where λ^m is given by $\lambda^m=\sqrt{W-E^m}$ and W is the work function. With the aid of the orthogonality conditions

$$\langle u_{25}^l|\partial/\partial z|u_{15}\rangle=\frac{Q}{2}i, \quad \langle u_{25}^u|\partial/\partial z|u_{15}\rangle$$

$$=\frac{Q'}{2}i, \quad \langle u_{25}^u|\partial/\partial z|u_{25}'\rangle=0,$$

Eq. (7) is rewritten as follows:

$$F_{1,z}^{\rm hh}+\frac{Q}{2}\,\eta_2^{\rm hh}F_{1,z}^{\rm hh}+\lambda^{\rm hh}F_1^{\rm hh}=0 \quad \text{at } z=q, \tag{8a}$$

$$F_{1,z}^{\rm hh}+\frac{Q}{2}\,\eta_2^{\rm hh}F_{1,z}^{\rm hh}-\lambda^{\rm hh}F_1^{\rm hh}=0 \quad \text{at } z=-q. \tag{8b}$$

Combining Eqs. (4) and (8) yields the confinement condition for the heavy hole of the silicon quantum film:

$$\frac{2\lambda k m^{\rm hh}}{k^2(m^{\rm hh})^2-\lambda^2}=\tan(2kq), \tag{9}$$

where $m^{\rm hh}$ is defined by $m^{\rm hh}=1-(Q\eta_2^{\rm hh})/2$.

The wave function of the high evanescent state [Eq. (A4) in the Appendix] and the boundary condition [Eq. (7)] yield the following confinement condition for the high evanescent state:

$$(m^{\rm he}\kappa^{\rm he}+\lambda^{\rm he})^2e^{2\kappa^{\rm he}q}=(m^{\rm he}\kappa^{\rm he}-\lambda^{\rm he})^2e^{-2\kappa^{\rm he}q}, \tag{10}$$

where $m^{\rm he}$ is defined by $m^{\rm he}=1-(Q\eta_2^{\rm he})/2$. The confinement condition for the low evanescent state is the same as Eq. (10) with the superscript "he" replaced by "le" and the parameter $m^{\rm le}$ defined by

$$m^{\rm le}=1+(P\eta_2^{\rm ke})/2-(R\eta_4^{\rm le})/\sqrt{2}+(P''\eta_5^{\rm le})/2.$$

Similarly, the confinement condition for the electron state can be written as follows:

$$2(\varsigma_{21}^2-\varsigma_{22}^2\lambda^2)\cos(2k^-q)+4\varsigma_{11}\varsigma_{12}\lambda\sin(2k^+q)-2(\varsigma_{11}^2$$
$$-\varsigma_{12}^2\lambda^2)\cos(2k^+q)-4\varsigma_{21}\varsigma_{22}\lambda\sin(2k^-q)-8(\eta_{21}^e\lambda^2$$
$$+m_{11}m_{21})(\eta_{22}^e\lambda^2+m_{12}m_{22})=0, \tag{11}$$

where λ is used for $\lambda^{\rm el}$ and the ς's and $k^{\pm}$ are defined by

$$\varsigma_{11}=m_{12}m_{21}-m_{11}m_{22}+(\eta_{22}^{\rm el}-\eta_{21}^{\rm el})\lambda^2,$$

$$\varsigma_{21}=-m_{12}m_{21}-m_{11}m_{22}-(\eta_{22}^{\rm el}+\eta_{21}^{\rm el})\lambda^2,$$

$$\varsigma_{12}=m_{22}-m_{21}+m_{11}\eta_{22}^{\rm el}-m_{12}\eta_{21}^{\rm el},$$

$$\varsigma_{12}=m_{22}-m_{21}-m_{11}\eta_{22}^{\rm el}+m_{12}\eta_{21}^{\rm el}$$

and $k^{\pm}=k_1\pm k_2$. Here the η's are given in the Appendix and the m's are defined by

$$m_{11}=\left(1-\frac{T'\gamma_1}{2}\right)k_1+\frac{T+T'\gamma_2}{2}\,\eta_{21}^{\rm el},$$

$$m_{12}=\left(1-\frac{T'\gamma_1}{2}\right)k_2+\frac{T+T'\gamma_2}{2}\,\eta_{22}^{\rm el},$$

$$m_{21}=\frac{T'}{2}+\eta_{21}^{\rm el}k_1, \quad m_{22}=\frac{T'}{2}+\eta_{22}^{\rm el}k_2.$$

The wave function in the vacuum surrounding the film can be expressed as follows:

$$\Psi_\nu^m=\begin{cases} A_\nu^m e^{ik_xx}e^{ik_yy}e^{-\lambda^m z} & \text{in } z\geqslant q \quad (12a) \\ B_\nu^m e^{ik_xx}e^{ik_yy}e^{\lambda^m z} & \text{in } z\leqslant -q. \quad (12b)\end{cases}$$

The continuity of the wave function at the film surface requires, for example, for $z\geqslant q$, that

TABLE I. Parity of the envelope function F_1.

State	F_1 Parity	Envelope function
high evanescent	even	$F_1^{\mathrm{he}}=A_1^{\mathrm{he}}(e^{-\kappa z}+e^{\kappa z})=2A_1^{\mathrm{he}}\cosh(\kappa z)$
	odd	$F_1^{\mathrm{he}}=A_1^{\mathrm{he}}(e^{-\kappa z}-e^{\kappa z})=-2A_1^{\mathrm{he}}\sinh(\kappa z)$
electron	even	$F_1^{\mathrm{el}}(z)=2A_1^{\mathrm{el}}[\cos(k_1z)+r\cos(k_2z)]$
		$F_2^{\mathrm{el}}(z)=2iA_1^{\mathrm{el}}[\eta_{21}^{\mathrm{el}}\sin(k_1z)+r\eta_{22}^{\mathrm{el}}\sin(k_2z)]$
	odd	$F_1^{\mathrm{el}}(z)=2iA_1^{\mathrm{el}}[\sin(k_1z)+r\sin(k_2z)]$
		$F_2^{\mathrm{el}}(z)=2A_1^{\mathrm{el}}[\eta_{21}^{\mathrm{el}}\cos(k_1z)+r\eta_{22}^{\mathrm{el}}\cos(k_2z)]$
low evanescent	even	$F_1^{\mathrm{le}}=2A_1^{\mathrm{le}}\cosh(\kappa z)$
	odd	$F_1^{\mathrm{le}}=-2A_1^{\mathrm{le}}\sinh(\kappa z)$
heavy hole	even	$F_1^{\mathrm{hh}}(z)=2A_1^{\mathrm{hh}}\cos(kz)$
	odd	$F_1^{\mathrm{hh}}(z)=2iA_1^{\mathrm{hh}}\sin(kz)$

$$F_1^{\mathrm{hh}}(q)u_{25'}^{l}(\mathbf{r})-i\eta_2^{\mathrm{hh}}F_{1,z}^{\mathrm{hh}}(q)u_{15}(\mathbf{r})+\eta_3^{\mathrm{hh}}F_1^{\mathrm{hh}}(q)u_{25'}^{u}(\mathbf{r})$$
$$=A_\nu^m e^{ik_xx}e^{ik_yy}e^{-\lambda^m q}. \tag{13}$$

The constant coefficients A_v^m and B_v^m are obtained by averaging the position dependence over one monolayer with its center line at the surface, i.e., $z=q$. The wave function over the space can now be normalized. For accuracy, the parity should be taken into account in terms of the envelope function $F_1^{\mathrm{hh}}(z)$. Table I shows the parity of the envelope functions. The normalization of the wave functions yields the coefficients in Table I.

The square of the matrix elements of the transition momentum[16] is

$$|P_{i\to f}^j|^2=\left|\left\langle f\left|-i\frac{\partial}{\partial x_j}\right|i\right\rangle\right|^2=\left|\left[\int_{-q}^{q}d\mathbf{r}+\int_{q}^{\infty}d\mathbf{r}+\int_{-\infty}^{-q}d\mathbf{r}\right]\right.$$
$$\left.\times\left[\Psi^{f*}\left(-i\frac{\partial}{\partial x_j}\right)\Psi'\right]\right|^2, \tag{14}$$

where $P_{i\to f}^j$ is the dipole element between the states (i) and (f). Calculation of the square of the transition momentum matrix between states is laborious and the details are omitted. Table II gives the polarization of the transition between the states.

III. RESULTS AND DISCUSSION

The energy level of each state can be calculated from the corresponding confinement condition using the parameters given in Table III. The result for a work function of 4 eV is shown in Fig. 1. Because of the parity, there can be eight possible states, the high and low evanescent states, electron state, and heavy-hole state, each having odd and even states. It is notable that the high evanescent state is size insensitive and that the even and odd states have almost the same energy level for a film thickness larger than 20 Å. The even and odd states of the electron are almost identical. The even low evanescent state does not exist for a work function of 4 eV. For a film thickness smaller than 20 Å, the size dependency of the energy level is apparent for all the states but is mainly due to the odd heavy-hole state.

Figure 2 shows the dependency of the energy level on the work function for the key states involved in typical PL for a film thickness of 10 Å. The work function represents the state of the film surface, such as the presence of adsorbed species, and thus is related to surface effects. It is notable in this regard in Fig. 2 that the electron and heavy-hole states are relatively invariant with the work function whereas the evanescent states are sensitive to the work function or the surface effects. This finding is an indication that the evanes-

TABLE II. Polarization of the transition.

Transition states		Polarization
even high evanescent,	even electron	transverse
even high evanescent,	odd low evanescent	transverse
odd high evanescent,	odd electron	transverse
odd high evanescent,	even heavy hole	transverse
even electron,	even heavy hole	longitudinal

TABLE III. Parameters used for the calculation. The energy and matrix elements of the momentum are in rydbergs and atomic units, respectively.

Parameter	Value	Parameter	Value
$E(\Gamma_{25'}^{l})$	0.00	R	0.830
$E(\Gamma_{2'}^{l})$	0.256	p''	0.100
$E(\Gamma_{15})$	0.252	P'	−0.090
$E(\Gamma_1^{u})$	0.520	Q'	−0.807
$E(\Gamma_1^{l})$	−0.950	R'	1.210
$E(\Gamma_{12'})$	0.710	P'''	1.320
$E(\Gamma_{25'}^{u})$	0.940	T	1.080
$E(\Gamma_{2'}^{u})$	0.990	T'	0.206
P	1.200	W	4.0 eV
Q	1.050		

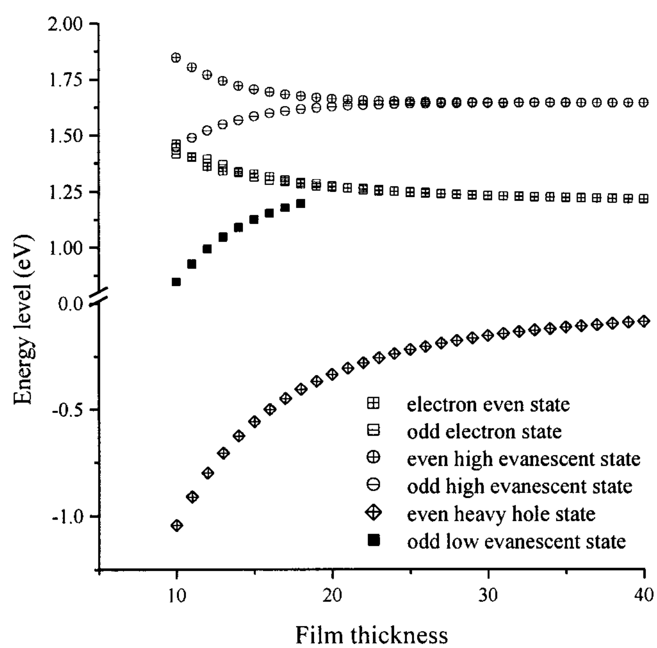

FIG. 1. Energy level of each state as a function of film thickness. The work function is 4.0 eV.

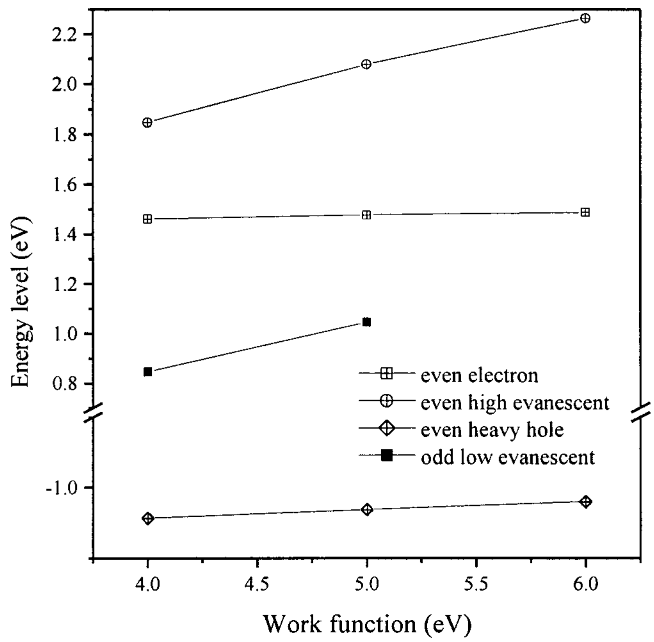

FIG. 2. Dependence of the energy level on the work function. The film thickness is 10 Å.

cent states represent most of the surface effects. The low evanescent state disappears at 6 eV.

There are five possible optical transitions that can take place when the work function is 4 eV; only four optical transitions are possible when it is 6 eV, the odd low evanescent state disappearing at 6 eV. The transition energies for these four possible transitions ($W = 6.0\,\mathrm{eV}$) are shown in Fig. 3. The result indicates that even at a film thickness of 30 Å a blue PL band can coexist with a red band in the visible

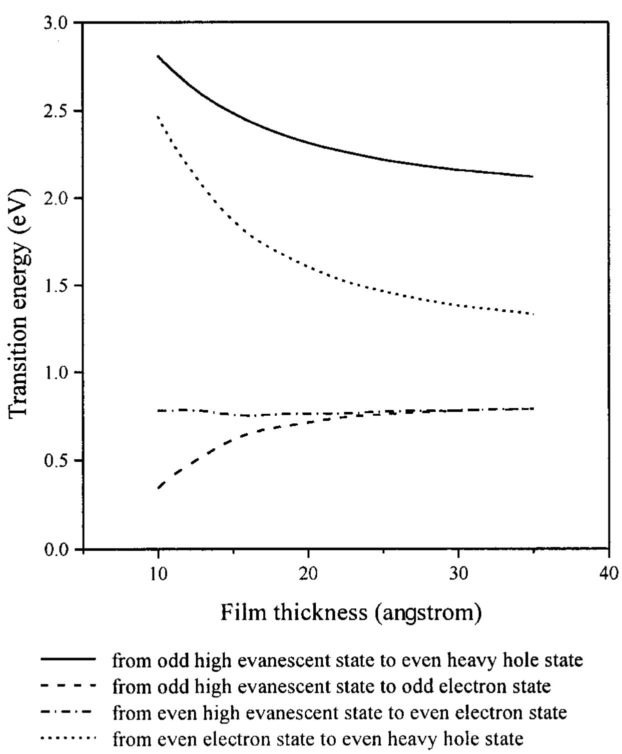

FIG. 3. Multiple transition energies in silicon quantum film. The work function is 6.0 eV.

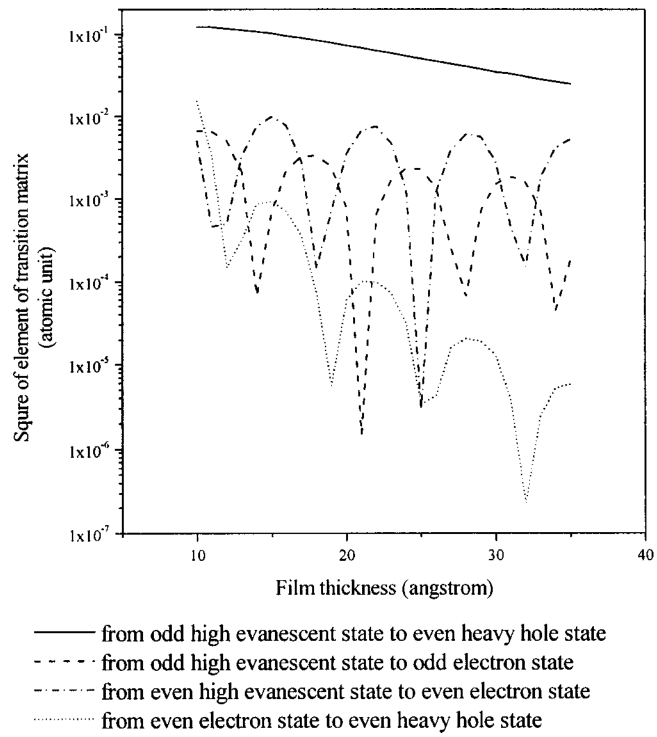

FIG. 4. Square of the transition momentum element for each of four possible transitions as a function of film thickness. The work function is 6.0 eV.

range: the blue is due to the transition from the high evanescent state to the heavy-hole state, which is longitudinally polarized PL (see Table II), and the red to the transition from the electron to the heavy-hole state. According to the result here, the blue longitudinally polarized PL band in a 30 Å silicon quantum well observed by Steigmeir *et al.*[17] might be due to the transition from the high evanescent to the heavy-hole state, which is longitudinally polarized.

Figure 4 gives the square of the matrix elements of the transition momentum, which is the transition probability, for each of the four possible transitions. It shows that the square of the transition momentum for the blue band is much larger than that for the red band. Therefore, the blue band is the fast-decaying band and the red band is the slowly decaying band, as observed by Kanemitsu[7] in nanocrystallites.

It may seem odd in Figs. 3 and 4 that optical transitions between odd and odd states or even and even states are discussed. In reality, however, transitions between the same-parity states of the envelope function are due to the opposite parity of the Bloch functions.

In summary, a formulation based on the full-zone $\mathbf{k}\cdot\mathbf{p}$ method has revealed the presence of evanescent states in thin silicon films. The presence of these evanescent states explains why both blue and red PL bands can coexist. The blue band decays fast and the red slowly. These states also explain why the blue band can appear for films thicker than 30 Å. The evanescent states are sensitive to the work function, even the existence of some of the states depending on the magnitude of the work function. This fact is an indication that the evanescent states represent surface effects as opposed to size effects.

APPENDIX: WAVE FUNCTIONS

The complex band structure of a [001] Si quantum film is such that the propagation state and an evanescent state coexist near the conduction-band minimum energy. The propagation states that represent the real crystal momentum are classified into the hole state and the electron state. The evanescent states that represent the purely imaginary crystal momentum are classified into a high evanescent state in the Δ_5 bands and a low evanescent state in the Δ_2 bands, high and low indicating the energy level of the evanescent state. Spurious solutions are excluded in our calculation. Therefore, only one of the wave vectors is chosen for the evanescent state.

The column vector of the envelope function of the high evanescent state in the Δ_5 bands becomes

$$\mathbf{F}^{\mathrm{he}}=[F_1^{\mathrm{he}} \quad -\eta_2^{\mathrm{he}}F_{1,z}^{\mathrm{he}} \quad \eta_3^{\mathrm{he}}F_1^{\mathrm{he}}]^T. \tag{A1}$$

Here the superscript T is for the transpose of the row vector, and the envelope function F_1^{he} is defined by

$$F_1^{\mathrm{he}}=A_1^{\mathrm{he}}e^{-\kappa^{\mathrm{he}}z}+B_1^{\mathrm{he}}e^{\kappa^{\mathrm{he}}z},$$

where the η's are given by

$$\eta_2^{\mathrm{he}}=\frac{-Q[(E_{25'}^u-(\kappa^{\mathrm{he}})^2)]}{[E_{15}-(\kappa^{\mathrm{he}})^2][E_{25'}^u-(\kappa^{\mathrm{he}})^2]+Q'^2(\kappa^{\mathrm{he}})^2},$$

$$\eta_3^{\mathrm{he}}=\frac{-QQ'(\kappa^{\mathrm{he}})^2}{[E_{15}-(\kappa^{\mathrm{he}})^2][E_{25'}^u-(\kappa^{\mathrm{he}})^2]+Q'^2(\kappa^{\mathrm{he}})^2}$$

and the E's are defined by $E_j=E(\Gamma_j)-E^m$. The column vector of the envelope functions $\mathbf{F}^{\mathrm{he}}$ is valid only in the energy range between $E(\Gamma_{25'}^l)$ and $E(\Gamma_{15})$.

The column vector of the envelope function of the electron state in the Δ_1 bands becomes

$$\mathbf{F}^{\mathrm{el}}=[F_1^{\mathrm{el}} \quad F_2^{\mathrm{el}} \quad i\gamma_1F_{1,z}^{\mathrm{el}}+\gamma_2F_2^{\mathrm{el}}]^T, \tag{A2}$$

where the envelope functions F^{el} and the γ's are defined by

$$F_1^{\mathrm{el}}=A_1^{\mathrm{el}}e^{ik_1z}+B_1^{\mathrm{el}}e^{-ik_1z}+A_2^{\mathrm{el}}e^{ik_{21}z}+B_2^{\mathrm{el}}e^{-ik_2z},$$

$$F_2^{\mathrm{el}}=\eta_{21}^{\mathrm{el}}A_1^{\mathrm{el}}e^{ik_1z}-\eta_{21}^{\mathrm{el}}B_1^{\mathrm{el}}e^{-ik_1z}+\eta_{22}^{\mathrm{el}}A_2^{\mathrm{el}}e^{ik_{21}}z-\eta_{22}^{\mathrm{el}}B_2^{\mathrm{el}}e^{-ik_2z},$$

$$\gamma_1=\frac{\eta_{32}^{\mathrm{el}}\eta_{21}^{\mathrm{el}}-\eta_{31}^{\mathrm{el}}\eta_{22}^{\mathrm{el}}}{k_1\eta_{22}^{\mathrm{el}}-k_2\eta_{21}^{\mathrm{el}}},$$

$$\gamma_2=\frac{k_1\eta_{32}^{\mathrm{el}}-k_2\eta_{31}^{\mathrm{el}}}{k_1\eta_{22}^{\mathrm{el}}-k_2\eta_{21}^{\mathrm{el}}},$$

and the η's are given by

$$\eta_{21}^{\mathrm{el}}=\frac{-Tk_1}{E_1^u+k_1^2}, \quad \eta_{22}^{\mathrm{el}}=\frac{-Tk_2}{E_1^u+k_2^2},$$

$$\eta_{31}^{\mathrm{el}}=\frac{-T'k_1}{E_1^l+k_1^2}, \quad \eta_{32}^{\mathrm{el}}=\frac{-T'k_2}{E_1^l+k_2^2}.$$

The column vector of the envelope function of the low evanescent state in the Δ_2 bands becomes

$$\mathbf{F}^{\mathrm{le}}=[F_1^{\mathrm{le}} \quad -i\eta_2^{\mathrm{le}}F_{1,z}^{\mathrm{le}} \quad \eta_3^{\mathrm{le}}F_1^{\mathrm{le}} \quad -i\eta_4^{\mathrm{le}}F_{1,z}^{\mathrm{le}} \quad -i\eta_5^{\mathrm{le}}F_{1,z}^{\mathrm{le}}]^T, \tag{A3}$$

where the envelope function F_1^{le} is defined by

$$F_1^{\mathrm{le}}=A_1^{\mathrm{le}}e^{-\kappa^{\mathrm{le}}z}+B_1^{\mathrm{le}}e^{\kappa^{\mathrm{le}}z}$$

and the η's are given by

$$\eta_2^{\mathrm{le}}=\frac{-P}{E_{2'}^l-\alpha_3^{\mathrm{le}}-(\kappa^{\mathrm{le}})^2},$$

$$\eta_3^{\mathrm{le}}=\frac{-PP'(\kappa^{\mathrm{le}})^2}{[E_{2'}^l-\alpha_3^{\mathrm{le}}-(\kappa^{\mathrm{le}})^2][E_{25'}^l-\alpha_1^{\mathrm{le}}-\alpha_2^{\mathrm{le}}-(\kappa^{\mathrm{le}})^2]},$$

$$\eta_4^{\mathrm{le}}=\frac{\sqrt{2}R}{E_{12}-(\kappa^{\mathrm{le}})^2}-\frac{\sqrt{2}PP'R'(\kappa^{\mathrm{le}})^2}{[E_{12}-(\kappa^{\mathrm{le}})^2][E_{2'}^l-\alpha_3^{\mathrm{le}}-(\kappa^{\mathrm{le}})^2][E_{25'}^l-\alpha_1^{\mathrm{le}}-\alpha_2^{\mathrm{le}}-(\kappa^{\mathrm{le}})^2]},$$

$$\eta_2^{\mathrm{le}}=\frac{-P''}{E_{2'}^u-(\kappa^{\mathrm{le}})^2}+\frac{PP'P'''(\kappa^{\mathrm{le}})^2}{[E_{2'}^u-(\kappa^{\mathrm{le}})^2][E_{2'}^l-\alpha_3^{\mathrm{le}}-(\kappa^{\mathrm{le}})^2][E_{25'}^l-\alpha_1^{\mathrm{le}}-\alpha_2^{\mathrm{le}}-(\kappa^{\mathrm{le}})^2]}.$$

Here, the α's are defined by

$$\alpha_1^{\mathrm{le}}=\frac{-P'''^2(\kappa^{\mathrm{le}})^2}{E_{2'}^u-(\kappa^{\mathrm{le}})^2}, \quad \alpha_2^{\mathrm{le}}=\frac{-2R'^2(\kappa^{\mathrm{le}})^2}{E_{12}-(\kappa^{\mathrm{le}})^2},$$

$$\alpha_3^{\mathrm{le}}=\frac{-P'^2(\kappa^{\mathrm{le}})^2}{E_{25'}^u-\alpha_1^{\mathrm{le}}-\alpha_2^{\mathrm{le}}-(\kappa^{\mathrm{le}})^2}.$$

The column vector of the envelope functions $\mathbf{F}^{\mathrm{le}}$ is valid in the energy range between $E(\Gamma_{25'}^l)$ and $E(X_{lc})$ since the Δ_2 bands have only purely imagine crystal momentum in this range.

The wave functions of the high evanescent state Ψ^{he}, the electron state Ψ^{el}, and the low evanescent state Ψ^{le} are given by

$$\Psi^{\mathrm{he}}=F_1^{\mathrm{he}}u_{25'}^{l}-i\,\eta_2^{\mathrm{he}}F_{1,z}^{\mathrm{he}}u_{15}+\eta_3^{\mathrm{he}}F_1^{\mathrm{he}}u_{25'}^{u}, \tag{A4}$$

$$\Psi^{\mathrm{el}}=F_1^{\mathrm{el}}u_{15}+F_2^{\mathrm{el}}u_1^{u}+(i\,\gamma_1F_{1,z}^{\mathrm{el}}+\gamma_2F_2^{\mathrm{el}})u_1^{l}, \tag{A5}$$

and

$$\Psi^{\mathrm{le}}=F_1^{\mathrm{le}}u_{25'}^{l}-i\,\eta_2^{\mathrm{le}}F_{1,z}^{\mathrm{le}}u_{2'}^{l}+\eta_3^{\mathrm{le}}F_1^{\mathrm{le}}u_{25'}^{u}-i\,\eta_4^{\mathrm{le}}F_{1,z}^{\mathrm{le}}u_{12}-i\,\eta_5^{\mathrm{le}}F_{1,z}^{\mathrm{l3}}u_{2'}^{u}. \tag{A6}$$

*Author to whom correspondence should be addressed.
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