Excitons and excitonic fine structures in Si nanowires: Prediction of an electronic state crossover with diameter changes

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Si nano ires ha e attracted considerable attention as promising candidates for electronic, thermoelectric, photonic, and photo oltaic de ices, et there appears to be onl limited nderstanding of the nderl ing electronic and e citonic str ct res on all pertinent energ scales. Using atomistic pse dopotential calc lations of single-particle as ell as man -bod states, e ha e identi ed remarkable properties of Si nano ires in three energ scales: (i) In the high-energ –□1-eV scale, e nd an n s al electronic state crosso er hereb the nat re of the lo est nocc pied molec lar orbital (LUMO) state changes its s mmetr ith ire diameters for [001]-oriented ires b t not for [011]-oriented ires. This change leads to orbitall allo ed transitions becoming orbitall forbidden belo a certain critical diameter for [001] ires. (ii) In the intermediate-energ –□10^{-1}-eV scale, e describe the d e to the electron-hole e change interaction, hereas the spin-allo ed states in the orbitall forbidden diameter region remain dark. The diameter dependence of the ne-str ct re splitting of e citonic states scales as $1/D^{2.3}$ in [001] ires and as $1/D^{2.6}$ in [011] ires. S rface-polari ation effects are fo nd to signi cantl enhance electron-hole Co lomb interaction, b t ha e a small effect on the e change ne-str ct re splitting. The present ork pro ides a road map for a ariet of electronic and optical effects in Si nano ires that can g ide spectroscopic st dies.

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I. INTRODUCTION

Si nano ires ha e attracted considerable interest as promising candidate str ct res for electronic,[1,2] thermoelectric,[3,4] photonic,[5,6] and photo oltaic de ices,[7 11] re ected b n mero s papers on gro th,[12 14] str ct ral characteri ation,[15] transport,[16,17] and optical[15,18 23] properties. Yet, there appears to be limited nderstanding of the nderl ing electronic and e citonic properties. S ch nderstanding o ld span three energ scales: (i) in the high-energ □1-eV scale one needs to nderstand the nat re of con ned energ le els and their dependence on ire orientation and diameter (single-particle

here $\mathbf{M}_v = \sum_{h_i,e_j} C^{(v)}(h_i,e_j)\langle\psi_{h_i}|\widehat{\mathbf{P}}|\psi_{e_j}\rangle$ is the dipole transition matri , E_v is the e citon energ and the broadening of spectral lines, σ is chosen as 50 μeV. The e citon deca lifetime (τ_v) is calc lated according to[39]

$$\frac{1}{\tau_v} = \frac{4\alpha E_v n|M_v|^2}{m_0^2 h c^2}, \tag{7}$$

here n is the refracti e inde (□4.0 for photon

TABLE I. Direct prod ct of interband dipole matri elements $\Box h|\mathbf{P}_i|e\Box$ in Si [001] ires (D_{2d} s mmetr) and [011] ires (C_{2v} s mmetr). $\mathbf{P}_i$ represents the dipole operator along the ire a is (P_{001} for [001] ires and P_{011} for [011] ires) and in-plane direction (P_{110} for [001] and P_{100} for [011]). The s mmetric A_1 representation (dipole-allo ed transition) is gi en in bold. For [001] ires the LUMO A_1 is allo ed in P_{001} and E is allo ed in P_{110}. For [011] ires A_1 is allo ed in P_{011}.

[001]:	$\Box h\|P_{001}(B_2)\|e\Box$	$\Box h\|P_{110}(E)\|e\Box$
	$\Box B_2 \Box B_2 \Box A_1\Box = \mathbf{A_1}$	$\Box B_2 \Box E \Box A_1\Box = E$
	$\Box B_2 \Box B_2 \Box B_1\Box = B_1$	$\Box B_2 \Box E \Box B_1\Box = E$
	$\Box B_2 \Box B_2 \Box E\Box = E$	$\Box B_2 \Box E \Box E\Box = \mathbf{A_1} \Box A_2 \Box B_1 \Box B_2$
[011]:	$\Box h\|P_{011}(B_1)\|e\Box$	$\Box h\|P_{100}(A_1)\|e\Box$
	$\Box B_1 \Box B_1 \Box A_1\Box = \mathbf{A_1}$	$\Box B_1 \Box A_1 \Box A_1\Box = B_1$

corresponds to the electrostatic potential e cl ding the s rface-polari ation effect, and is the sol tion of the Poisson eq ation,

$$(\mathbf{r})\Box^2 \; {}^{\mathrm{dir}}_{e_j,e_j^{\Box}}(\mathbf{r}) = -4\pi e^2 \sum_{\sigma} \psi^{\Box}_{e_j}(\mathbf{r},\sigma)\psi_{e_j^{\Box}}(\mathbf{r},\sigma). \quad (11)$$

Eq ations (10) and (11) are sol ed in real space b sing a nite-difference discreti ation of the gradient operator and a conj gate-gradient minimi ation algorithm.[42,43]

In the follo ing e rst present res lts for [001] ires from the abo e (i), (ii), and (iii) energ scales, and then sho res lts for [011] ires. We then disc ss the effects of dielectric mismatch on e citon binding and e change interaction.

A. The *eV* energy scale: Single-particle states

B lk Si has si eq i alent cond ction-band alle s $_X$ (along the -X direction), from hich the LUMO of ires is deri ed. The con nement plane of [001] ires contains fo r of these si $_X$ alle s, folded to the point of the ire Brillo in one. For [001] ires belonging to the D_{2d} point gro p, s mmetr anal sis[44] indicates that these fo r $_X$-deri ed states correspond to the A_1, B_1, and E representation, here both A_1 and B_1 are nondegenerate and E is do bl degenerate. The highest occ pied molec lar orbital (HOMO) al a s has nondegenerate B_2 s mmetr for all ire si es. Fig res 1(a) and 2 sho e ol tion of the LUMO and HOMO state hen the ire diameter is aried. At large diameter $D = 7.6$ nm, as q ant m con nement and inter alle co pling are negligible, the splitting bet een A_1, B_1, and E is tin , lea ing all these states practicall degenerate. With decreasing diameters, the enhanced inter alle co pling lifts the degenerac of these fo r states. This makes the B_1 state the lo est-energ one at diameter $D = 3.3$ nm to $D \Box 2.5$ nm (see Fig. 2). For lo er diameters, the A_1 state becomes the LUMO [e.g., $D = 2.2$ nm in Fig. 1(a)]. In contrast to the LUMO, the HOMO keeps the B_2 s mmetr for all the diameters. These HOMO and LUMO states ha e characteristic a e f nctions corresponding to their speci c s mmetries, as sho n in the right part of Fig. 1.

The s itching of s mmetr of the LUMO state ith diameter has a strong effect on the optical properties of these ires. Table I sho s the direct prod ct $\Box h|\mathbf{P}_i|e\Box$ for electron-hole dipole transition matri elements, in terms of the irred cible representations of the D_{2d} gro p ($|e\Box = A_1$; B_1; E and $|h\Box = B_2$). The dipole operator $\mathbf{P}_i$ consists of t o components: P_{001}

TABLE II. S mmetr anal sis of the e citonic states generated from HOMO and LUMO single-particle orbitals of [001] and [011] Si ires. Single-gro p representations are con erted to corresponding do ble-gro p representations to incl de the spin degree of freedom for e citons.

	HOMO	LUMO	E citons (HOMO□LUMO)
[001]:			
D = 7.6 nm	$B_2 \longrightarrow \ {}_6$	$E \longrightarrow \ {}_6 + \ {}_6$	${}_6$ □ ${}_6 = A_1$□ A_2□ E
D = 3.3 nm	$B_2 \longrightarrow \ {}_6$	$B_1 \longrightarrow \ {}_6$	${}_6$ □ ${}_6 = A_1$□ A_2□ E
D = 2.2 nm	$B_2 \longrightarrow \ {}_6$	$A_1 \longrightarrow \ {}_7$	${}_6$ □ ${}_7 = B_1$□ B_2□ E
[011]:			
D = 3.3 nm	$B_1 \longrightarrow \ {}_5$	$A_1 \longrightarrow \ {}_5$	${}_5$ □ ${}_5 = A_1$□ A_2□ B_1□ B_2

B. Intermediate energy scale: Exitonic states

Based on the gro p theor Table II describes ho single-particle HOMO and LUMO states contrib te to prod ce e citons. Here e con ert single-gro p representations to corresponding do ble-gro p ones adding the spin degrees of freedom. It can be seen that three gro ps of e citonic states emerge from different s mmetr of the LUMO state:

(1) At diameter D = 7.6 nm [Fig. 3(a)], the spin-orbit

TABLE III. Calc lated gro nd-state e citon energ $E(i)$ and e citon ne-str ct re splittings for [001] ires (Fig. 3) and [011] ires (Fig. 6). $E(i)$ (i = 1, 2, 3, and 4) represent the energ of e citonic transition corresponding to the notation (1, 2, 3, and 4) in Figs. 3 and 6.

		[001]:		**[011]:**
D (nm)	7.6	3.3	2.2	3.3
$E(1)$ (eV)	1.182	1.460	1.764	1.335
$E(2)$-$E(1)$ (μeV)	21.3	238.9	399.4	3.4
$E(3)$-$E(2)$ (μeV)	25.1	721.3	2668.6	20.8
$E(4)$-$E(3)$ (μeV)	92.4			1017.6

SO co pling), there is strong con g ration mi ing bet een these t o $_6$

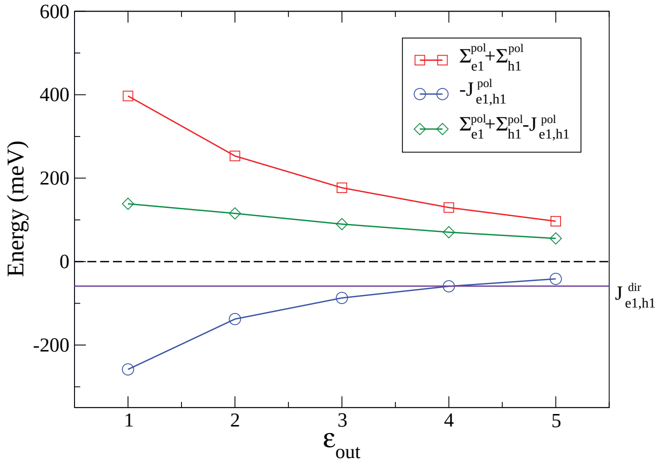

FIG. 8. (Color online) The s rface-polari ation-ind ced self-energ , $^{pol}_{i}$ [$i = e1$ (LUMO) and $h1$ (HOMO)], Co lomb interaction $-J^{pol}_{e1,h1}$ (negati e al e means decreasing e citon energies), and the s m $^{pol}_{e1}$ + $^{pol}_{h1}$ $- J^{pol}_{e1,h1}$ are sho n as a f nction of o t for a [001] ire of diameter D = 3.3 nm. The direct Co lomb interaction (e cl ding s rface-polari ation effect) $J^{dir}_{e1,h1}$ is sho n as a solid (hori ontal) line for comparison.

sing in = 11.85 (Ref. 40) for the Si ire and o t = 1 5 for the s rro nding material. The calc lations are performed for the [001] ire ith diameter D = 3.3 nm. Fig re 72oe2R()Tj/F51Tf1.0580TD(e)Tj/F11Tf.46370TD[(1)-163.5(()]T