

## Energy band mixing in core-shell-structured Si/FeSi<sub>2</sub> nanocomposites

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Using the bandmixing model of direct and indirect gaps, we calculate the energy levels of electrons and holes confined in the Si/FeSi<sub>2</sub> nanocomposite consisting of nanocrystalline Si core, interfacial FeSi<sub>2</sub> layer, and outer Fe<sub>2</sub>O<sub>3</sub> crust. The obtained results explain very well the intensity enhancement and pinning behavior of the observed photoluminescence peaks after the nanocomposite is stored in air. We also theoretically obtain the photoluminescence excitation characteristics. Good agreement is achieved between the theory and experiments. © 2006 American Institute of Physics.

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An upsurge of research activities in the physics and applications of nanostructured materials has led to more attention to electronic states and luminescence properties of nanoparticle composites.<sup>1-9</sup> For the typical luminescent nanomaterial, porous Si (PS), its photoluminescence (PL) origin was initially suggested to be due to the quantum confinement effect,<sup>1</sup> which completely depends on Si nanocrystal sizes. Further studies indicate that its PL property is not only determined by the quantum confinement but also controlled by the surface chemical bonds.<sup>3</sup> Many investigators attributed the PL to optical transition in the surface/interface states.<sup>3-5,9</sup> From a spectroscopic viewpoint, the PL spectra resulting from quantum confinement and surface states should have a large difference in shape. However, we cannot identify this difference in many PL results.<sup>2,3</sup> Interestingly, Zhang *et al.*<sup>10</sup> fabricated the Fe-passivated PS via a hydrothermal method and observed nondegrading PL that has been desired for many years. They found that after the sample was stored in air, the PL intensity increases but the peak position and spectral shape remain unchanged. Based on the formation of both Fe-Si bonds and outer  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin layer, they ascribed the nondegrading PL to the band-to-band recombination in the quantum confined Si cores. The surface Fe-Si bonds reduce Si dangling bonds and prevent the Si core from further oxidization. As a result, the PL intensity increases and the peak position remains the same. However, two additional problems must be addressed: (1) How do the surface dangling bonds affect the light-emitting process during the surface passivation? (2) The band gap of Fe-Si bonds is lower than that of Si.<sup>11,12</sup> Why and how can the passivation layer confine the photoexcited carriers in the Si core? The aforementioned problems seem difficult to overcome on the basis of surface state models or molecular bonding theory.

In fact, the surface passivation layer should also be regarded as a nanoparticle when the core has a very small size. Both the surface layer and core constitute a nanoparticle

composite. Its luminescence should be a result of the interaction between electronic states of the two nanoparticles.<sup>7,13</sup> Such nanocomposites generally exist in luminescent semiconductor nanomaterials.<sup>14</sup> The Fe-passivated PS presented by Zhang *et al.*<sup>10</sup> is a typical example (we call it as the Si/FeSi<sub>2</sub> nanocomposite). It is very complicated to build an effective theory to describe the electronic states of this sort of nanoparticle composite. In the theory of linear combination of atomic orbitals, the calculated energy spectrum can only portray the interaction among various atoms. The band attribution of each nanoparticle cannot be reflected. The envelope function in the effective mass model describes the slowly varying behavior of a wave function at band edge and gives many satisfactory results in heterostructure and superlattice. But in these nanosystems consisting of nanoparticles with different band structures, the electron wave function cannot be expanded by only one energy valley.

For a nanocomposite, the lattice periodicity is broken by different band structures of various nanoparticles, so that many energy valleys should be included in the Schrödinger equation. The surface no longer forms local surface states. It directly changes the quantum confinement characteristics and band attribution of electrons and holes. For simplicity, the band mixing model only considers direct and indirect valley components to investigate the light-emitting behavior. When strong direct gap components are dominant, the PL peaks are largely strengthened. The band mixing model not only can explain the light-emitting mechanism of the nanocomposites but also opens a fascinating way to tailor quantum confined sizes and nanometer environment for optimization of luminescent properties. In this work, we calculate electronic states of the core-shell-structured Si/FeSi<sub>2</sub> nanocomposites using the band mixing model. The obtained results can describe very well the results reported by Zhang *et al.*<sup>10</sup> and our experiments on the Si/FeSi<sub>2</sub> nanocomposites.

For the Si/FeSi<sub>2</sub> nanocomposite, the Schrödinger equation can be written<sup>7,13</sup>

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TABLE I. The calculated electron energy levels  $E_c$  and their  $C$  coefficients of the Si/FeSi<sub>2</sub> nanocomposite. The transition energy between electron and hole levels is  $\Delta E = E_c + E_v + E_g$ , where  $E_g = 1.1$  eV is the band gap of bulk Si and  $E_v = 0.308$  eV is the hole level.

$i$	$E_c$ (eV)	$C$	$\Delta E$ (eV)
1	0.051 92	0.044 03	...
2	0.418 9	11.78	1.827
3	0.677 8	0.080 96	...
4	1.650	3.429	3.058
5	1.809	0.291 9	...
6	2.840	4.772	4.248

$$\begin{pmatrix} H_D & H_{DI} \\ H_{ID} & H_I \end{pmatrix} \begin{pmatrix} \Psi_D \\ \Psi_I \end{pmatrix} = E \begin{pmatrix} \Psi_D \\ \Psi_I \end{pmatrix},$$

where  $H_D$  and  $H_I$  are the Hamiltonians for direct and indirect gap waves,  $H_{DI}$  ( $H_{ID}$ ) the interaction Hamiltonian, and  $\psi_D$  and  $\psi_I$  the wave functions for direct and indirect gap waves. Similar to the case in electrochemically etched PS

$$\begin{pmatrix} -\frac{\hbar^2}{2m_D} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2} \right] + V_D & V_{DI} \\ V_{ID} & -\frac{\hbar^2}{2m_I} \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2} \right] + V_I \end{pmatrix},$$

where  $m_D$  and  $m_I$  are the effective masses at direct and indirect valleys,  $V_D$  and  $V_I$  the potential energies for direct and indirect wave functions, and  $V_{DI}$  and  $V_{ID}$  the coupling potentials between direct and indirect valleys, respectively. Inside each nanolayer, the direct and indirect waves exist independently so that  $V_{DI}$  and  $V_{ID}$  are zero. We introduce a transition layer between different layers, where  $V_{DI} = V_{ID} = 0.1$  eV is chosen to induce the band coupling between different valleys. It is found that the values of  $V_{DI}$  and  $V_{ID}$  only have a weak influence on the calculated states. Simply, the energies in the two transition regions are assumed to vary linearly with the core radius. Using the finite-difference method,<sup>15</sup> we can solve the above Schrödinger equation and thus obtain the confined band mixing energy levels. To effectively characterize the band attribution, a coupling coefficient  $C = \bar{\Psi}_D / \bar{\Psi}_I$  is introduced. Since the phase of  $\Psi_D$  is different from that of  $\Psi_I$ , we define  $C$  to be the amplitude ratio of  $\Psi_D$  to  $\Psi_I$ . Then the states may be regarded as direct or indirect gap state according to whether  $C$  is larger or less than 1. In view of the description in Ref. 10, the Fe-passivated PS nanocrystal should consist of three regions: nc-Si core, interfacial FeSi<sub>2</sub> layer, and outer Fe<sub>2</sub>O<sub>3</sub> crust. FeSi<sub>2</sub> is an interesting material with very close indirect (0.78 eV) and direct (0.83 eV) gaps.<sup>11</sup> Theoretical calculation indicates that the effective masses of indirect and direct valleys are rather large,  $0.8m_o$ .<sup>11</sup> We take the hole mass as  $0.8m_o$  too. Since no valid data have been given so far for the band offsets in the Si/FeSi<sub>2</sub> heterostructure, we take  $\Delta E_c = 0.17$  eV and  $\Delta E_v = 0.1$  eV. For Fe<sub>2</sub>O<sub>3</sub>, we suppose that it is also an indirect gap material and

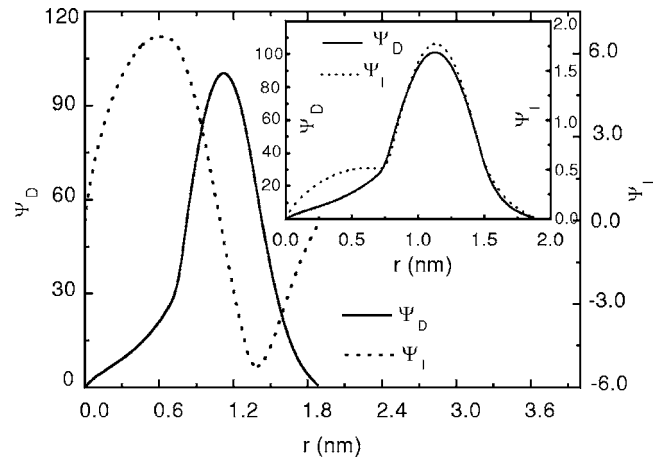


FIG. 1. Wave functions of the lowest antibonding  $E_2$  state. The inset illustrates the wave functions of the antibonding  $E_2$  states in the case with the shortest  $AB$  distance.

nanowires,<sup>1</sup> the cylinder coordinate is taken and thus the Hamiltonian can be described as follows:

has direct and indirect band gaps of 3 and 2 eV,<sup>16,17</sup> respectively. Its effective electron and hole masses are assumed to be the same as those of FeSi<sub>2</sub>. In our calculation, we take the thicknesses of nc-Si core (diameter), interfacial FeSi<sub>2</sub> layer, and outer Fe<sub>2</sub>O<sub>3</sub> crust to be 1.4, 0.8–1.3, and >1.8 nm, respectively.

Table I gives the calculated electron energy levels  $E_c$  and their  $C$  coefficients of the Si/FeSi<sub>2</sub> nanocomposite. The heterostructure shows a series of alternately bonding (small  $C$ ) and antibonding (large  $C$ ) state levels due to the band mixing. Strong light emission mainly depends on the antibonding states. Figure 1 shows the wave functions of the lowest antibonding  $E_2$  state. We can see that for the indirect valleys the Si core and FeSi<sub>2</sub> layer are the wells and so the indirect gap wave function is localized in the two layers, while for the direct valleys the Si core and Fe<sub>2</sub>O<sub>3</sub> layer are the barriers and so the direct gap wave function is confined inside the FeSi<sub>2</sub> well. Since the effective electron and hole masses of the FeSi<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> layers are almost the same, the calculated hole level is  $E_v = 0.308$  eV, comparable to the electron levels. Thus, the transition energy  $\Delta E_2$  between electron and hole levels is 1.827 eV (678 nm), which is very consistent with the energy of the PL peak observed by Zhang *et al.*

In our calculation, we have preset a large transition region,  $AB$ , between FeSi<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> layers. This corresponds to the case in the as-fabricated Fe-passivated PS. After the sample is annealed or stored in air, the Fe<sub>2</sub>O<sub>3</sub> layer thickens and so the transition layer thins.<sup>10</sup> The heterostructure interface gradually becomes sharp. Now we change the distance

TABLE II. The calculated electron and hole energy levels for the  $E_2$  states and their  $C$  coefficients in the cases with different  $A$  and  $B$  positions.

$A$ (nm)	$B$ (nm)	$E_c$ (eV)	$C$	$E_v$ (eV)	$\Delta E_2$ (eV)
1.30	1.80	0.419	11.78	0.308	1.827
1.34	1.70	0.410	16.53	0.312	1.821
1.38	1.60	0.408	26.35	0.318	1.826
1.44	1.50	0.406	54.14	0.323	1.830
1.46	1.48	0.404	56.63	0.323	1.827

between positions  $A$  and  $B$  to calculate the electron and hole energy levels and their  $C$  coefficients of the  $E_2$  state. The corresponding results are presented in Table II. It can be seen that when positions  $A$  and  $B$  gradually approach, the  $C$  coefficient largely increases, but the energy levels remain unchanged. This result indicates that the coupling coefficients of the antibonding states strongly depend on the distance between positions  $A$  and  $B$ . The inset of Fig. 1 displays the wave functions of the antibonding  $E_2$  state in the case with the shortest  $AB$  distance. One can see that the direct and indirect gap wave functions are both suppressed into the  $\text{FeSi}_2$  well, but the direct gap wave function has far greater intensity. This corresponds to the PL intensity enhancement for the stored sample. From Table I, we can further find that the  $E_4$  level of the antibonding states has an energy of 3.058 eV (405 nm). This is the energy for the first antibonding excitation state. It should be observable in the PL excitation (PLE) spectral experiments. Unfortunately, the PLE data were not given in Ref. 10. To check the PLE spectral feature, we fabricated similar Fe-passivated PS samples and examined the PL and PLE spectra. The obtained results are shown in Fig. 2. One can see that the PL peak is pinned at  $\sim 660$  nm, but its intensity increases with the storage time and saturates after  $\sim 4$  months. In addition, we can clearly see that the pinned PL band has a strong PLE peak at  $\sim 415$  nm, which is very consistent with our calculation. This result indicates that the band mixing model is suitable for explaining electronic state characteristics of the  $\text{Si}/\text{FeSi}_2$  nanocomposites.

In our current  $\text{Si}/\text{FeSi}_2$  nanocomposites, the Si core has a small size and thus the  $\text{FeSi}_2$  and  $\text{Fe}_2\text{O}_3$  layers cannot be

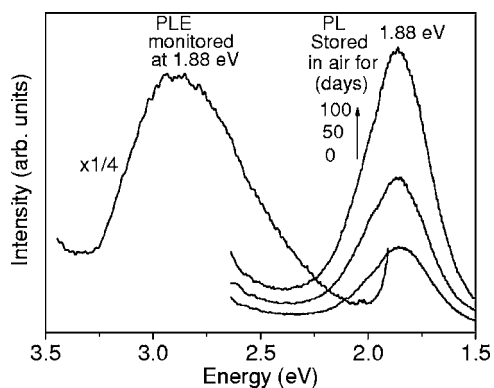


FIG. 2. PL and PLE spectra of the as-prepared  $\text{Si}/\text{FeSi}_2$  nanocomposite and those stored in air for 50 and 100 days. The PLE spectrum is taken under the monitoring energy of 1.88 eV (660 nm).

regarded as surface chemical bonds. We found in the calculations that the energy bands of the surface layers have a large influence on the band mixing, but hardly change the energy levels. This is why the PL spectra of PS have similar shapes when the surface states vary.<sup>3,8</sup> In addition, according to the analysis by Zhang *et al.*, the  $\text{FeSi}_2$  and  $\text{Fe}_2\text{O}_3$  layers passivate the surface of Si core and thus keep the core size constant. This leads to the pinned PL. In our calculation results, the energy level of fundamental state  $E_1$  is really low due to the quantum confinement by the deep  $\text{FeSi}_2$  well, but it belongs to an indirect gap state with small  $C$  coefficient and so is not connected with any light emission. For the  $E_2$  level, it is the antibonding state with large  $C$  coefficient and so has high emission efficiency. Very close indirect and direct gaps in  $\text{FeSi}_2$  produce alternate indirect and direct gap states, which open a way to tailor nanostructure for optimization of luminescent properties. Luminous wavelength is not decided by the quantum confinement only, thus it is incorrect to attribute the pinned PL peak to constant core size.

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