Electronic states and shapes of silicon quantum dots*

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A curviform surface breaks the symmetrical shape of silicon quantum dots on which some bonds can produce localized electronic states in the bandgap. The calculation results show that the bonding energy and electronic states of silicon quantum dots are different on various curved surfaces, for example, a Si–O–Si bridge bond on curved surface provides localized levels in bandgap and its bonding energy is shallower than that on the facet. The red-shifting ofthe photoluminescence spectrum on smaller silicon quantum dots can be explained by the curved surface effect. Experiments demonstrate that silicon quantum dots are activated for emission due to the localized levels provided by the curved surface effect.

Keywords: Si quantum dots, curved surface effect, surface bonds, localized levels

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1. Introduction

The investigation of silicon quantum dots (Si QDs) is a very active field of research because it has the interesting fundamental physical properties of these mesoscale objects and promising applications in advanced electronic devices and optoelectronic devices.[1–3] Si QDs provide nanoscale electronic confinement resulting in the opening of bandgaps and the appearing of quasi-direct gaps, which lead to the blue shift of their photoluminescence (PL) emission with crystallite size decreasing. But the PL peaks stand at some fixed positions of wavelength for smaller Si QDs prepared in oxygen, nitrogen or air atmosphere.[4,5] Numerous models have been proposed to explain the change of the PL. Wolkin *et al.*[6] indicated that the disappearance of the blue shift is related to the trapping of an electron by an Si=O bond producing localized levels in the bandgap of nanocrystals smaller than 3 nm, which was argued because no Si=O bond has been detected in FTIR transmission spectra. Moreover, Hadjisavvas *et al.*[7] and Cruz *et al.*[8] found that the shape of larger nanocrystals are often observed to be faceted, while that of smaller nanocrystals are always found to be spherical.

The central questions which arise are why some bonds on the surface of smaller QDs can produce localized states in the gap to break the QC effect and what is the relation between the localized level and the shape of QDs. Our calculation results show that localized levels can be produced in the bandgap by a Si–O–Si bridge bond on the curved surface of smaller Si QDs, but no localized state occurs in the gap for an Si–O–Si bridge bond on the facet. Therefore, besides size, the shape of the Si QD is more essential for producing a localized electronic state in the bandgap. This may be called the curved surface effect for smaller Si QDs. Analysis of the PL spectrum on a curved surface can show the characteristic of the type-II emission due to the curved surface effect.

2. Method and calculation

We choose some models in order to simulate various kinds of surface structures of Si QDs prepared in different atmospheres. The models based on supercells have the advantage of being simple and emphasize the quantum confinement effect and deformation of the surface structure. The electronic behavior is investigated by an *ab initio* nonrelativistic quantum mechanical analysis in this work. The density-functional theory (DFT) calculation is carried out by using the local density approximation (LDA), and the gradient-corrected exchange–correlation function (GGA) is used for the self-consistent total energy calculation.

For comparing their bonding energy and density of states, some special structures including a facet and a curviform surface are built on a Si QD. An opened bandgap and a quasi-direct gap structure are obtained for a good passivation of Si–H bonds. Figure 1 shows a structure and a density distribution of states which has obvious localized levels in the gap due to an Si–O–Si bridge bond on the curved surface of the Si QD. And Fig. 2 shows the structure of an Si–O–Si bridge bond on the facet of the Si QD and its density of states in which no localized state is found in the gap. It is found that the bonding energy on the facet (Fig. 3(a)) is deeper than that on the

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curved surface (Fig. 3(b)) for an Si–O–Si bridge bond. But for an Si=O bond, everything is almost the same as that shown in Fig. 4, and the bonding energy and density of states have little change from the facet to the curved surface.

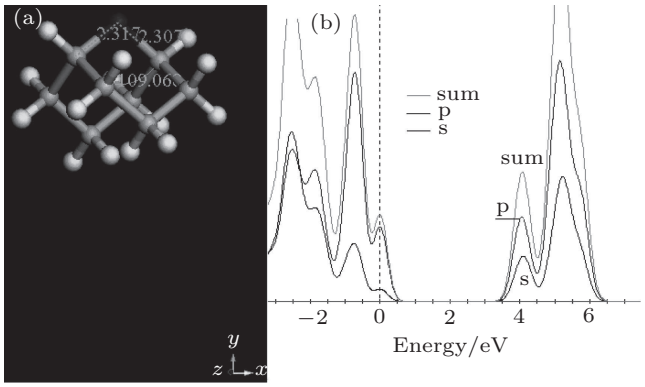


Fig. 1. Si–O–Si bridge bonds on curved surfaces of Si QDs and their densities of states.

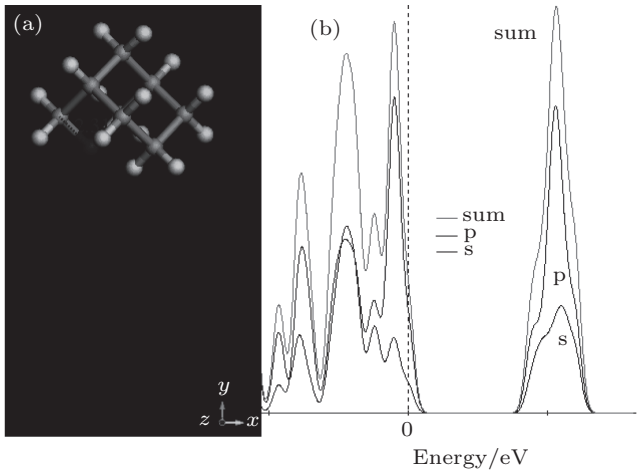


Fig. 2. Si–O–Si bridge bonds on facets of Si QDs and their densities of states.

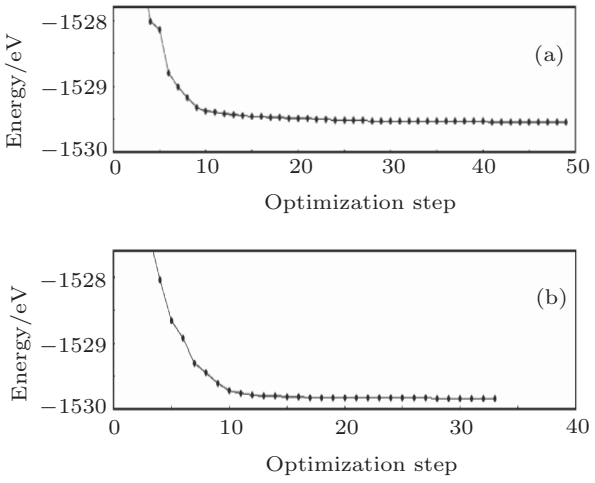


Fig. 3. Bonding energy of the Si–O–Si bridge bond on a curved surface (a), and on the facet (b) of an Si QD.

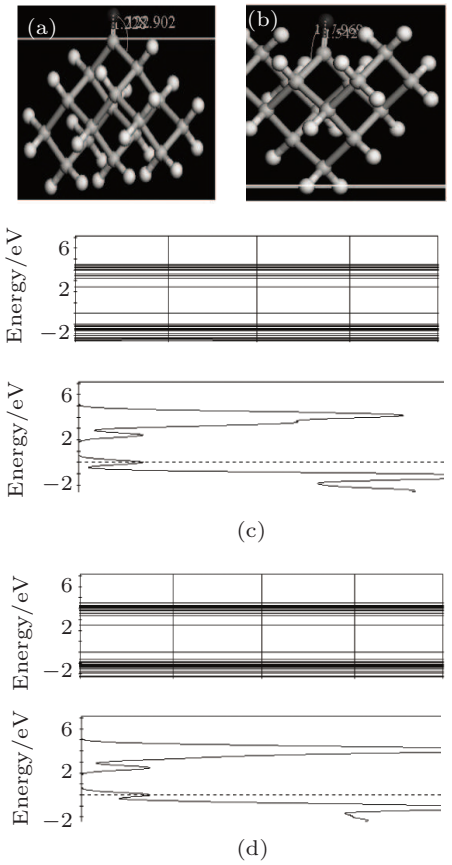


Fig. 4. Si=O bond structures on curved surfaces (a) and on facets (b) of Si QDs, and their densities of states.

3. Experiment

The QDs were fabricated by plasma produced from the interaction between silicon and a pulse laser. We prepared the Si QDs by using a pulse laser (wavelength: 1064 nm, pulse width (FWHM): 60 nm∼80 nm, repetition rate: 1000/s∼3000/s).[9] A wafer of P-type silicon with a room temperature resistivity of 20 Ω·cm was used as starting material which was cleaned in a Summa cleaner for 20 min. The nanosecond pulse of laser was normally focused on the silicon sample placed in oxygen, nitrogen or air atmosphere. The intensity of the laser pulse was about 5×10^8 W·cm^{-2} on silicon, which was sufficient to produce the plasma on the sample. After irradiation, many Si QDs were prepared by plasma, and distributed on the wall of the cavity hit by laser beam. In plasma, the dangling bonds were formed on the surfaces of Si QDs. Passivation of the dangling bonds on the surface could be obtained by different gas atoms in different atmospheres. Some surface bonds could not provide a good passivation in smaller crystallites, which provided the localized states in the bandgap. After annealing, the range of QD sizes became narrower and the defect states decreased so that the emission from some localized levels became stronger.

By using a RENISHAW Micro-Raman System, the PL spectra of the samples were measured under 514-nm excita-

tion. Figure 5 shows the PL spectrum and the relevant deconvoluted fit peaks for the sample prepared by nanosecond pulse laser in air atmosphere, in which fit peak 1 is related to an emission band due to the quantum confinement effect (QDs size: 1 nm∼5 nm), the fit peaks 2, 3, and 4 are the emissions of the localized states from some surface bonds respectively. After suitable annealing, peaks 2 and 3 become sharper and narrower because of the decrease of defect states and the arrangement of QDs sizes as shown in Fig. 6(a).

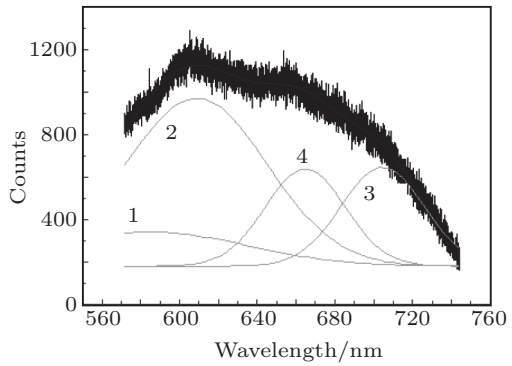


Fig. 5. PL spectrum on Si QDs prepared in air atmosphere, in which peak 1 relates to type-I emission band, peaks 2, 3, and 4 relate to type-II emission due to localized levels, respectively.

4. Results and discussion

Figure 6(b) shows a physics process of emission on Si QDs, in which the right side shows the opening band structure produced by quantum confinement (QC) effect, the type-I emission from near 800 nm to the ultraviolet is related to the electron jumping back to valence band in QDs with different sizes. This kind of emission forms a weaker and wider emission band produced by direct recombination of electron–holes between the opened conduction band and the valence band. In another way, the electron is pumped to the opened conduction band, and it tunnels into the localized states with different levels related to different surface bonds to form the active center. The lifetime of the states on the bottom of the conduction band opened is shorter, which is suitable for pumping. Here, it is important that some bonds on the curved surfaces of smaller QDs can provide the localized states, for example, the localized state of 1.78 eV and the localized state of 2.03 eV in the gap. The population inversion could be formed between the valence band and the localized levels for stimulated emission which belongs to the emission of type-II.[10,11] The annealing is an important step in activation for emission. The suitable annealing can reduce the arrangement of sizes of Si QDs to improve the emission of type-II as shown in Fig. 6(a).

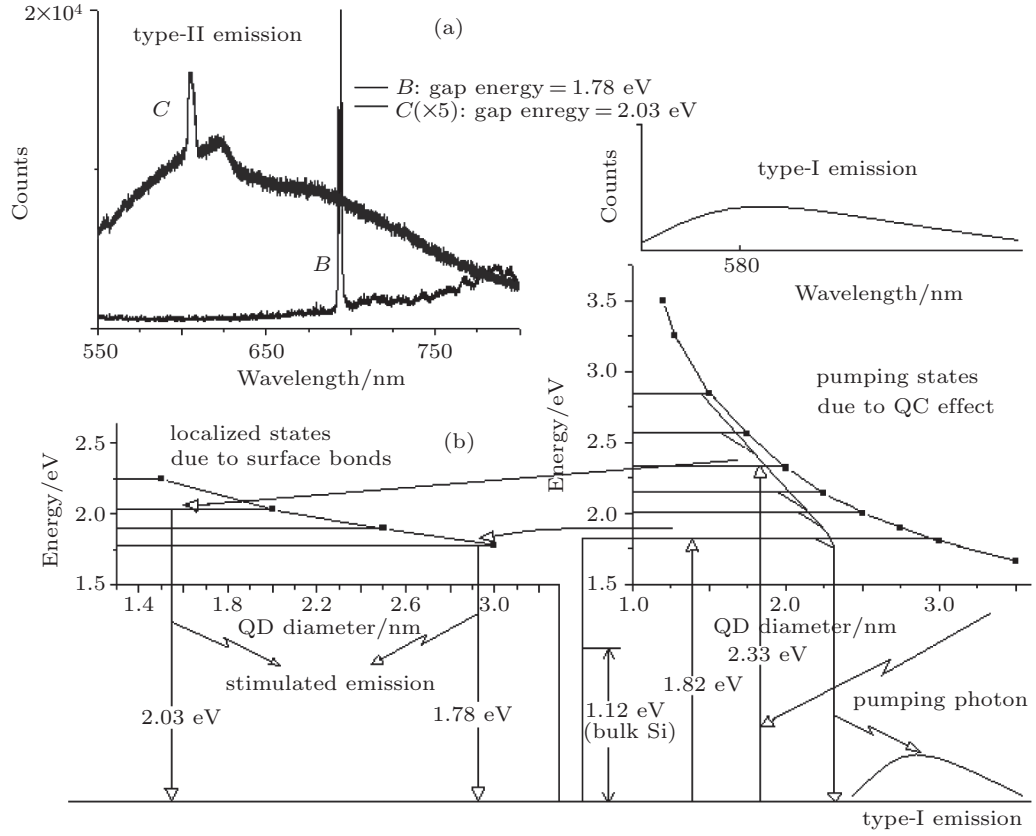


Fig. 6. (a) Type-II emission after annealing and type-I emission on Si QDs before annealing; (b) physics model and emission on Si QDs.

The calculation results indicate that the curviform surface breaks the symmetrical shape of Si QDs on which some bonds can provide localized states in the bandgap. For describing this curved surface (CS) effect of QDs, a curviform bonding factor A is defined as shown in the following form, which will affect the bonding energy and the localized states in the gap:

$$A = B^{1/(1+d)}/R. \tag{1}$$

In the formula, R is the curvature radius of the surface, and B is the bonding cover factor on the surface whose index d is cover dimension, such as $d = 0$ for Si=O bond, $d = 1$ for Si–O–Si bridge bond and $d = 2$ for Si–N bond. They relate to the point, line and face forms of the bonding cover, respectively. It is clear that a bonding cover of lower dimensions has more asymmetrical properties so that it is easy to form lower localized levels in the gap. The energy $E_{\rm L}$ of the localized level on the Si QD with the CS effect can be stated in the following form

$$E_{\rm L} = C/r^m - \beta A, \tag{2}$$

where β is the bond coefficient, r the radius of QD, and C the coefficient of the QC effect, m the index, which is about 2 for Si QDs embedded in oxide. In formula (2), the first term relates to the QC effect, and the second term represents the CS effect on smaller Si QDs, which provide localized levels lower than those on the bottom of conduction band.

A curviform energy factor A' can be defined in the following form

$$A' = B^{(1+d)}/R, \tag{3}$$

while the bonding energy $E_{\rm B}$ with the CS effect can be described by A' as follows:

$$E_{\rm B} = -E_{\rm B0} + \zeta A', \tag{4}$$

where ζ is the bonding coefficient and $E_{\rm B0}$ is the bonding energy for some bond on the facet of Si QDs. Here, the bond of higher-dimensional d has a bigger change of bonding energy. The bonding energy is deeper on tge facet and its bond is more stable for Si QDs with larger sizes (> 3 nm ~ 4 nm). For smaller Si QDs (< 2 nm ~ 3 nm), the facet on the surface disappears and some bonds on the curved surface begin to produce localized states in the bandgap. Therefore the CS effect on smaller QDs is the most important factor for forming the localized levels in the gap. The CS effect can explain the reason why the red-shift of PL spectra occurs on smaller Si QDs (< 3 nm) when oxidized.

The coefficients ζ and β in the above formulas could be modulated according to the results of experiment.

Figure 7 shows the CS effect on smaller QDs. For example, as shown with curve E, the localized levels due to Si–O–Si bond on the curved surface begin to form in the bandgap when the diameter of Si QDs is smaller than 2.5 nm.

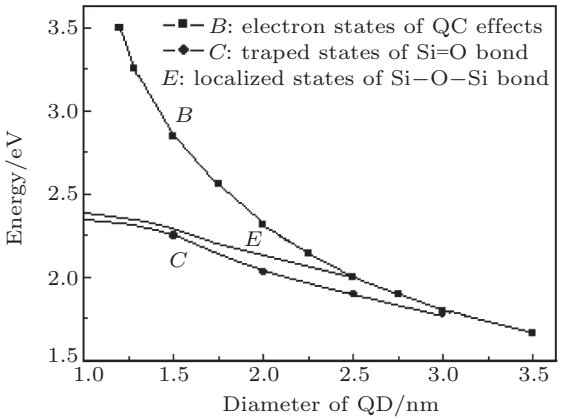


Fig. 7. Electronic states in Si QDs versus QD size, in which curve B relates to the surface passivation of Si–H bonds, curves C and E relate to localized levels of the Si–O–Si bridge bond and the Si=O bond on a curved surface with the CS effect, respectively.

5. Conclusion

The results of calculation and experiment demonstrate the CS effect on smaller Si QDs, by which two problems can be solved. The first one is that some bonds, such as the Si–O–Si bridge bond, on curved surfaces of smaller Si QDs provide the localized levels in the bandgap to form emission centers which break the blue-shift of PL spectra. Therefore, the CS effect plays an important role for the PL emission of smaller Si QDs prepared in oxygen, nitrogen or air atmosphere. The second one is that the facets are distributed on bigger Si QDs, on which it is difficult for surface bonds to produce localized states, so the QC effect plays a main role for the PL spectra of bigger Si QDs.

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