Curved surface effect and emission on silicon nanostructures*

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The curved surface (CS) effect on nanosilicon plays a main role in the activation for emission and photonic manipulation. The CS effect breaks the symmetrical shape of nanosilicon on which some bonds can produce localized electron states in the band gap. The investigation in calculation and experiment demonstrates that the different curvatures can form the characteristic electron states for some special bonding on the nanosilicon surface, which are related to a series of peaks in photoluminecience (PL), such as $L_{\rm N}$, $L_{\rm NO}$, $L_{\rm O1}$, and $L_{\rm O2}$ lines in PL spectra due to Si–N, Si–NO, Si=O, and Si–O–Si bonds on curved surface, respectively. Si–Yb bond on curved surface of Si nanostructures can provide the localized states in the band gap deeply and manipulate the emission wavelength into the window of optical communication by the CS effect, which is marked as the $L_{\rm Yb}$ line of electroluminescence (EL) emission.

Keywords: silicon nanostructures, curved surface effect, characteristic line, localized states

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1. Introduction

The investigation of silicon nanocrystals is a very active field of research because of the interesting fundamental physical properties of these mesoscale objects and promising applications in advanced optoelectronic devices.[1–8] Silicon nanocrystals provide nanoscale electronic confinement resulting in the opening of the bandgap and the occurrence of a quasi-direct gap, which blue-shifts their PL emission with decreasing crystallite size due to the quantum confinement (QC) effect. But the photoluminescence (PL) peaks stand at some fixed positions of wavelength for smaller Si quantum dots (QDs) prepared in nitrogen, air or oxygen atmospheres.[9–11]

As is well known, the PL emission on a sample prepared in Ar or high vacuum belongs to the emission, in which its blue-shift relies on the QC effect. It is noted that the optical properties of Si QDs are very sensitive to surface passivation, and that the size-independent PL peaks on samples prepared in oxygen, nitrogen or air atmospheres become obviously stronger. It is a task to establish the origin and exact mechanism of the enhancement of PL emission and even the optical gain from silicon nanostructures.[12] The enhancement of PL emission can be observed on the Si QDs surface with larger curvature, which is passivated in nitrogen or oxygen. Here, we do not know whether the shape or the size plays a main role in PL enhancement. Besides the intrinsic matter of Si QDs, it may also depend on the specific localized states produced in the band gap by oxide or nitride passivation on the curved surface.

2. Experiments

The enhancement of PL emission and the optical gain on Si QD are nearly always observed no matter what method is used to prepare it (e.g., heavily oxidized porous silicon,[13] magnetron sputtering[14] or plasma-enhanced chemical vapor deposition[15]). However, it may be better to make Si QDs embedded in oxide or nitride, in which the laser-material interaction process can produce nanostructures on silicon in various atmospheres.[16]

A wafer of P-type silicon with room temperature resistivity of 2 Ω·cm is used as the starting material which is cleaned in a Summa cleaner for 20 min. The pulse laser etching (PLE) laser is normally focused on the silicon sample placed in nitrogen, air or oxygen atmospheres. The intensity of the laser pulse is about 5×10^8 W·cm^{-2} on silicon, which is sufficient to produce the plasma vibrating on silicon. Nanostructures are prepared by plasma vibration to be distributed on the wall of the Purcell cavity. Then pulse laser deposit (PLD) processing builds a nitride or oxide layer on the nanostructures. After rapidly annealing, the construction with Si QDs embedded in the nitride or oxide layer is formed by the aggregating of rich silicon. The experiments demonstrate that it is important for preparing nanostructures to control the standing waves of plasma[16] in PLE and the ions beam of depositing in PLD.

Passivation of the dangling bonds on QD surface could

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be made by different gas atoms. Some surface bonds may not provide a good passivation in smaller crystallites, which can produce the localized states in the band gap for emission. The suitable annealing can reduce the non-radiation defect states and improve the emission.

By using RENISHAW Micro-Raman Systems, the PL spectra of the samples can be measured under 514-nm excitation at room temperature. The sharp PL peaks on samples prepared in nitrogen, air or oxygen atmospheres are compared. It is interesting that the shape of a single tip appears at 605 nm related to Si–N bond on the sample prepared in nitrogen as shown in Fig. 1(a); the peak with special shape occurs at 560 nm related to Si–NO bond on the sample prepared in air as shown in Fig. 1(b); figures 1(c) and 1(d) show the sharp peaks with the shape of twin tips at 693 nm related to Si=O bond and at 604 nm related to Si–O–Si bond on the samples prepared in oxygen. The peak position is kept at some wavelength which is independent of QD size. It is exciting that they have the threshold behaviors and the optical gains on samples prepared in nitrogen or oxygen atmosphere, which are measured with the variable stripe length (VSL) method.

As shown in Fig. 2(a), the PL peaks near 700 nm are measured on the samples in which the Yb ions are deposited on Si QDs by PLD. It is noted that the central wavelength of PL peak can be manipulated into the region of optical communication when the sample is prepared to a PIN junction with Si–Yb–Si structure after suitable annealing. The electroluminescence (EL) peaks near 1300 nm are observed in Fig. 2(b).

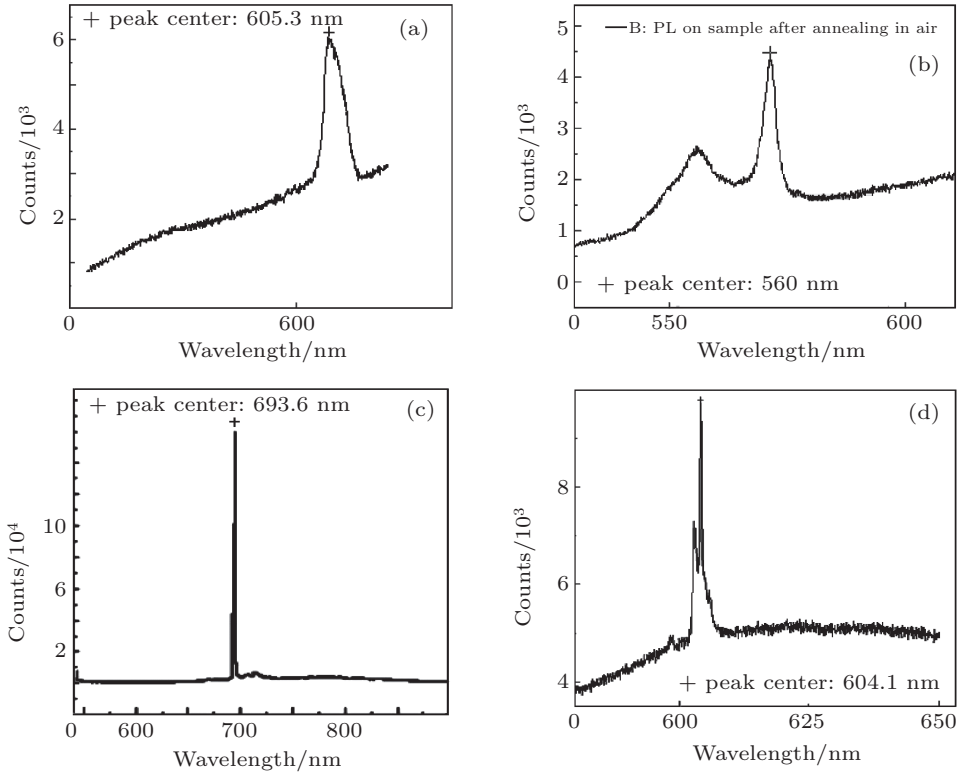


Fig. 1. Sharp PL peaks on samples, related to (a) Si–N bond, (b) Si–NO bond, (c) Si=O bond, and (d) Si–O–Si bond.

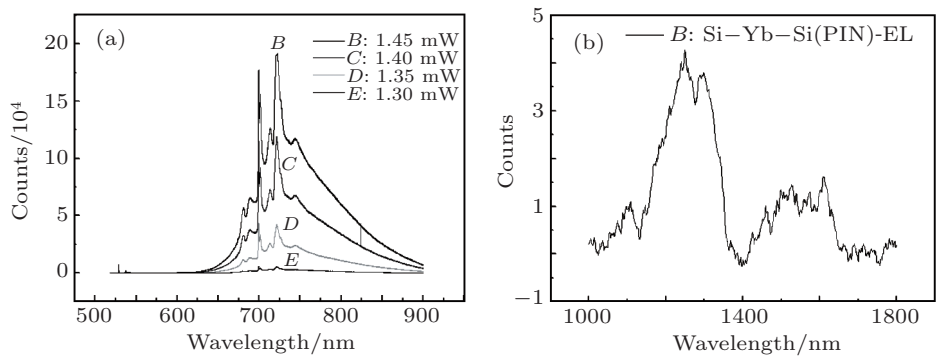


Fig. 2. (a) The PL peaks near 700 nm on the sample in which the Yb ions are deposited on Si nanostructures by PLD. (b) The EL peaks near 1300 nm on sample with PIN junction deposited by Yb.

The analysis of experimental results indicates that it is difficult to explain the size-independent PL peaks on samples prepared in the above ways, by using the quantum confinement effect model.

3. Calculation

Some models are chosen for simulating various kinds of surface structures of Si quantum dots prepared in different atmospheres. The models are simple and emphasize the quantum confinement effect and deformation of the surface structure, which are based on supercells. We investigate their electronic behavior by an *ab initio* non-relativistic quantum mechanical analysis in this work. The density-functional-theory (DFT) calculation is carried out by using the local density approximation (LDA) for the self-consistent total energy calculation.

In order to compare their bonding energy and density of states, some special surface structures including a facet and a curved surface are built on the same silicon quantum dot. An opened bandgap and a quasi-direct gap structure are obtained for a good passivation of Si–H bonds. Figure 3(a) shows an Si–N bond on the surface with larger curvature, which can provide the localized levels in band gap as shown in Fig. 3(b). Figure 3(c) shows that a band structure with four energy levels is formed, in which the population inversion could occur to generate stimulated emission. The calculation result is in good agreement with the experimental result, which is related to the PL peak in Fig. 1(a). Therefore the peak at 605 nm due to Si–N bond on curved surface of Si quantum dot is called L_{N} line. But an Si–N bond on the facet of Si quantum dots cannot provide any localized level in gap as shown in Fig. 4. An Si–NO bond on curved surface of Si quantum dot is built which is related to the passivation in air as shown in Fig. 5, which is related to the PL peak at 560 nm called L_{NO} line in Fig. 1(b).

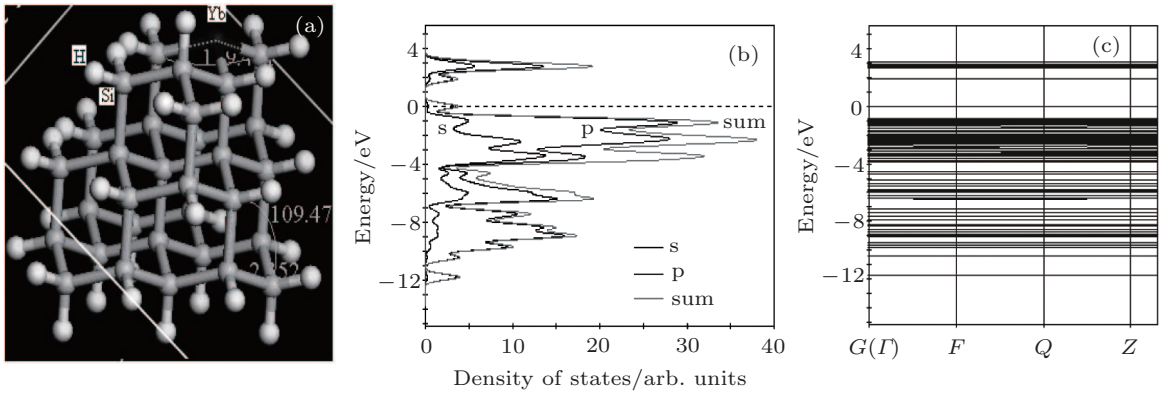


Fig. 3. Si–N bond structure on curved surface of Si QD (a), its band construction (b), and its density of states (c).

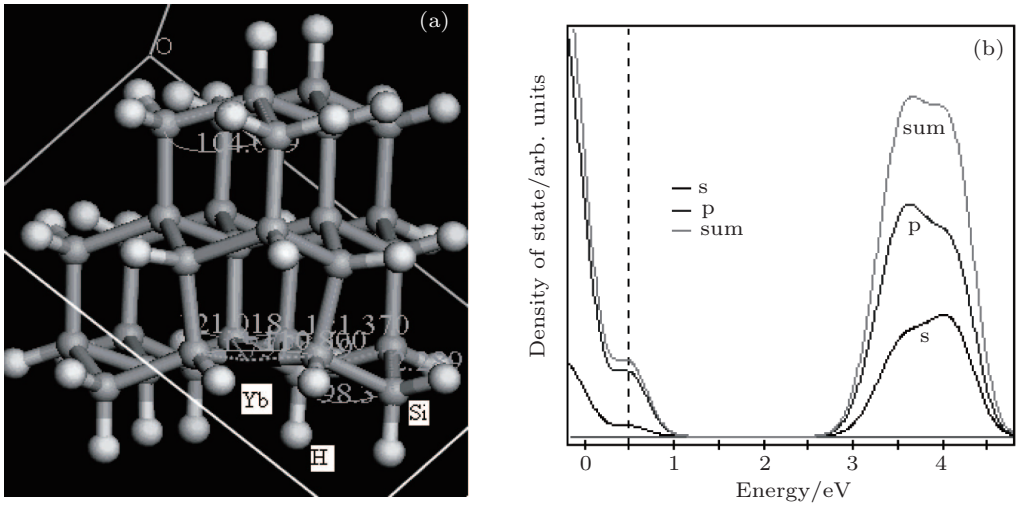


Fig. 4. The Si–N bond structures on facet of Si QD, and its density of states.

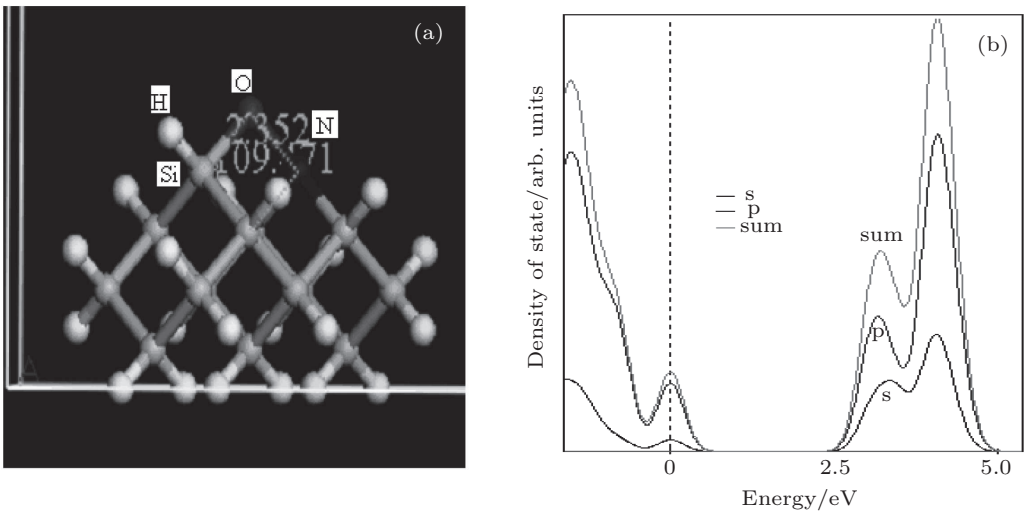


Fig. 5. An Si–NO bond structure on curved surface of Si QD which is related to the passivation in air.

We can make a comparison between their localized states due to Si=O bond on the curved surface (Fig. 6(a)) and those on the facet (Fig. 6(b)) of the same QD. Figure 1(c) shows the stimulated peak at 693 nm marked as L_{O1} line related to the localized states produced by Si=O bond on the curved surface. As shown in Fig. 7, some electronic states localize in band gap due to an Si–O–Si bridge bond on the curved surface of Si nanostructure (quantum line with a diameter of 1 nm), to which related is the stimulated emission at 604 nm marked as L_{O2} line as observed in Fig. 1(d). Figure 8 shows the Si–Yb bond structures on curved surface (a) and on facet (b) of Si QDs, and their densities of states. The localized state structure in Fig. 8(a) is related to the EL peak marked as L_{Yb} line at 1250 nm as shown in Fig. 2(b).

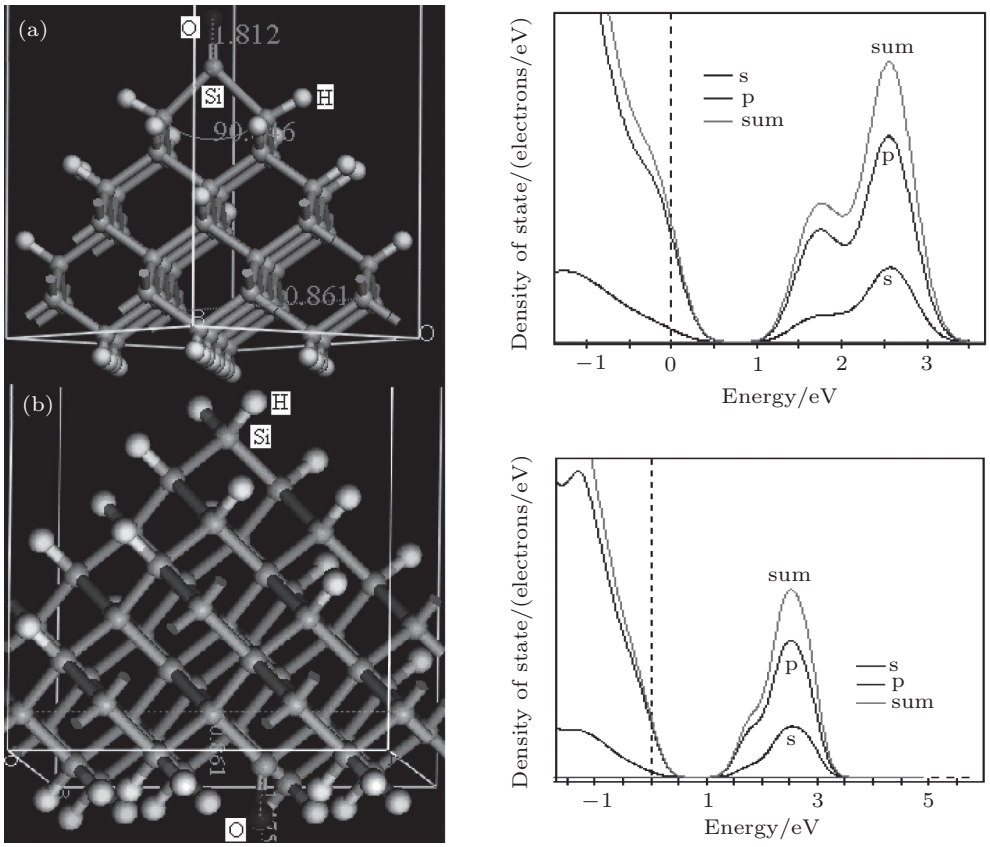


Fig. 6. The Si=O bond structures (a) on curved surface and (b) on facet of Si QDs, and their densities of states.

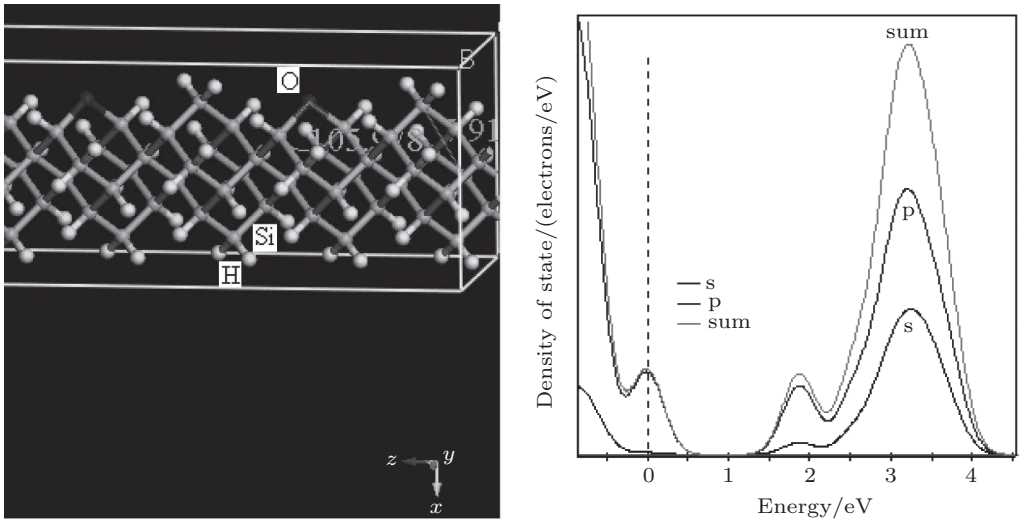


Fig. 7. The Si–O–Si bridge bond structure on Si nanostructure (quantum line with a diameter of 1 nm) and its density of states.

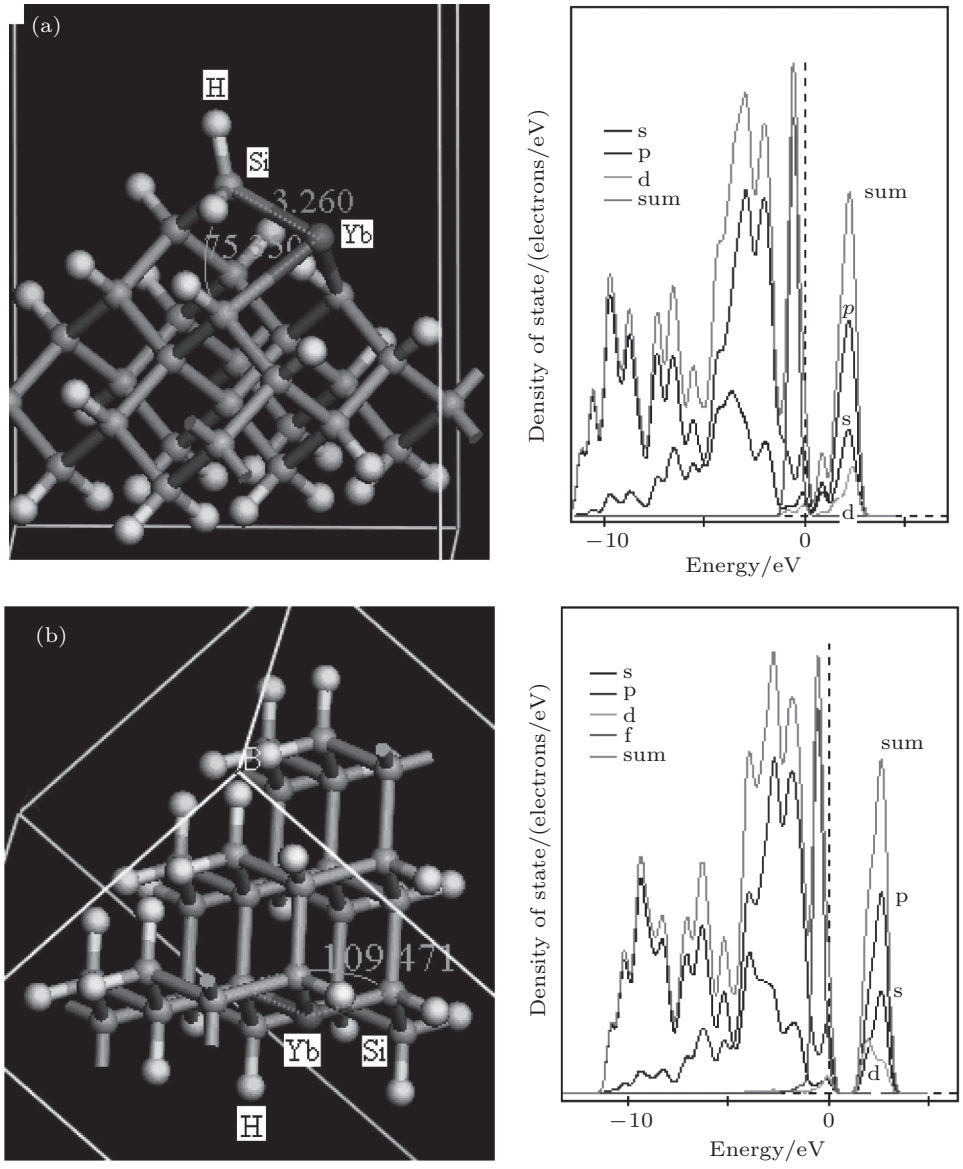


Fig. 8. The Si–Yb bond structures (a) on curved surface and (b) on facet of Si QDs, and their densities of states.

4. Results and discussion

Since Canham's first reported[17] on bright, room-temperature PL from porous silicon and Pavesi's first reported about optical gain from nanocrystalline silicon,[18] various PL spectra from silicon nanostructures independent of the preparation methods have attracted a lot of research interest in the field. Experimental results show that complicated PL spectra and obvious optical gain appear on silicon nanostructures prepared by pulsed laser in various atmospheres.[19]

It is under debate that whether the enhancement of PL and the optical gain are intrinsic to silicon nanostructures or due to specific defects related to some passivation on surface. In physical conception, the emission in PL spectrum from silicon nanostructures involves two kinds. The first is the emission associated with opening of band gap and discrete energy levels in nanostructures. This kind of emission produces a broad band in PL spectrum, which relates to the continuous distribution of the sizes of Si QDs. In the emission, the blue-shift of central wavelength is induced by QC effect. The second one belongs to the localized states emission associated with electronic tunneling from the levels of conduction band to the localized states related to nitride or oxide passivation. Here, the state in the conduction band elevated by QC effect forms a pumping level from which electron can transfer into the localized states in gap. The experiments demonstrate that a lot of localized states due to nitride or oxide passivation on Si QDs do enhance the PL emission, and make the central wavelength stand at the stable position for the localized state in band gap. After annealing, a lot of defect states no-radiated disappear and some special localized states remain there, in which the optical gain can be obtained.

The questions arising here are what relation between the localized levels and the shape of QDs is. Our calculation results show that the localized levels can be produced in band gap by Si–N bond on the curved surface of smaller Si QD, but not any localized state occurs in gap for Si–N bond on the facet as shown in Figs. 3 and 4. It is important that Si–N bonding on surface with larger curvature can produce the localized states to build up a four-energy system for nanolaser as shown in Figs. 3(b) and 3(c). In the same way, Si–NO bond, Si=O double bond, and Si–O–Si bridge bond have the same behavior on Si nanostructures as shown in Figs. 5, 6, and 7, respectively. Therefore, besides size, shape of Si nanostructures is more essential for producing localized state in gap. This may be called curved surface effect (CS effect) for Si nanostructure. The analyses of PL spectra on curved surface and their characteristic peaks can show the properties of the emission due to the CS effect.

In order to describe the CS effect of QDs, a curviform bonding factor A is defined as follows: $A = B^{1/(1+d)}/R$, which affects the energy level of the localized states in gap. In this formula, R is the curvature radius of surface, B is the bonding cover factor on surface, and 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 point, line, and face forms of bonding cover on surface, respectively. The bonding cover of lower dimension has more asymmetrical properties, for example, point form of bonding cover on surface. In the CS effect, the energy E_{L} of the localized levels on surface is more sensitive to the surface curvature $1/R$ for higher-dimensional bonding, but it is more sensitive to the bonding cover $B^{1/(1+d)}$ for lower-dimensional bonding, which may be expressed in the following form:

$$E_{\mathrm{L}} = C/r^m - \beta A, \tag{1}$$

where β is the bond coefficient, r is the radius of QD and C is the coefficient of QC effect, in which the index m is about 1.7 for Si QDs embedded in oxide. In the formula, the first term relates to the QC effect, and the second term refers to the CS effect of Si QDs, which provides the localized levels in band gap. Here, the CS effect involves the QC effect. Here, it is important that the factor A coming from the simulation calculation involves the surface curvature and the surface systematization, which determine the position and the generation of the localized states in gap.

A curviform energy factor A' can be defined as shown in the following form: $A' = B^{(1+d)}/R$, which refers to the bond energy on surface. While the bonding energy E_{B} with the CS effect can be described by A':

$$E_{\mathrm{B}} = -E_{\mathrm{B0}} + \zeta A', \tag{2}$$

where ζ is the bonding coefficient and E_{B0} is the bonding energy for some bond on facet of Si QDs. Here, the bond of higher dimension d has a bigger change of bonding energy. In physical conception, the second term in the above formula is related to the activating energy for emission. The coefficients ζ and β in the above formulas could be modulated according to the experimental results.

The formulas of the CS effect originate from the simulation calculation in the first principles investigation, which is in good agreement with the experimental results, for example, the wider and weaker band appears in PL spectrum on the Si nanostructure prepared in high vacuum or Ar atmosphere, in which not any sharp peak can be found in the emission. But on the Si nanostructure prepared in pure nitrogen the enhanced sharp peak occurs at 605 nm marked as L_{N} line due to Si–N bond, for the preparation in air the L_{NO} line due to Si–NO bond appears at 560 nm and in pure oxygen the L_{O1} line due to Si=O bond and L_{O2} line due to Si–O–Si bond occur at 693 nm and 604 nm, respectively. These characteristic lines in PL spectra can be explained by CS effect model.

As well as the nitrogen can do, Yb ion on curved surface of Si nanostructures can provide the localized states in band

gap deeply as shown in Fig. 8, and can manipulate the emission wavelength into the window of optical communication by the CS effect, which is marked as L_{Yb} line of EL emission in Fig. 2.

The facet shape almost disappears on the surface of smaller Si QDs, so the QD is smaller and the curvature of surface is bigger for spherical QDs. Therefore the CS effect is often submerged in the size effect, which makes a confusion that the QC effect fails for smaller QDs, for example, for QDs with the diameter smaller than 3 nm.[9] In physical conception the QC effect depends on size of Si QD because of the confinement of energy which is described from the first term in formula (1), but the levels of the localized states slowly arise for abiding the second term in formula (1) on smaller Si QDs with spherical shape. The size of Si QD is not important, the most essential factor is the curvature of surface bonded. It can be understand why the enhancement and the red-shift of PL occur on curved surface of various Si nanostructures passivated by oxide or nitride, such as on porous silicon oxidized, hole-net silicon oxidized and silicon QDs oxidized or nitrified.

5. Conclusion

In this paper, we prepare Si QDs and nanostructures in various atmospheres by using nanosecond laser. It is found in PL spectra that the emission in Si QDs prepared in vacuum is weaker and broader, which is dependent on nanostructures size, and the localized states emission from localized states is produced by nitride or oxide passivation. It is exciting that after choosing the suitable preparing conditions, the stimulated emissions at 694 nm and 604 nm are observed on sample prepared in oxygen, and even on sample prepared in nitrogen, and a stimulated peak at 605 nm is discovered. The four sharper and enhanced peaks in visual wavelength region are useful for highlight emitter of LED based on silicon, which are marked as L_{N}, L_{NO}, L_{O1}, and L_{O2} lines related to different localized states in gap, respectively. It is important that the emission wavelength in PL and EL could be manipulated into the region from 1200 nm to 1500 nm by the CS effect, which is marked as L_{Yb} line.

The results of calculation and experiment demonstrate the CS effect on Si QDs, by which their emission mechanism can be obtained. The red-shift and enhancement of localized states emission from localized states due to nitride or oxide passivation on surface can be interpreted by the CS effect. And the CS effect also plays a main role in the stimulated emission on Si QDs and nanostructures passivated by nitride or oxide. The most important result is that the energy level of the localized states depends on the surface curvature of passivation bonding in CS effect which is different from QC effect, which is dependent on the size of QD. The CS effect is very useful to activate nanolaser matter and manipulate photonic properties on silicon chip in future.

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