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CS effect and characteristic emission on silicon nanostructures prepared in various atmospheres

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ABSTRACT

The curved surface (CS) effect breaks symmetrical shape of nanosilicon on which some bonds can produce localized electron states in band gap. The different curvature can form the characteristic electron states for some special bonding on nanosilicon surface, which are related to a series peaks in photoluminescence (PL), such as L_N , L_{NO} , L_{O1} and L_{O2} line in PL spectra due to Si–N, Si–NO, Si=O and Si–O–Si bond on curved surface, respectively. Si–Yb bond on curved surface of Si nanostructures can manipulate the emission wavelength into the window of optical communication by the CS effect, which is marked as L_{Yb} line.

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1. Introduction

The investigation of silicon nanocrystals is a very active field of research because it has the interesting fundamental physical properties of these mesoscale objects and promising applications in advanced optoelectronic devices [1–5]. Silicon nanocrystals provide nanoscale electronic confinement resulting in opening of bandgap and occurring of quasi-direct gap, which pushes their PL emission in blue-shifting with decreasing of crystallite sizes due to the quantum confinement (QC) effect. But some photoluminescence (PL) peaks stand at stable positions of wavelength so that the blue-shifting disappears in smaller silicon quantum dots (Si QDs) prepared in nitrogen, air or oxygen atmospheres [6–8].

The PL emission on samples prepared in Ar or high vacuum occurs in Si QDs, and the spectra blue-shifting with decreasing QDs size relies on QC effect. It is noted that the optical properties of Si QDs are very sensitive to surface passivation, the size-independent PL peaks on samples prepared in nitrogen, oxygen or air atmospheres become stronger obviously. 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 [9]. The PL enhancement can be observed on the Si QDs surface with larger curvature, which is passivated in nitrogen or oxygen. Here, we think that the shape of Si QDs 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 band gap by oxide or nitride passivation on curved surface of Si QDs.

The enhancement of PL emission and the optical gain on Si QDs are nearly always observed independent of the preparation method (e.g., heavily oxidized porous silicon [10], magnetron sputtering [11] or plasma enhanced chemical vapor deposition [12]). However, it may be a better way to make Si QDs embedded in oxide or nitride that the laser-material interaction process can produce nanostructures by the pulse laser etching (PLE) on silicon in various atmospheres [13].

The PLE laser is focused on a wafer of P-type silicon placed in nitrogen, air or oxygen atmospheres. The intensity of the laser pulse is about $5 \times 10^8 \text{ W cm}^{-2}$ on silicon, which is sufficient to produce the plasma vibrating on silicon. Nanostructures are prepared by plasma vibrating to distribute on the wall of the Purcell cavity. Then the pulse laser deposit (PLD) processing builds nitride or oxide layer on the Nanostructures. After rapidly annealing, the construction with Si QDs embedded in nitride or oxide layer are formed by aggregating of rich silicon. The experiments demonstrate that it is important for preparing nanostructures to control the stand waves of plasma in PLE and the ions beam of depositing in PLD.

Passivation of the dangling bonds on QDs surface could be made in various atmospheres. Some surface bonds may not provide a good passivation in smaller crystallites, which can produce the localized states in band gap for emission.

PL spectra of the samples can be measured under the 514 nm excitation at room-temperature by using RENISHAW Micro-Raman Systems. The sharp PL peaks on samples prepared in nitrogen, air

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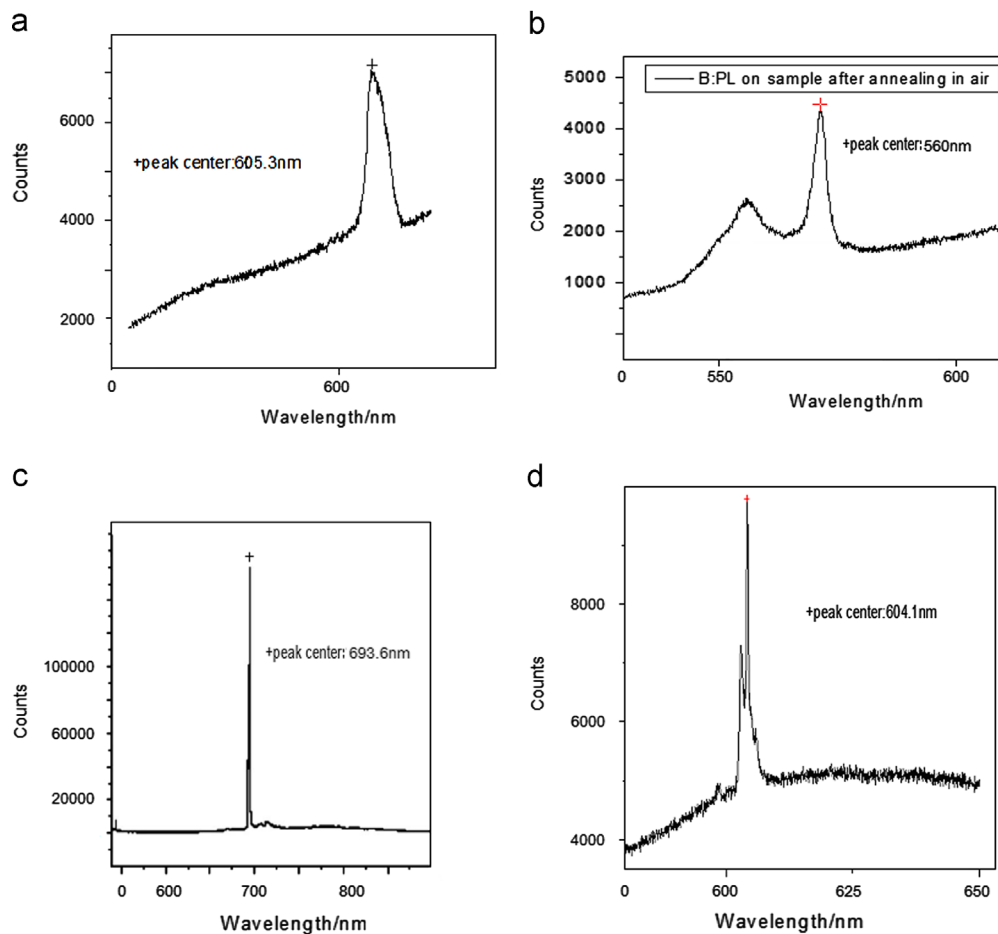


Fig. 1. Sharp PL peaks on samples related to (a) Si–N bond, (b) Si–NO bond, (c) Si=O bond, and (d) Si–O–Si bond.

or oxygen atmospheres are compared. It is interesting that the shape of single tip appears at 605 nm related to Si–N bond on the samples 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 samples prepared in air, as shown in Fig. 1(b); fig. 1(c) and (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 on sizes of QDs. It is exciting that they have the threshold behavior and the optical gain on samples prepared in nitrogen or oxygen atmospheres, 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 beam is deposited on Si QDs by PLD. It is noted that the center wavelength of PL peak can be manipulated into the wavelength region of optical communication by curved surface effect. The transparent pole films are deposited on the samples prepared by PLD for measuring electroluminescence (EL) spectrum [4]. The EL peaks near 1300 nm are observed in Fig. 2(b).

Having analyzed the experimental results, it is difficult to explain the size-independent PL peaks on these samples by using QC effect model [6].

Some models have been chosen for simulating various kinds of surface structures of Si QDs prepared in different atmospheres. We investigate their electronic behavior by an ab initio non-relativistic quantum mechanical analysis in this work. The DFT calculation was carried out by using the local density approximation (LDA) for the self-consistent total energy calculation.

Some special surface structures including a facet and a curved surface are built on a same silicon quantum dot for comparing their bonding energy and density of states. An opened bandgap and a quasi-direct gap structure are obtained for a good passivation of Si–H bonds. Fig. 3(a) shows a Si–N bond on the surface with larger curvature, which can provide the localized levels in band gap as shown in Fig. 3(b). Fig. 3(c) shows that a band structure with four energy levels is formed, in which the population inversion could occur between two groups of localized states in gap to generate stimulated emission. The calculation result in the energy levels is in good agreement with the experimental result, which is related to the PL peak measured in experiment in Fig. 1(a). Here, the peak at 605 nm due to Si–N bond on curved surface of Si QD is called L_N line. But a Si–N bond on the facet of Si QDs cannot provide any localized level in gap, in which the bond angle on facet is about 140° much bigger than the bond angle 110° on curved surface, as shown in Fig. 4. A Si–NO bond on curved surface of Si QD passivated in air is built, as shown in Fig. 5, which is related to the PL peak at 560 nm called L_{NO} line in Fig. 1(b).

We can make a comparison between their localized states due to Si=O bond on the curved surface (Fig. 6(a)) and on the facet (Fig. 6(b)) of the same QD. Fig. 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 a Si–O–Si bridge bond on curved surface of Si nanostructure (quantum line with diameter of 1 nm), related to which the stimulated emission at 604 nm marked as L_{O2} line was observed in Fig. 1(d). The calculation results show that the localized states in band gap produced from

these bonds on curved surface of Si QDs are related to the emission peaks in energy, respectively.

In same way, Fig. 8(a) and (b) show the Si–Yb bond structures on curved surface with the bond angle of 75° and on facet with bond angle of 109° in Si QDs, and their density of states. The localized states structure in Fig. 8(a) is related to the EL peak marked as L_{Yb} line at 1250 nm in Fig. 2(b). But there are almost not localized states to be discovered on facet in Fig. 8(b).

Since Canham's first report of bright, room temperature PL from porous silicon [14] and Pavesi's first report about optical gain

from nanocrystalline silicon in 2000 [15], 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 pulse laser in various atmospheres [16].

It is debated that whether the enhancement of PL and the optical gain are intrinsic to silicon nanostructures or are due to specific defects related to some passivation on surface. In physical conception, the emission in PL spectra from silicon nanostructures involves two kinds. The first one occurs in Si QDs associated with opening of band gap and discrete energy levels in nanostructures. This kind of emission produces a broad band in PL spectra, which relates to the continuative distribution of the sizes of Si QDs. In the emission spectra, the blue-shift of center wavelength abides by QC effect. The second one occurs on surface of Si QDs 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 center wavelength stand at the stable position for the localized state in band gap. It is noted that after annealing, the defect states no-radiated disappear and the some special localized states are remained, in which the optical gain can be obtained.

Here, the arising questions 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 the four energy system for nanolaser, as shown in Fig. 3(b) and (c). In 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. 5–7. 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) on Si nanostructures. The analysis for PL spectra on curved surface and their characteristic peaks can show the properties of the type-II emission due to the CS effect.

A curviform bonding factor A is defined for describing the CS effect of QDs as followed: $A=B^{1/(1+d)}/R$, which affects the energy level localizing in gap. In the form, 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

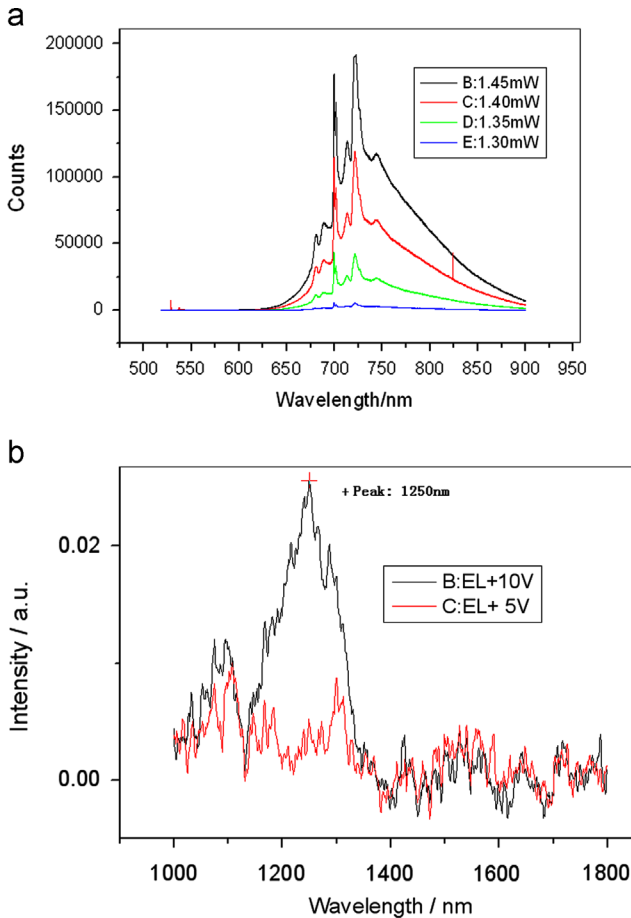


Fig. 2. (a) The PL peaks near 700 nm on the sample in which the Yb ions beam is deposited on Si nanostructures by PLD. (b) The EL peaks near 1300 nm on sample with PIN junction deposited by Yb.

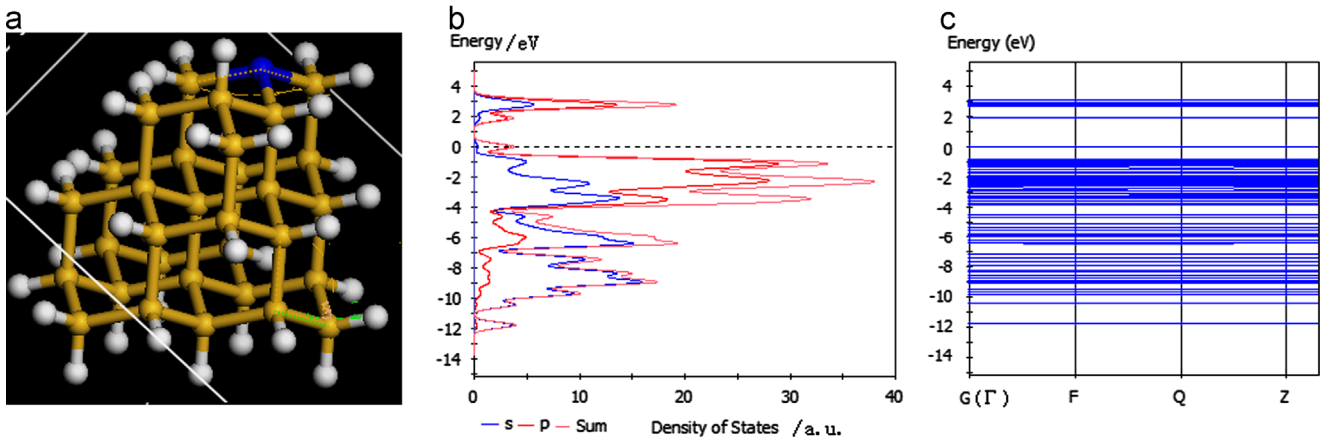


Fig. 3. Si–N bond structure on curved surface of Si QD, whose bond angle is about 98° (a), its band construction (b) and its density of states (c).

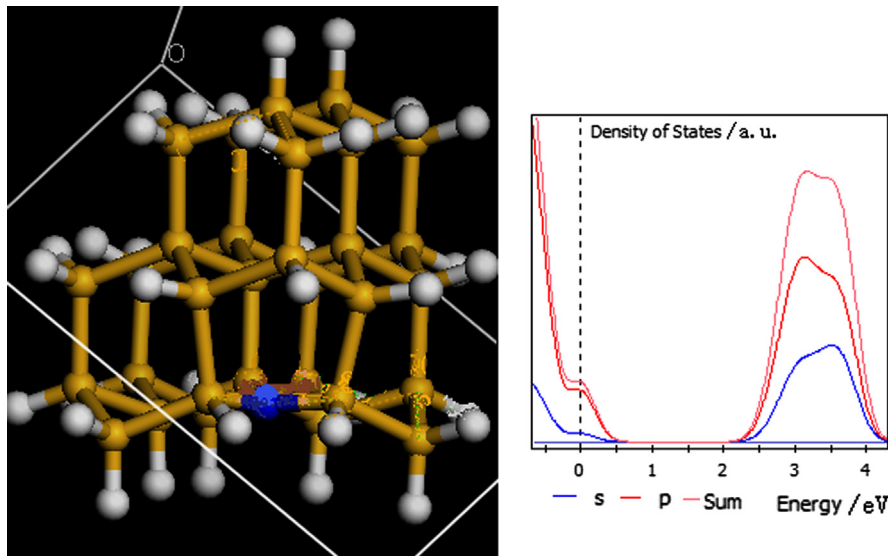


Fig. 4. Si–N bond structures on facet of Si QD, whose bond angle is about 120° and its density of states.

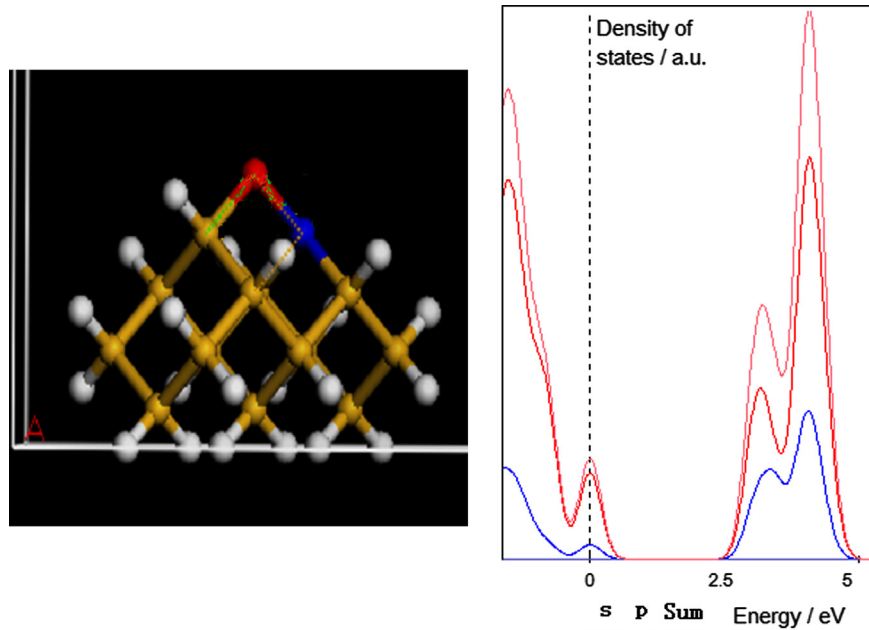


Fig. 5. A Si–NO bond structure on curved surface of Si QD which is related to the passivation in air.

bridge bond and $d=2$ for Si–N bond. They relate to point, line and face forms of bonding cover on surface. The bonding cover of lower dimension has more asymmetrical properties, such as point form of bonding cover on surface. In the CS effect, the energy E_L of the localized states 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 is stated by followed form:

$$E_L = C/r^m - \beta A \quad (1)$$

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 presents the CS effect of Si QDs, which provide the localized levels in band gap. 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 of the localized states in gap.

In order to describe the bond energy on surface, a curviform energy factor A' is defined: $A' = B^{1/(1+d)}/R$. While the bonding energy E_B with the CS effect can be described by A' :

$$E_B = -E_{B0} + \zeta A' \quad (2)$$

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 formula (2) is related to the activating energy for emission. The coefficient ζ and β in above formulas could be modulated according to the experimental results.

The formulas of the CS effect are originated from the simulation calculation in the first principle investigation, which have a good agreement with the results of experiment in energy, such as on the

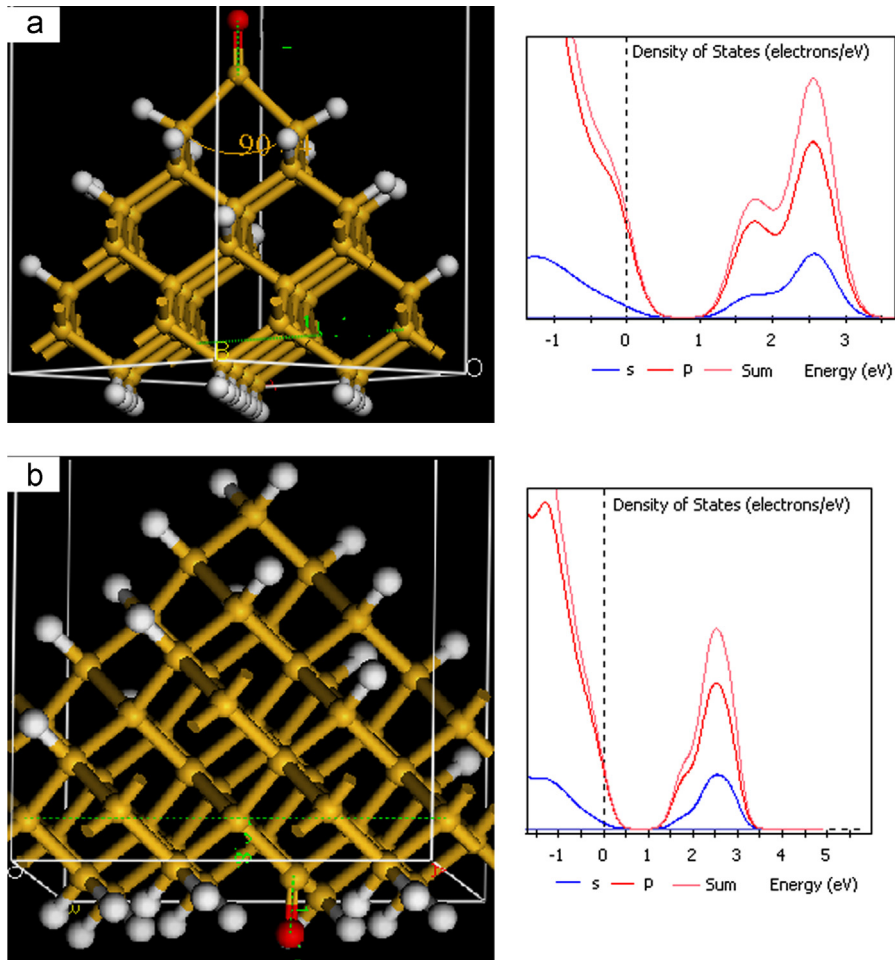


Fig. 6. Si=O bond structures (a) on curved surface and (b) on facet of Si QDs, and their density of states.

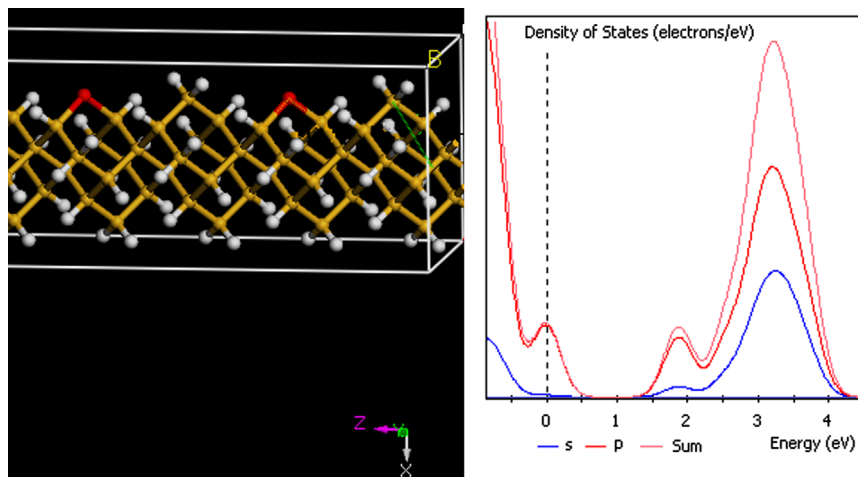


Fig. 7. Si-O-Si bridge bond structure on Si nanostructure (quantum line with diameter of 1 nm) and its density of states.

Si nanostructures prepared in pure nitrogen the enhanced sharp peak occurs at 605 nm marked as L_N line due to Si-N bond, for preparing 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 on curved surface, respectively. These characteristic lines in PL spectra can be explained by CS effect model.

As well as the nitrogen 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 calculation results in the CS effect model show a good relationship in energy between the electronic states localized in

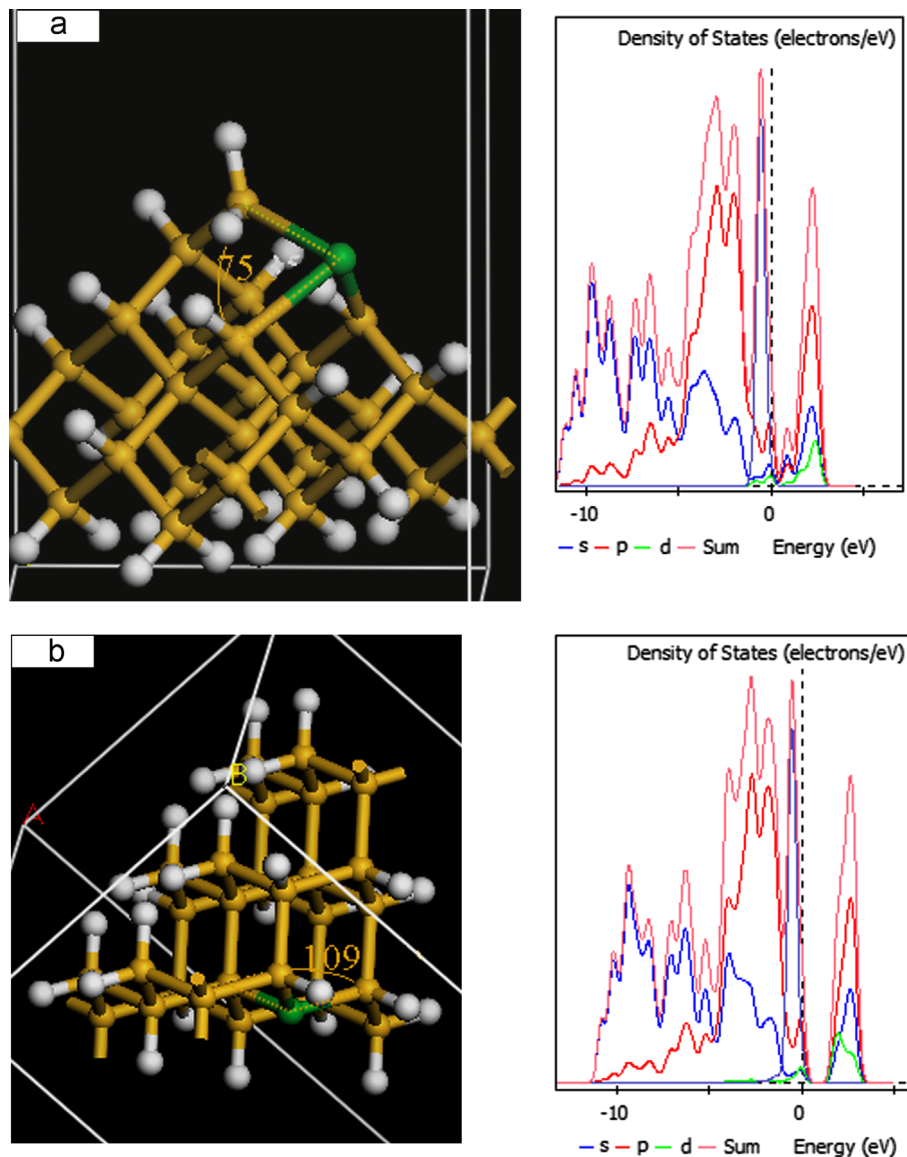


Fig. 8. Si–Yb bond structures (a) on curved surface, whose bond angle is about 75° and (b) on facet of Si QDs, whose bond angle is about 109° and their density of states.

band gap due to different bonds on curved surface and the characteristic line of PL spectra measured on the samples prepared in various conditions.

The CS effect is often submerged in the size effect, which makes a confusion that the QC effect fails for smaller QDs, such as for QDs with the diameter smaller than 3 nm [6]. In physical conception the QC effect depends on sizes of Si QDs because of confining for energy which is described from the first term in the formula (1), but the levels of the localized states slowly arise for abiding the second term in the formula (1) on smaller Si QDs with sphere shape. In fact, the sizes of Si QDs is not important for smaller QDs, the most essential factor is the curvature of surface bonded. It can be understood 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.

Taken together, we prepare Si QDs and nanostructures in various atmospheres by using nanosecond laser. It is found in PL spectra that the emission on surface of Si QDs comes from localized states produced by nitride or oxide passivation. It is exciting that after selecting the suitable preparing conditions, the stimulated emission at 694 nm and 604 nm is observed on

samples prepared in oxygen, and even on samples prepared in nitrogen a stimulated peak at 605 nm is discovered. The four sharper and enhanced peaks in visual wavelength are useful for highlight emitter of LED based on silicon, which are marked as L_N , L_{NO} , L_{O1} and L_{O2} line related to different localized states in gap, respectively. It is important that the emission wavelength in PL and EL can be manipulated into the region from 1200 nm to 1500 nm by the CS effect, which is marked as L_{Yb} line related to Si–Yb bond on curved surface of Si QDs.

The results of calculation and experiment demonstrate the CS effect on Si QDs, by which the emission mechanism on them can be obtained. The red-shift and enhancement of the emission on nitride or oxide surface of Si QDs from localized states 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, in which the four energy levels system occurs in band construction for building nanolaser. 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 depending on the sizes of QDs. The CS effect is very useful to activate nanolaser matter and manipulate photonic properties on silicon chip in future.

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