Activation of silicon quantum dots for emission*

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Emission of silicon quantum dots is weak when their surface is passivated well. Oxygen or nitrogen on surface of silicon quantum dots can break the passivation to form localized electronic states in band gap to generate active centers where stronger emission occurs. From this point of view, we can build up radiative matters for emission. By controlling the surface bonds of silicon quantum dots, emissions of various wavelengths can be obtained. Our experimental results demonstrate that annealing is important in treatment of the activation, and stimulated emissions at about 600 and 700 nm take place on active silicon quantum dots.

Keywords: activation for emission, silicon quantum dots, localized states

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1. Introduction

Bulk silicon shows very inefficient band-to-band radiative electron-hole recombination because of its indirect band gap. Light emission and amplification in silicon have thus focused on the use of silicon engineered materials such as nanocrystals.[1−4] A great number of experimental evidences of high-intensity emission from silicon quantum dots (QDs) generated broad interest in last decade.[3−7] Various experiments confirm the following behaviors of Si QD observed at room temperature in different atmospheres: 1) wider and weaker photoluminescence (PL) emission appears in the wavelength range from near infrared to ultraviolet in pure hydrogen or in vacuum, and blue-shifted PL peak is observed with decreasing nanocrystal size; 2) exposure to oxygen, nitrogen or air atmosphere may not provide a good passivation on Si QD, and stronger emission would occur in a narrower wavelength range; 3) stimulated peaks are observed at 605 and 693 nm after suitable annealing and preparing samples in oxygen.

Experiments and calculations indicate that stronger emission is due to the activation of Si QD. Besides Si=O bond and Si–O–Si bridge bond, Si–NO or Si–N bond can break the passivation on the surface of Si QD to generate radiative centers for emission.[8,9] In this paper, it is found that the surface bonds of Si QD with different shapes and sizes can affect the passivation and the activation, which is the possible reason different behaviors are detected in different atmospheres, depends on the pressure.[6]

It is important that the localized states formed by Si=O bond on the surface of QD split from conduction band into gap to form the radiative centers when the size of QD is less than 3 nm. This is the reason why the stimulated emission occurs in smaller QD and the spontaneous emission appears in bigger QD. However, only when the size of QD is much less (about 2 nm), the localized states formed by Si–NO or Si–N bond on the surface of QD split into band gap to form the radiative centers. It is also found in calculation that the hydrogen bond on the surface of smaller Si QD (less than 1 nm) may not provide a good passivation.

2. Experiment

We prepared the Si QD by using a pulse laser (wavelength: 1064 nm, pulse width (FWHM): 60–

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80 ns, repetition rate: 1000–3000 s^{-1}). The quantum dots were fabricated by plasma produced from interaction between silicon and pulse laser.[3,7] The nanosecond laser pulse was normally focused on the silicon sample placed in oxygen, nitrogen, or air atmosphere. The intensity of the laser pulse is about 5×10^8 W/cm^2 on silicon which is sufficient to produce the plasma on sample. A wafer of P-type silicon with room-temperature resistivity of 20 Ω·cm was used as initial material which was cleaned in a Summa cleaner for 20 min. After irradiation, a lot of silicon QDs are prepared by plasma, which distribute on the wall of the cavity hit by laser beam. In plasma, the dangling bonds are formed on the surface of Si QD. Passivation of the dangling bonds on surface could be obtained with different gas atoms in different atmospheres. Some surface bonds may not provide a good passivation in small crystallites so that some defect states remain. There are more dangling bonds and defect states before annealing. Then the samples were loaded into an annealing furnace at 1000 °C for 5–30 min in oxygen, nitrogen, or air atmosphere. After annealing, the range of QD size becomes narrower and the defect states decrease. The combination between suitable annealing and irradiation of pulse laser in different atmospheres is a good way to achieve the activation of Si QD for emission.

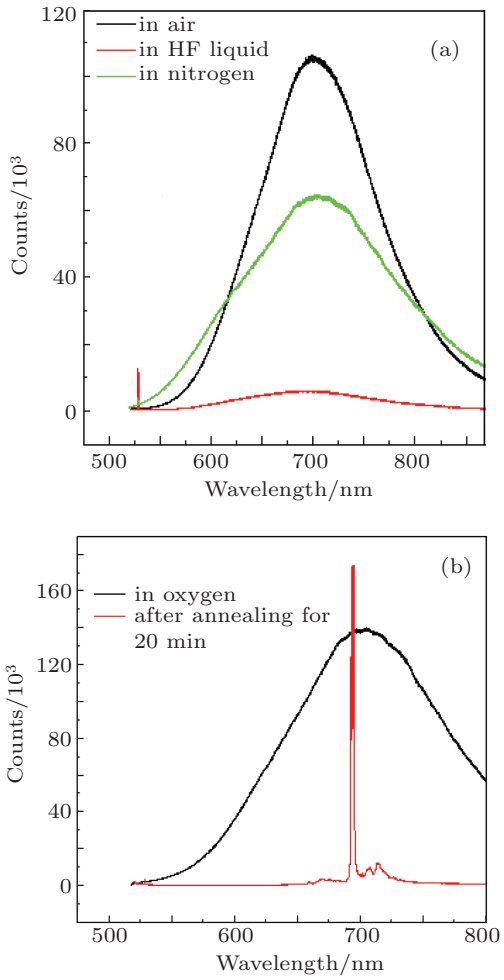


Fig. 1. (colour online) (a) Photoluminescence spectra on Si QD prepared in HF liquid, nitrogen, and air atmosphere. (b) Photoluminescence spectra on Si QD prepared in oxygen and annealed for 20 min.

The PL spectra of samples under 514-nm excitation were measured by using RENISHAW Micro-Raman Systems. The PL spectra of Si QD prepared in HF liquid, nitrogen, and air atmospheres are compared, as shown in Fig. 1(a). The PL spectra of the sample in oxygen and the annealing effect for emission are shown in Fig. 1(b). There is almost no photoluminescence observed for Si QD with a good passivation of hydrogen in HF liquid, and conversely the Si QD prepared in nitrogen or air atmosphere has an enhanced PL emission. The stimulated emission is observed on Si QD prepared in oxygen after annealing for 20 min, and sharper peak is obtained due to the resonance of Purcell cavity. Thus, it is obvious that the preparing atmospheres and annealing play important roles in the activation of Si QD.

3. Simulation calculation

For the structures of QD prepared in different atmospheres, we have chosen some models in order to simulate the experiment process. The models based on supercells are simple and emphasize the quantum confinement (QC) effect and deformation of the surface structure. The electronic behavior is investigated through *ab initio* non-relativistic quantum mechanical analysis. The density-functional-theory (DFT) calculation were carried out by using the local density approximation (LDA) and non-local gradient-corrected exchange-correlation function (GGA) to obtain self-consistent total energy. It is considered that both LDA and GGA underestimate the band gap for semiconductors and insulators.

Figure 2 shows the Si QD structure and its density of states for smaller nanocrystals. We can make a comparison between Si–H bonds with a good passivation and Si=O bond breaking passivation on surface to form the localized states in gap. The calculation

results demonstrate the quasi-direct band effect (see the left part of Fig. 2) and the opening effect of band gap caused by the quantum confinement. An Si–O–Si bridge bond also breaks the passivation of Si QD to form the localized states in gap, as shown Fig. 3. However, the Si–OH bond does not affect the passivation on surface of Si QD. Figures 4 and 5 show that a Si–N bond or a Si–NO bond can also break the passivation to build the localized states in gap, and thus the radiative centers are built. On this basis, we can explain the physical mechanism of the activation of Si QD in nitrogen or air atmosphere. It is interesting that different bonds on surface affect the passivation of Si QD in different sizes. For example, 3-nm Si=O bond and 2-nm Si–O–Si bridge (Si–N) bond can break the passivation, forming the localized states to activate Si QD.

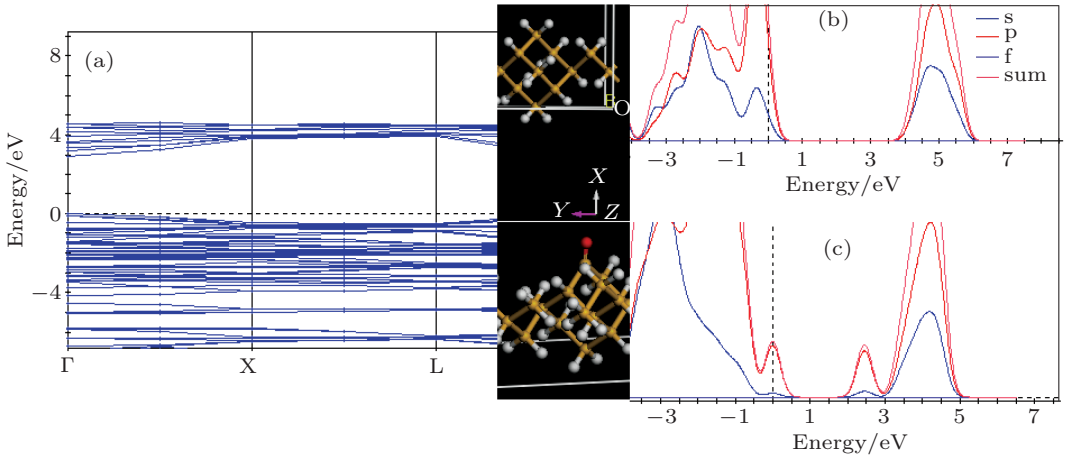


Fig. 2. (colour online) (a) Si QD structure and band structures, (b)density of states for Si–H bonds, and (c) density of states for smaller nano-crystals of Si=O bonds.

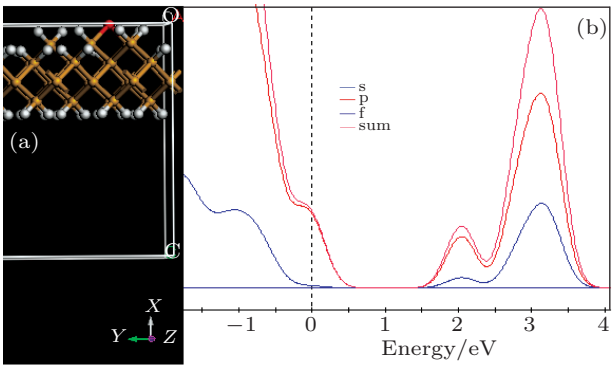


Fig. 3. (colour online) (a) Si QD structure and (b) density of states caused by a Si–O–Si bond on surface.

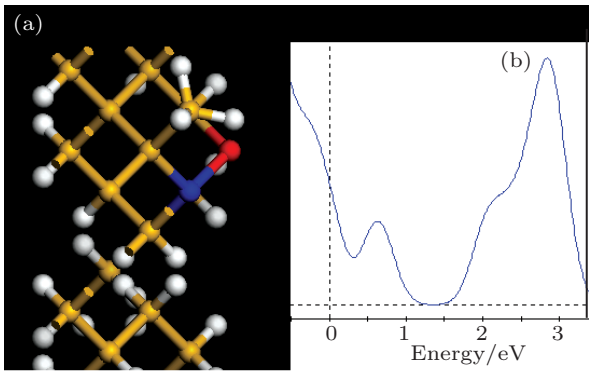


Fig. 5. (colour online) (a) Si QD structure and (b) density of states caused by a Si–ON bond on surface.

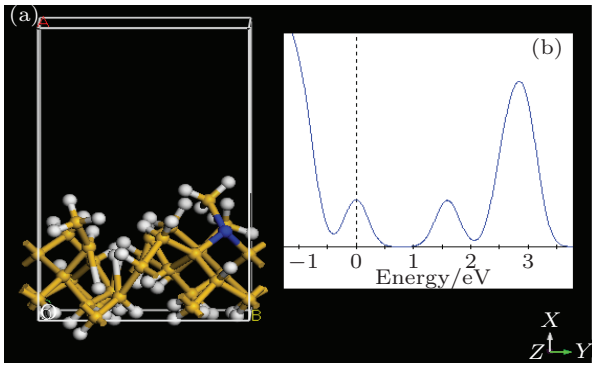


Fig. 4. (colour online) (a) Si QD structure and (b) density of states caused by a Si–N bond on surface.

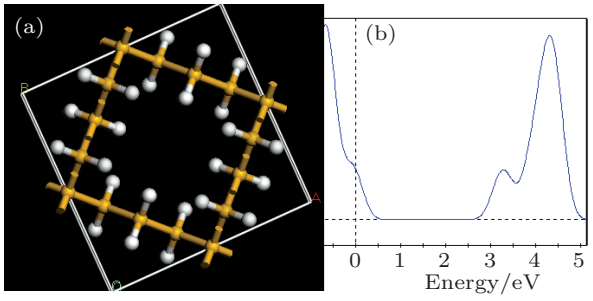


Fig. 6. (colour online) (a) Cube tube structure with one layer wall of silicon and (b) density of states caused by Si–H bond on surface.

In addition, the shape change of Si QD can affect the passivation. The calculation result indicates that the Si–H bonds on surface of smaller cube tube structure with one layer wall of silicon cannot provide a good passivation, as shown in Fig. 6.

4. Discussion

Under the transmission electron microscopy (TEM), we can observe the quantum-dot structure embedded in silicon oxide (the concentration of QD is about 10^{12} cm^{-2}, see the inset of Fig. 7), which was fabricated by nanosecond laser pulse in oxygen and then annealed at 1000 °C for 20 min. In Fig. 7, curve B describes the QC effect of Si QD and the gap energy increases with decreasing QD size. The curve C shows that the localized states form in the gap due to Si=O bond when the QD size reaches about 3 nm. The curve E indicates that the Si–O–Si bond breaks passivation to form localized states in gap when QD size is about 2.5 nm. It is shown from curve D that the localized states caused by Si–N bond on surface enter in gap when the QD size is decreased to about 2 nm.

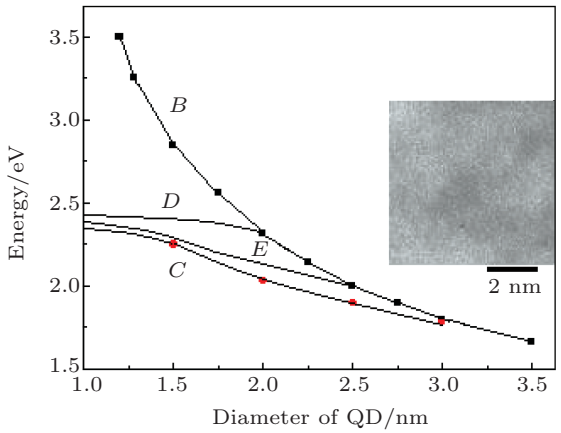


Fig. 7. (colour online) Curve B: the relation between the energy of band gap opened and the sizes of Si QD passivated with Si–H bonds on surface. Curve C: the evolution of the level of the localized states in gap due to a Si=O on surface. Curve E: the evolution of the level of the localized states in gap due to a Si–O–Si on surface. Curve D: the evolution of the level of the localized states in gap due to a Si–N on surface. Inset: TEM image of quantum dots embedded in oxidized silicon.

The experiments and calculation results indicate that the activation effects of Si=O and Si–O–Si bonds are very sensible, but the activated saturation could occur with the increase of bonds on surface. In contrast, the activation effect of Si–N bond is weak, and its activated saturation does not appear in general.

It is found that the shape of Si QD as well as its size affect the activation of surface bonds for emission. For example, the Si–H bonds on surface of slice or tube structures can break the passivation when the QD size is less than 1 nm. Therefore, through experiment and calculation, we can give an activation coefficient involving three factors: passivation factor of surface bond, size factor, and shape factor of QD which means some kind of symmetry breaking.

Figure 8(b) shows a physics process of the activation of Si QD for emission. First, the electron is pumped to the conduction band opened by the QC effect. Then, it can tunnel into the localized states with different levels related to different surface bonds to form active center. For example, Si=O bond forms the localized state of 1.78 eV and Si–N bond forms the localized state of 2.03 eV in gap. The population inversion could be formed between the valence band and the localized states for stimulated emission of type-II. The direct-recombination luminescence of electron-hole pairs between extended conduction band and valence band belongs to the emission of type-I, which forms a weaker and wider emission band. The annealing is an important step in activation for emission. The suitable annealing can decrease the range of size of Si QD to improve the emission of type-II, as shown in Fig. 8(a).

As shown in Fig. 9(a), a nano-laser is designed, which includes three main components: Si QD in Purcell cavities, active centers caused by surface bonds of Si QD, and two-dimensional (2D) photonic crystal with array of Purcell cavities. Here, there are two key points which need to be emphasized. First, activated silicon quantum dots can become the active matter of nanometer laser whose wavelength is adjusted by controlling the surface bonds. Second, the functions of selecting mode and resonance can be realized by coupling the electronic localized states of activated Si QD and the defect states of 2D photonic crystal. Both states can enter to the gap of photonic band, as shown in Fig. 9(b).

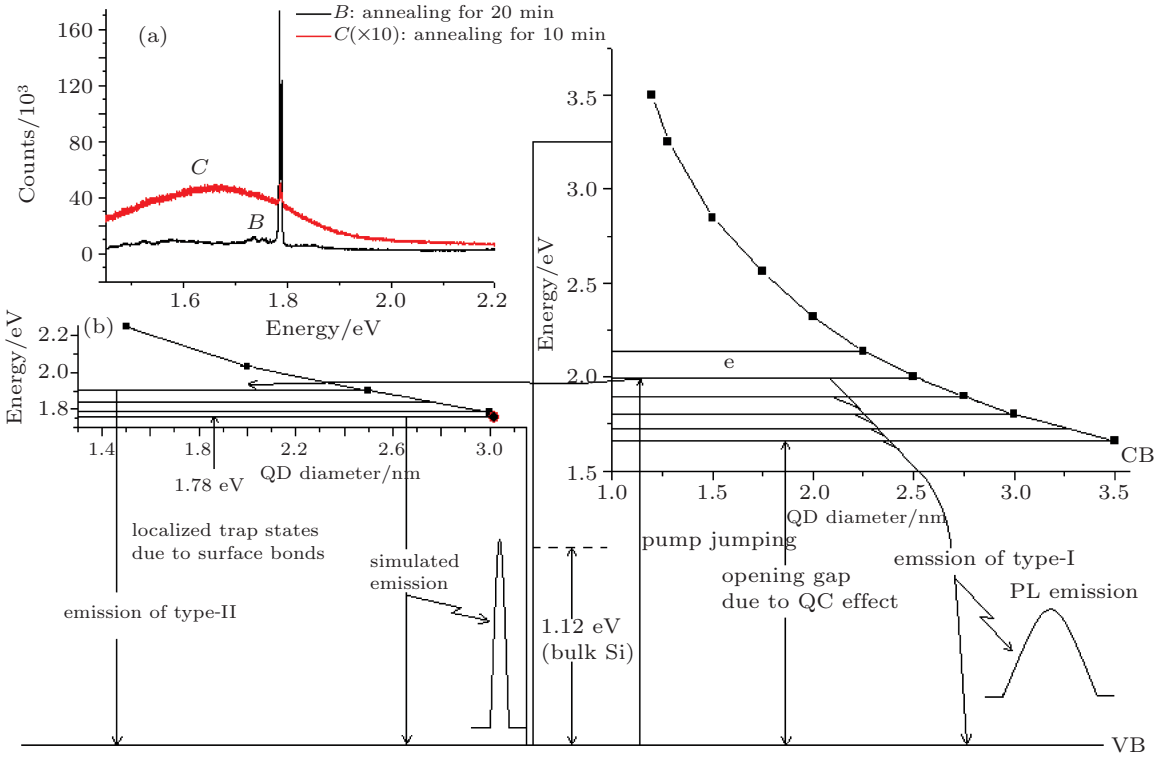


Fig. 8. (colour online) (a) PL spectra. (b) Diagram of the activation process of Si QD for emission.

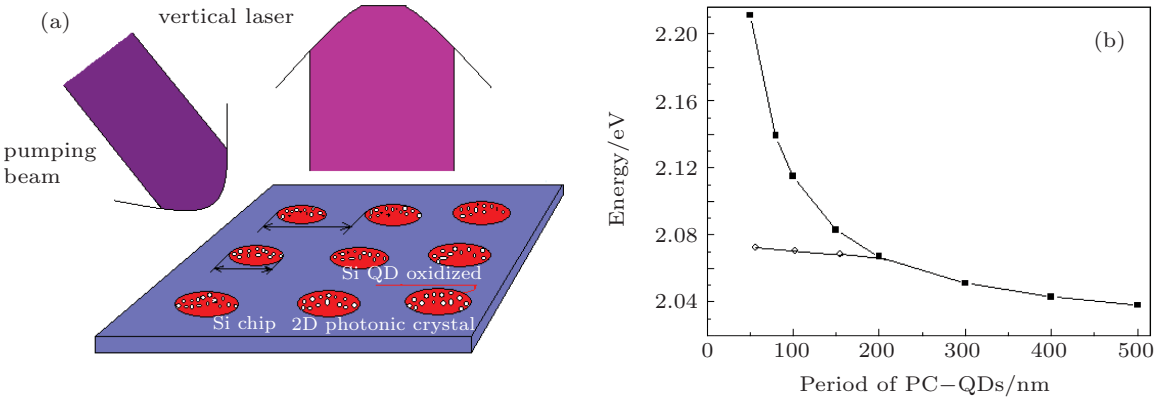


Fig. 9. (colour online) (a) Nano-laser structure including three main components: Si QD in Purcell cavities, active centers caused by surface bonds of Si QD (in every cavity), and 2D photonic crystal with array of Purcell cavities. (b) Lines with squares: the relation between the gap energy of photonic band opened and the sizes of perfect photonic QD. Lines with circles: the evolution of the defect states in 2D photonic crystal.

5. Conclusion

In conclusion, we prepare silicon quantum dots by using plasma of nanosecond laser (PNL), and achieve activation for emission in nitrogen, oxygen, and air atmospheres. The calculation shows that the activation is due to the localized electronic states of surface bonds in gap, which form in Si QD with different size and in different shape. The experimental and calculation results demonstrate that the active matter at various wavelengths of emission can be obtained by different surface bonds and suitable annealing. The activation of Si QD could have a good application in nano-laser. Moreover, this kind of activation has a switch effect on the emission of an active center in single quantum dot. The radiation of single quantum dot is characterized by its size and localized states. This would open a wide range of applications in the quantum communication, the quantum information process, and the quantum computing scheme in future.

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