Role of nitrogen and oxygen in emission of Si quantum dots formed by pulse laser*

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Silicon quantum dots fabricated by nanosecond pulsed laser in nitrogen, oxygen or air atmosphere have enhanced photoluminescence (PL) emission with the stimulated emission observed at about 700 nm. It is difficult to distinguish between the photoluminescence peaks emitted from samples prepared in different atmospheres. The reason for the appearance of similar peaks may be the similar distribution of the localised states in the gap for different samples when silicon dangling bonds of quantum dots are passivated by nitrogen or oxygen. It is revealed that both the kind and the density of passivated bonds on quantum dot surface prepared in oxygen or nitrogen have a strong influence on the enhancement of PL emission.

Keywords: nitrogen and oxygen, quantum dots, stimulated emission, localised states
PACC: 7845, 6820

1. Introduction

Silicon quantum dots (QDs) show quite different properties from those of their bulk counterparts.[1−3] Si nanocrystals are embedded in SiO_2 whose optical gain has been demonstrated,[4,5] thus opening a way for the interesting fundamental physical properties of these mesoscaled objects, and the use of Si in photonics would promote the full integration of photon. Numerous models have been proposed to explain the origin of the photoluminescence (PL) obtained in an experiment but the general mechanism is still under a wide debate. Besides the quantum confinement effect on QD, it was noticed that the passivated bonds on QD surface determine the level of localised electronic states in band gap, similar to the valence electron of the shell structure in an atom, which could give the explanation why there is no PL emission observed in a 'clean' Si QD. After a lot of investigations, the following interesting questions are still open to debate:[6−9] (i) Why do the main peaks in PL bands appear to be almost the same for QD samples prepared in different atmospheres (oxygen, nitrogen or air)? (ii) Why are there different variation trends in PL emission with the change of the density in oxygen or nitrogen? (iii) In which atmosphere (oxygen, nitrogen or air) prepared samples have the best enhancement in PL emission?

In this article, we use nanosecond pulsed laser to prepare QD structure on silicon in oxygen, nitrogen or air atmosphere. In this way, the various nanostructures and the passivated bonds on Si surface could be prepared easily. Especially, it can be controlled to make N–Si bonds in laser plasma. However, it is important to understand the physical process and obtain the information of the interaction between silicon and the pulsed laser. It was found that no difference can be observed between the PL peaks for samples prepared in different atmospheres; this may come from the similar distribution of the localised states in the gap. The peaks all occur at about 700 nm. The calculated results show that the same distribution of localised states can be formed in the gap when silicon dangling bonds on QD surface are passivated by nitrogen or oxygen. The results obtained in experiment and calculation reveal that both the kind and the density of the passivated bonds on QD surface in oxygen or nitrogen have a strong influence on the enhancement

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of the PL emission. We hope our work be helpful to the application of silicon QD in photonics.

2. Experiment

In ablation process, we used a pulsed laser (wavelength 1064 nm, pulse width 8 ns FWHM, repetition rate 800 Hz), which was normally focused onto the silicon sample placed in air, oxygen or nitrogen atmosphere. The intensity of the laser pulse was about 5×10^8 W$\cdot$cm^{-2} with an irradiation spot of 30 μm in diameter on silicon, which was sufficient to produce the laser plasma. A p-type Si wafer with room temperature resistivity of 10–20 $\Omega \cdot$ cm was used as starting material which was cleaned in a Summa cleaner for 20 min. After irradiation, the samples selected for comparison were loaded into an oxidation furnace at 1000 °C for 10–30 min.

In the TEM image, we can observe the QD structure embedded in silicon oxide as shown in Fig. 1, which was fabricated by nanosecond pulsed laser in oxygen. Figure 2 shows the distribution of elements on the sample by using line-scanning technique in x-ray energy analysis (the upper curve denotes the relative intensity of oxygen component, and the lower curve denotes the relative intensity of silicon component).

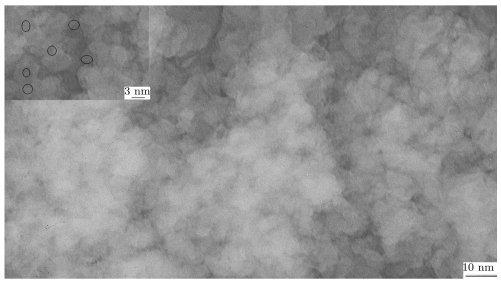


Fig. 1. TEM image of QD on silicon fabricated by pulse laser in oxygen atmosphere.

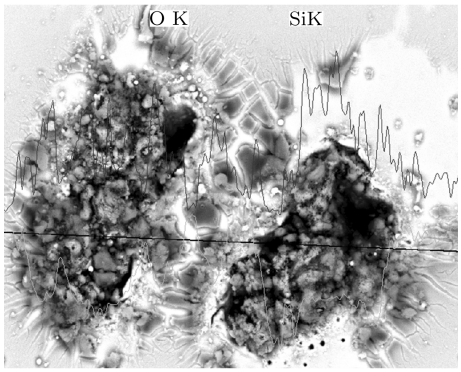


Fig. 2. Elements distribution on the sample by using curve-scanning technique of x-ray energy (top curve: intensity of oxygen; bottom curve: intensity of silicon).

The experimental result shows that controlling time of incident laser irradiation on silicon sample in oxygen atmosphere is important for enhancing PL emission as shown in Fig. 3. We could deduce that the density of the oxygen bonds on Si QD relative to the durations of incident laser directly affects the enhancement of PL emission. It is found that the PL emission will decrease when the ablation time is over 9 s which is determined by the optimum value of the density of the oxygen bonds.

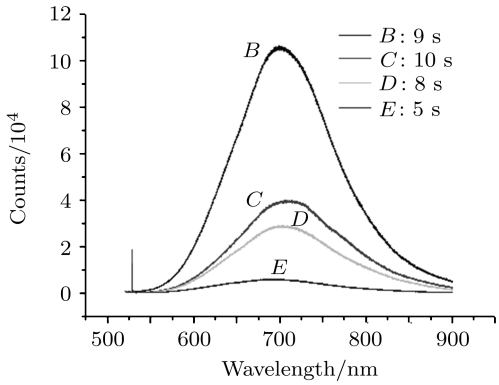
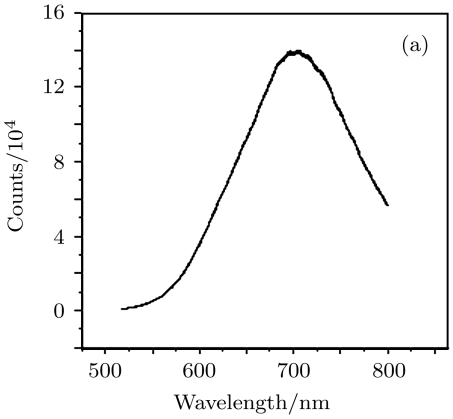


Fig. 3. PL intensity versus wavelength for different durations of laser irradiation incident on silicon sample in oxygen atmosphere.

Figures 4(a), 4(c), and 4(d) show the PL spectra of samples prepared in oxygen, nitrogen, and air atmospheres, respectively. It is very difficult to distinguish between the PL peaks emitted from samples prepared in different atmospheres, except for Fig. 4(b) in which the randomly stimulated emission can be observed at about 700 nm.[8] It could be guessed that those bonds on QD surface passivated in different atmospheres may produce the similar distribution of the electronic states.



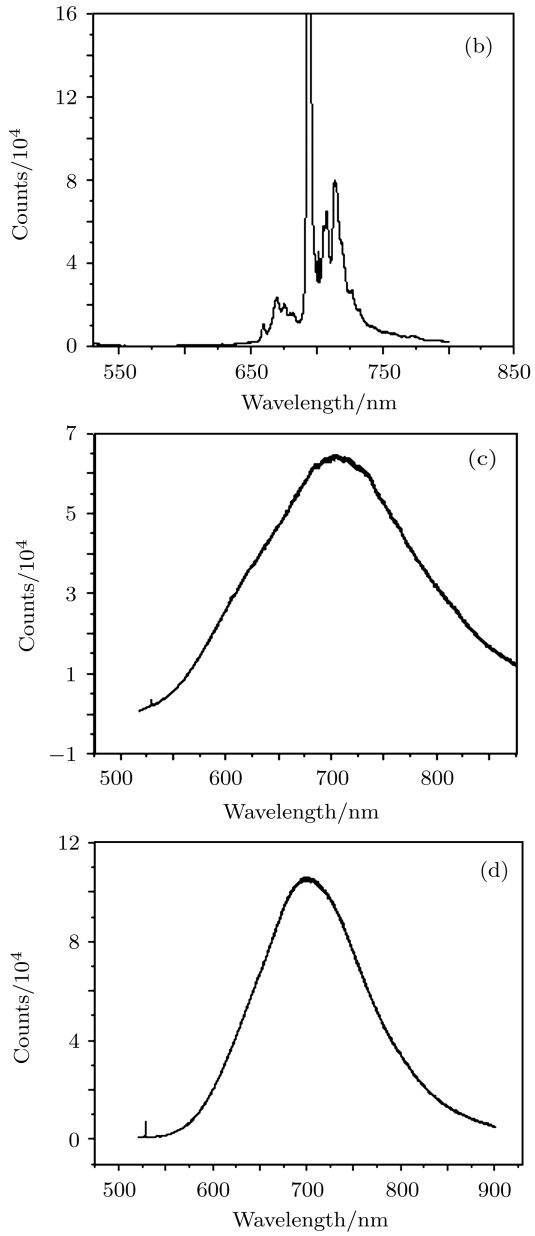


Fig. 4. PL spectra for Si QD formed by pulse laser in different atmospheres: (a) in oxygen, (b) annealing for 20min after irradiation in oxygen, (c) in nitrogen, (d) in air.

3. Calculation

According to the Fourier transform infrared (FTIR) spectroscopy, the surface layer on Si QD prepared in oxygen involves Si = O bonds, while N–Si bonds occur on the surface of samples prepared in nitrogen or air atmosphere. These bonds are important for forming localised electronic states in the gap.

We have chosen some models to simulate the experimental process in which the various structures of Si QD can be prepared in different atmospheres. Figure 5 shows a kind of Si QD structure prepared in oxygen and its density of states (DOS), in which the surface layer of QD involves Si = O bonds. In the model, the surface dangling bonds are saturated by hydrogen (white ball) and oxygen (black ball at the white point) atoms to simulate oxidation process. In Fig. 6, the DOS structure in the gap is shown to be destroyed with the increase of oxygen bonds on Si QD. The same structure of DOS in the gap can be formed on Si QD passivated by nitrogen atom (black ball at the white point), as shown in Fig. 7.

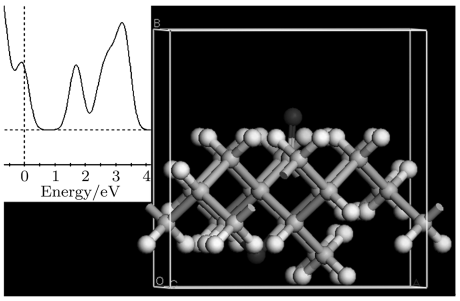


Fig. 5. Silicon QD structure prepared in oxygen and its DOS.

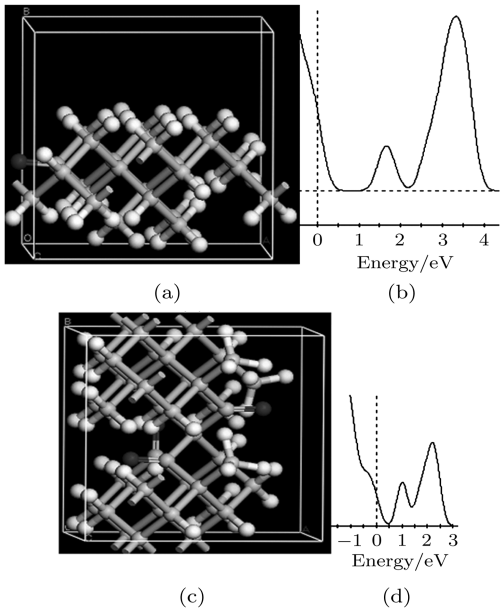


Fig. 6. Silicon QD structure and its DOS with the increase of Si = O bonds prepared in oxygen.

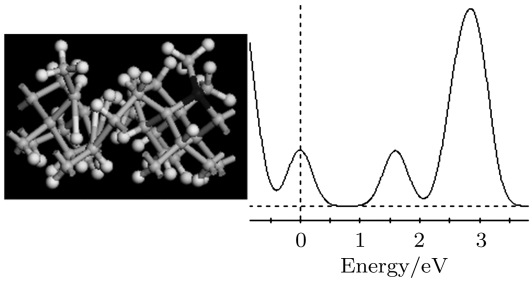


Fig. 7. Silicon QD structure prepared in nitrogen and its DOS.

The models based on supercells have the advantage that they are simple and give emphasize on the quantum confinement effect and deformation of the surface structure. The electronic behaviour is investigated in this work by an *ab initio* non-relativistic quantum mechanical analysis. The DFT calculation was carried out by using the local density approximation (LDA) and non-local generalised gradient approximation (GGA) for the self-consistent total energy calculation. It is considered that both LDA and GGA underestimate the band gap for semiconductors.

First, the nanocluster surface is initially saturated by hydrogen atoms whose structure produces the opening band gap due to the quantum confinement. Then the Si = O bonds is more likely to be formed and stabilises the surface, since it requires neither a large deformation energy nor an excess element, while the localised states are formed in the gap obviously, as shown in Fig. 5.

If the Si nanocrystallite is suitably passivated by oxygen through controlling the duration of irradiation and annealing, the localised states in the gap are perfectively formed. The best distribution of localised states can be obtained in which the density of Si = O bonds is about 3%, as shown in Figs. 6(a) and 6(b). But more Si = O bonds could break the distribution of localised states (Figs. 6(c) and 6(d)).

The same structure of localised states can also occur in the gap when the surface dangling bonds on Si QD are saturated by hydrogen and nitrogen atoms, as shown in Fig. 7. This model simulates the preparing process of the sample in nitrogen atmosphere. Nitrogen atoms are more active in the laser plasma than in other situation on Si QD surface. But the structure of the localised states in the gap is not easy to be broken in nitrogen.

Figure 8 shows that the same structure of localised states can also be formed in the gap when hydrogen (white ball), oxygen (gray ball) and nitrogen (black ball) atoms passivate dangling bonds on Si QD surface to simulate a preparing process of the sample in air atmosphere.

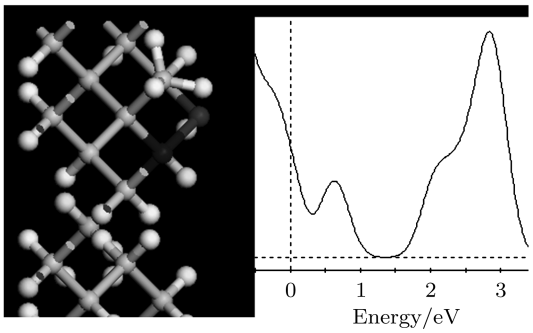


Fig. 8. Silicon QD structure prepared in air and its DOS.

4. Discussion

Having analysed the calculated results, we can propose a theoretical model generally. The band gap of Si QD is opened because of the quantum confinement effect. The localised trap states of electrons could be formed in the opened band gap if a Si QD is passivated by oxygen or nitrogen. As shown in Fig. 9, this model includes two systems: the right one is a photon pump system in which the valley level of the conduction band depends on QD size by quantum confinement, and the left one is a localised state system on QD surface in which oxygen or nitrogen bonds determine the energy level of the trapped electronic state which is independent of size. The trap states are discretely localised in the region of 1.6∼1.8 eV after considering the underestimation of the band gap in the LDA and GGA calculations.

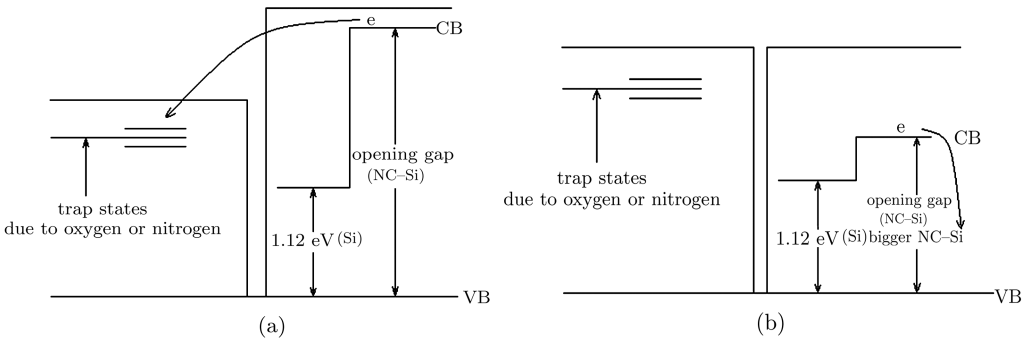


Fig. 9. Model for explaining the mechanism of stimulated emission on Si QD formed by nanosecond pulsed laser in different atmospheres. (a) Energy level construction which may produce the pinning and enhancing effect in PL emission. (b) Another level construction in which the pinning and enhancing effect in PL emission disappears at all.

In this model, it is a key factor for enhancing and pinning PL peaks at about 700 nm that the level position of the trap states coming from oxygen or nitrogen passivity is lower than that of the electronic states photoexcited in conduction band of Si QD. Figure 9(a) shows the energy levels construction in which the pinning and enhancing effect of PL emission may take place. At first the electrons from the conduction band are rapidly caught by the trap states in the gap. Then the population inversion between the valence band and the trap states may take place due to a longer lifetime of the trapped electrons. Generally speaking, when the QD scale is less than 3 nm, the bottom of the conduction band is usually higher than the level of localised electronic states, which is related to oxygen or nitrogen passivity on QD surface.

In the construction of Fig. 9(b), the pinning and enhancing effect in PL emission disappears at all when the level of the trap states is higher than that of the electronic states photoexcited in conduction band of Si QD

The calculated results indicate that at first the localised states in the gap increase rapidly with increasing oxygen bonds on Si QD surface, then the localised states structure will be broken down when the number of oxygen bonds is over some dead-spot (about 2–5% in density). This result can explain the ablation time effect for PL emission in the experiment, showing that 9s is an optimum time of laser irradiation on silicon sample in oxygen atmosphere (Fig. 3). But slower increasing of the localised states with the increase of nitrogen on Si QD surface cannot break the structure of the localised states. The calculated results agree with the experiments in which the PL emission keeps increasing with the density increase of nitrogen or air, but sometimes there is an inverse trend in oxygen atmosphere.

5. Conclusion

In summary, the results in calculation and experiment indicate that: (i) Si = O, Si–N or Si–NO bonds on Si QD can generate the same structure of localised states in the gap which can produce the same PL peaks. (ii) The localised states structure will be broken down when the density of oxygen bonds on Si QD is over some value (about 2–5%) which can explain why sometimes PL emission decreases with the increase in oxygen. (iii) The kind and the density of passivated bonds on Si QD prepared in oxygen, nitrogen or air atmosphere are the most important factors for PL enhancement and stimulated emission on silicon.

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