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Localized electronic states in gaps on hole-net structures of silicon*

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Hole-net structure silicon is fabricated by laser irradiation and annealing, on which a photoluminescence (PL) band in a the region of 650–750 nm is pinned and its intensity increases obviously after oxidation. It is found that the PL intensity changes with both laser irradiation time and annealing time. Calculations show that some localized states appear in the band gap of the smaller nanocrystal when Si=O bonds or Si–O–Si bonds are passivated on the surface. It is discovered that the density and the number of Si=O bonds or Si–O–Si bonds related to both the irradiation time and the annealing time obviously affect the generation of the localized gap states of hole-net silicon, by which the production of stimulated emission through controlling oxidation time can be explained.

Keywords: hole-net silicon, passivated bonds, localized gap states
PACC: 7845, 6820, 7320D

1. Introduction

Recent experiment data present evidence that surface effects on quantum dots produce a very substantial impact on the electronic and optical properties of nanocrystalline silicon. Various quantum dots (QDs) of silicon containing nanocrystal have attracted much attention to date,[1−6] mostly because of their intense visible photoluminescence (PL). Numerous models have been proposed to explain the PL. Presently, although a detailed understanding of the PL has not yet been achieved,[2] it is universally thought that the band gap opens as a result of quantum confinement, which pushes the PL into the visible band for nanocrystal. In the present work, a new kind of hole-net silicon is fabricated by laser irradiation and annealing. After oxidation, the central wavelength of the PL band is pinned in a region of 700–780 nm on the hole-net silicon. In our calculation the Si–O–Si bonds or Si=O bonds on the nanocrystal surface can produce localized gap states. It is found that controlling oxidation time in irradiation and annealing is very important for increasing the PL intensity. Calculations show that the density of Si=O bonds or Si–O–Si bonds related to both irradiation time and annealing time obviously affects the generation of the localized gap states. The results could interpret the production of stimulated emission by controlling oxidation time in irradiation and annealing.[7]

2. Experiment

We took some Si of P-type (100) oriented wafers with a 10–20 Ω·cm as the silicon sample. It was cleaned in a Summa cleaner for 20 min. A pulsed YAG laser (wavelength: 1064 nm, pulse length: 8 ns FWHM, repetition rate: 800) was normally focused onto the silicon sample in air. The irradiation intensity was about 5×10^8 W·cm^{-2} with a beam spot of 30 μm in diameter on the sample, which was sufficient to produce the laser plasma in air. Then the silicon sample was loaded into an oxidation furnace at 1000°.

The PL spectra of the samples under the 514 nm excitation were measured by using RENISHAW Micro-Raman Systems. Figure 1 shows the scanning electron microscope (SEM) image of net-hole silicon formed by irradiation and annealing. The experimental results show that stimulated emission (Fig.2(a)) and enhanced PL emission evolving with irradiation time (Fig.2(b)) could be obtained by controlling time in irradiation and annealing. The size of nanocrystal silicon (nc-Si) could be calculated from $D^2 = 88.34 \times 10^{-7}$ $(\lambda^2/\Delta\lambda)$ nm^2 (λ: Raman peak wavelength of the transverse-optical (TO) phonon, $\Delta\lambda$: wavelength deviation from the nc-Si peak to the bulk Si peak in Raman spectra),[8] which is about several nanometres.

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Fig.1. SEM image of hole-net silicon formed by irradiation and annealing.

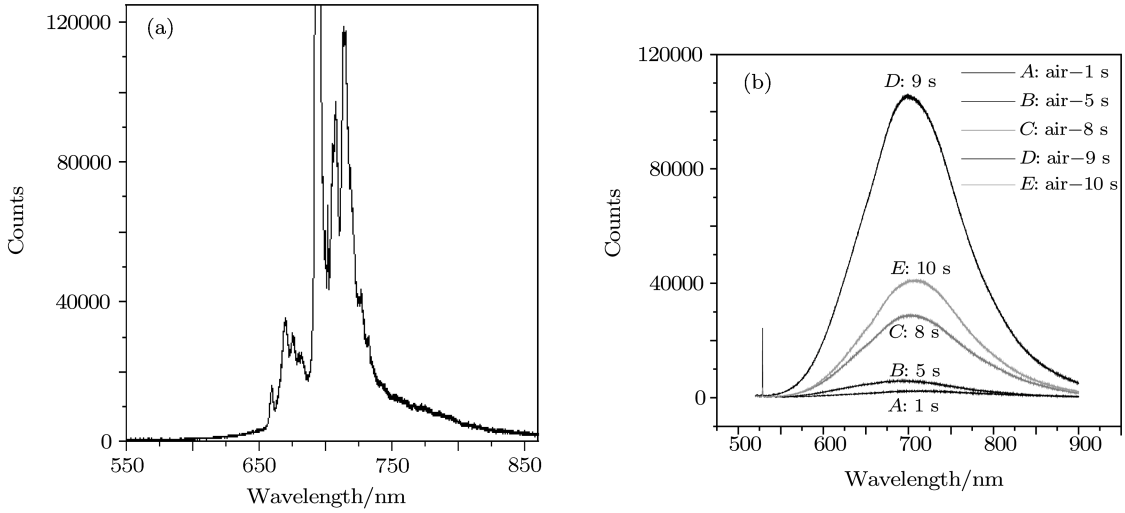
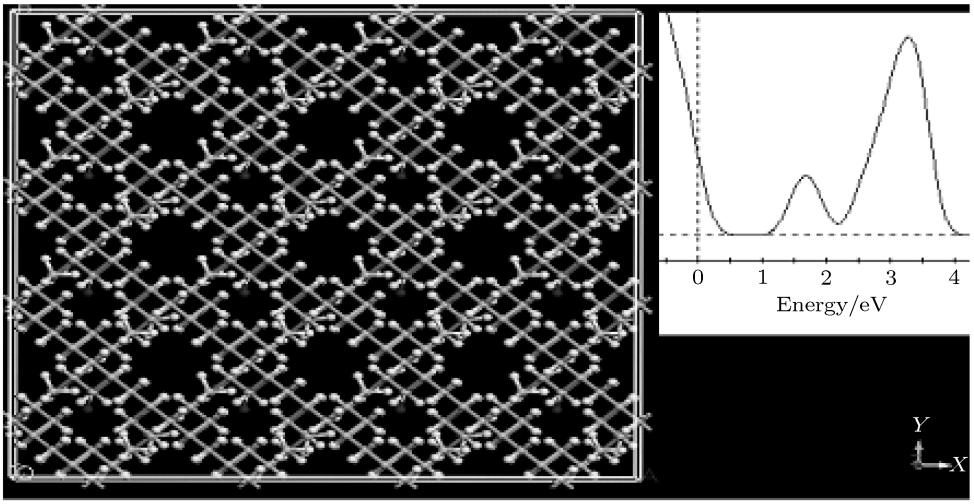


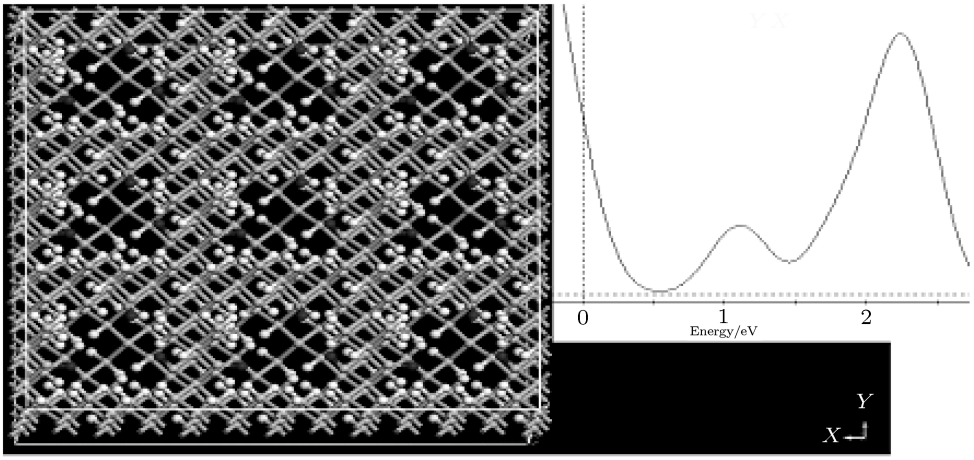
Fig.2. (a) Stimulated emission from porous silicon QD formed by controlling irradiation and annealing time; (b) Evolution of enhancing PL on porous silicon QD with irradiation time.

3. Calculation

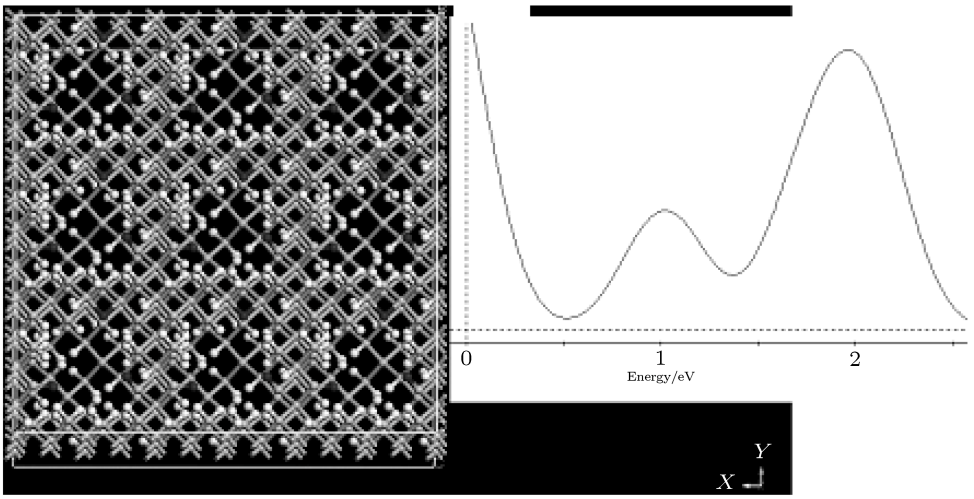
According to the nanocluster structures on hole-net silicon, formed by irradiation and annealing, we have chosen several structure models in order to simulate the surface passivation with Si–H bonds and the oxidation of various nanoclusters of silicon as shown in Figs.3–5. For numerical calculations, we start from a supercell built by joining several cubic c-Si cells, and then set different nanoclusters in the models.[9] The surface dangling bonds are saturated by using hydrogen atoms and oxygen atoms, in order to simulate different degrees of sample oxidation. The nanocluster model based on supercells has the advantage, i.e. it is simple and emphasizes the quantum confinement (QC) effect and deformation of the structure.[10,11] The electronic behaviour is investigated in the work by an *ab initio* non-relativistic quantum mechanical analysis. The density functional theory (DFT) calculations are carried out by using the local density approximation (LDA) and non-local generalized gradient approximation (GGA) exchange–correlation functional for the self-consistent total energy calculation. It is considered that both LDA and GGA underestimate the band gaps for semiconductors and insulators.



(a)

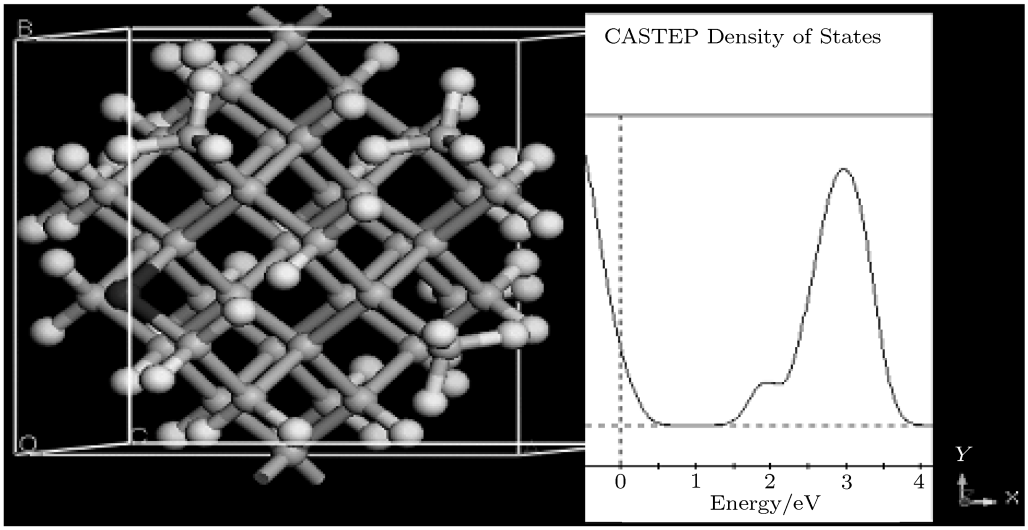


(b)

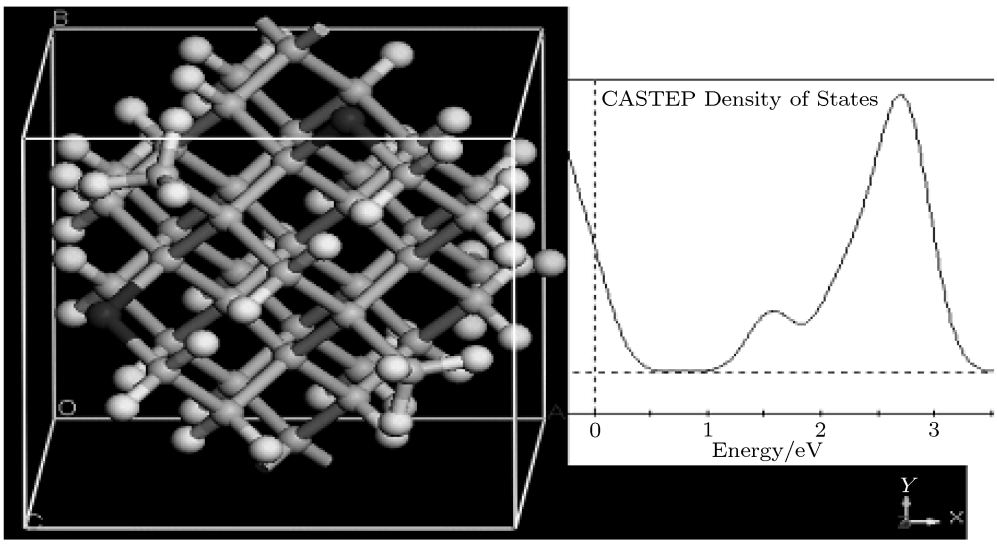


(c)

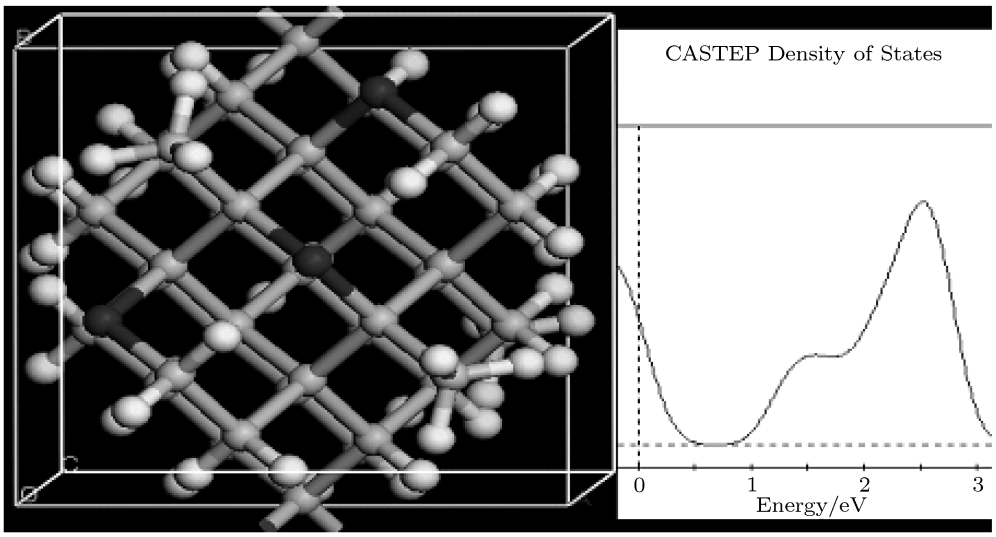
Fig.3. Variation of DOS with numbers of Si–O–Si bond and Si=O bond (oxygen atom: black ball) on porous: (a) One Si=O bond passivated on a power cell and its DOS; (b) Three Si=O bonds passivated on a power cell and their DOS; (c) Two Si=O bonds and one Si–O–Si bond passivated on a power cell and their DOS.



(a)



(b)



(c)

Fig.4. Variation of DOS with number of Si–O–Si bond (oxygen atom: black ball) on QD: (a) One Si–O–Si bond passivated on a power cell and its DOS; (b) Two Si–O–Si bonds passivated on a power cell and their DOS; (c) Three Si–O–Si bonds passivated on a power cell and their DOS.

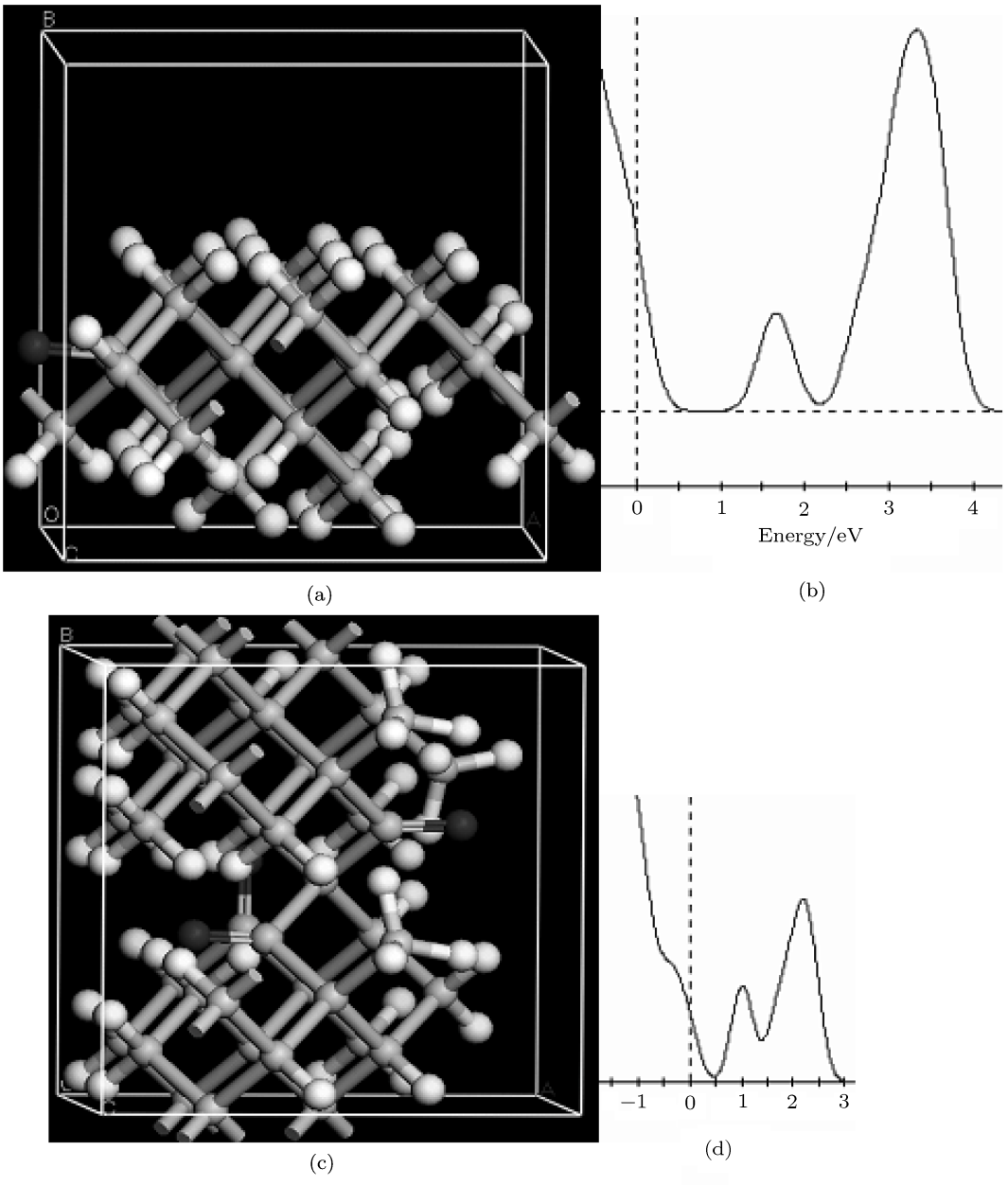


Fig.5. Variation of DOS with number of Si=O bond (oxygen atom: black ball) on QD: (a) One Si=O bond passivated on a power cell and its DOS; (b) Three Si=O bonds passivated on a power cell and their DOS.

The nanocluster surface is initially saturated by hydrogen atoms (white balls), and in the oxidation process they are gradually substituted by oxygen atoms (black balls) in various nanocluster models as shown in Figs.3–5. The *ab initio* calculation in the study was performed with the CASTEP codes developed at Cambridge University, UK, which is considered as one of the accurate DFT plane-wave pseudopotential programs.

4. Discussion

The nanocluster surface is initially saturated by hydrogen atoms whose structure produces the opening band gap. When nanocrystalline Si is oxidized, the Si–Si bonds are likely to weaken or break because of the large stress on the distortion surface and Si–O–Si bonds are formed which carry the oscillation of the density of states (DOS) in the band gap as shown in Fig.3(c) (negative dots) and Fig.4 (positive dots).

Then the Si=O double bond is more likely to be formed and stabilize the interface, since it requires neither a large deformation energy nor an excessive element, while the localized states are formed in gaps. Figures 3 (negative dots) and 5 (positive dots) show the passivation structures and the DOS in the nanocluster supercell saturated by Si=O bonds which generate the trap states localized in the band gap. The most important thing is that the number of Si–O–Si bonds or Si=O bonds on QD surface affects the distribution of the localized gap states obviously. As shown in Figs.3–5, the distribution shape of localized gap states is destroyed because of the narrowing gap when the number of Si–O–Si bonds or Si=O bonds reaches a level three power cell ($> 6\%$ of passivation atoms).

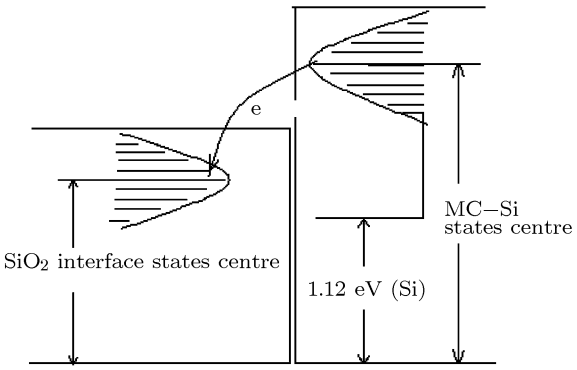


Fig.6. A model of a three-level system associated with the localized gap states in which the numbers of Si=O bonds and Si–O–Si bonds on silicon QD determine the position of the level of the localized gap states.

According to the results obtained from Fourier transform infrared spectroscopy (FTIR),[4] the oxide layer on Si nanocrystal involves Si=O bonds and Si–O–Si bonds. If the Si nanocrystallite is appropriately passivated by oxygen through controlling both the irradiation time and the annealing time, the localized gap states of electrons (or even the trapped exciton) are perfectively formed due to Si=O bonds or Si–O–Si bonds (2∼5% of passivation atoms). As shown in Fig.6, the model includes two systems: the left one is a localized gap state system in the oxidation layer in which the number of Si=O bonds and the Si–O–Si bonds determine the energy level of the state which is independent of size, and the right one is a photon pump system in the Si nanocrystal in which the level of the valence band valley is dependent on nanocrystal size by quantum confinement. The position of the localized gap state is in a region of 1.5–2.1 eV after considering the underestimation of the band gap in the LDA and GGA calculations.

5. Conclusion

The calculations and measurements in the paper indicate that (1) when the hole-net Si is appropriately oxidized by controlling both irradiation time and annealing time, the Si–O–Si bonds or Si=O bonds (density: 2–5% of passivation atoms) can produce the localized gap states very well; (2) the numbers of Si=O bonds and the Si–O–Si bonds on the surface determine the level position of the localized gap state which is size independent; (3) when the bottom level of the conductor band opened in nanocrystal Si is higher than the energy level of the localized gap states in silicon oxide, the recombination of the electron trapped in localized states and the hole on the valence band generates the pinning and enhances the effect of PL emission, and even produces a stimulated emission when population inversion occurs.

Acknowledgment

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