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Trap states in oxidation layer of nanocrystal Si*

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The photoluminescence (PL) of nanocrystal present in porous silicon shifts from the near infrared to the ultraviolet depending on the size when the surface is passivated with Si-H bonds. After oxidation, the centre wavelength of PL band is pinned in a region of 700–750 nm and its intensity increases obviously. Calculation shows that trap electronic states appear in the band gap of a smaller nanocrystal when Si = O bonds or Si–O–Si bonds are formed. The changes in PL intensity and wavelength can be explained by both quantum confinement and trap states in an oxidation layer of nanocrystal. In the theoretical model, the most important factor in the enhancement and the pinning effects of PL emission is the relative position between the level of the trap states and the level of the photoexcitation in the silicon nanocrystal.

Keywords: photoluminescence, porous silicon, trap states
PACC: 4255R, 4270Q

1. Introduction

Of all the forms of silicon containing nanocrystal, porous silicon is the one that has attracted the most attention to date,[1−3] mostly because of its intense visible photoluminescence (PL). Numerous models have been proposed to explain its PL. Presently, although a detailed understanding of the PL has not yet been achieved,[2] it is universally received that the band gap opens as a result of quantum confinement, which pushes the PL into the visible band for nanocrystal. The PL of nanocrystal present in porous silicon can be turned from the near infrared to the ultraviolet when the surface is passivated with Si-H bonds. After oxidation, the centre wavelength of PL band is pinned in a region of 700–750 nm. Wolkin *et al*[4] proposed a model for explaining the pinning wavelength effect that is related to the trapping of an electron by Si = O bonds that produce localized levels in the band gap of smaller nanocrystals. In our calculation the Si–O–Si bonds or Si = O bonds on the surface of nanocrystal can all produce the trap states. In Wolkin *et al*'s model, it is indicated that the quantum confinement alone can explain the PL on porous nanocrystals larger than 3 nm (displaying red or orange emission), and the oxidation of the nanocrystal plays an important role when the nanocrystal sizes are smaller than 3 nm. But it is another story in Qin and Li's model,[5] where two competitive processes take place in PL in which the oxidation states play a main role when the size of nanocrystal is larger than 3 nm, and the quantum confinement exerts a dominant influence when the size of nanocrystal is smaller than 3 nm. In the present paper, the discrepancy between them is resolved. As a matter of fact, the size 3 nm is a critical size in their models. However, our model indicates that the size 3 nm is not important but the relative position between the level of the trap state and the level of the photoexcitation in the silicon nanocrystal is the most important factor.

2. Experimental procedures

The samples A and B used in the study were prepared in the following procedures respectively.

Sample A preparation procedure. Take some p-type (100) oriented Si wafers with a 10–20 Ωcm as the

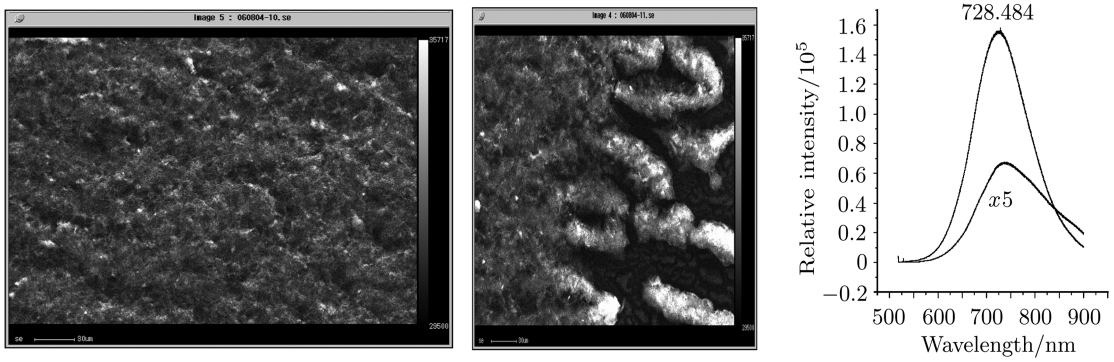
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silicon samples. Clean them in a Summa cleaner (a mixture of choline and methanol), and then anodize them in HF(49%): Ethanol(1:1.5) for 15 min at an anodizing current density of about 100 mA/cm^2.

Sample B preparation procedure. Anodize the silicon samples in HF(49%):Ethanol(1:1.5) for 15 min under the irradiation of a laser beam (spot diameter: 700 μm) with 532 nm wavelength and 20 mW power at an anodizing current density of about 60 mA/cm^2.

Etch all the samples, and then rinse them in ethanol, and finally expose them to air for several days.

Scanning electron microscopy (EPMA-1600) was used to observe the oxidation porous structures of the samples. The PL spectra of the samples under the 514 nm excitation were measured by using RENISHAW Raman Systems in which the spot diameter of laser beam can reach 1 μm. Figures1(a) and 1(b) show the images of SEM on the samples A and B, respectively. And their PL spectra are compared in Fig.1(c).



(a) (b) (c)

Fig.1. SEM images of sample A (a), the sample B (b), and their PL (c).

Figure 1(b) shows a kind of condensed rod structure in the region with irradiating and anodizing the sample B. It is clear that the laser irradiation causes the porous layer to crack, screw and condense into some rod states. It is the rod that emits more PL than the general porous samples as shown in Fig.1(c) which is due to largely increasing the surface on the rods and so greatly increasing porosities.

3. Calculation method

For numerical calculations, we start from a supercell built by joining up with four cubic c-Si cells in the $x-y$ plane, and then square empty columns are dug along the z-direction by removing 13 centre Si atoms,[6] which produce a weight porosity of about 40%. The surface dangling bonds are saturated by using hydrogen and oxygen atoms, in order to simulate different degrees of sample oxidation. This pore model based on supercells has the advantage of being simple and emphasizes the quantum confinement effect and the deformation of the structure. There is a preferential growth of pores along the [001] crystallographic directions in p-type (001)-oriented c-Si wafers.[7] So we chose the above model. The electronic behaviour has been investigated in the present work by an *ab initio* non-relativistic quantum mechanical analysis. The density functional theory (DFT) calculation has been carried out by using the local density approximation (LDA) and nonlocal gradient-corrected exchange-correlation functional (GGA) for the self-consistent total energy calculation. It is considered that both the LDA and the GGA underestimate the band gap by 30%–50% for semiconductors and insulators.

The *ab initio* calculation in the study have been performed by using the CASTEP codes developed at Cambridge University, UK.[8] which is considered as one of the accurate DFT plane-wave pseudopotential programs.

The pore surface is initially saturated by hydrogen atoms, and during the oxidation process they are gradually substituted by oxygen atoms as shown in Figs.2 and 3.

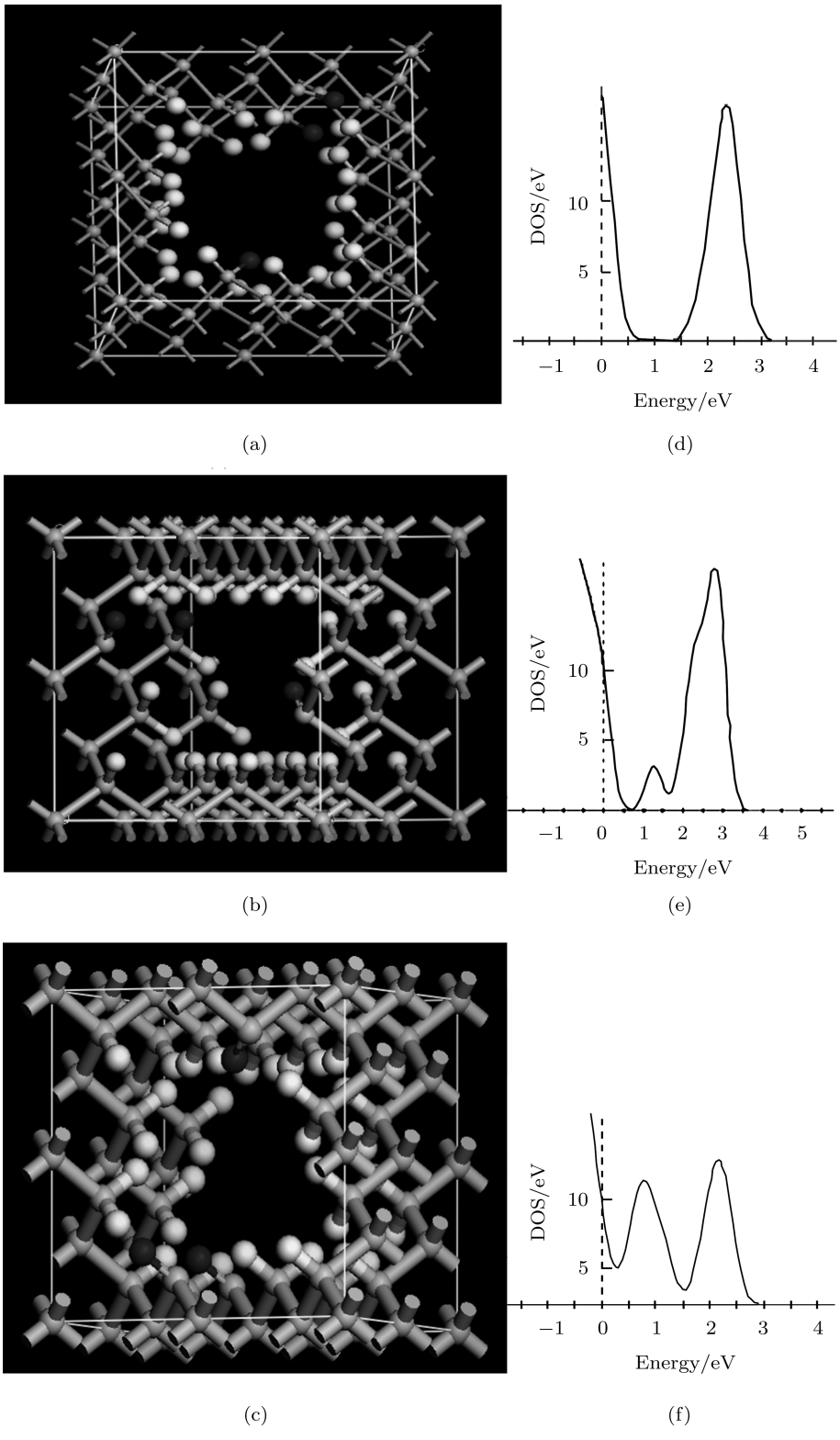


Fig.2. Three geometrically optimized supercells containing zero (a), one (b) and tree (c) Si = O double bonds, and their density of states (DOSs) (a), (b) and (c).

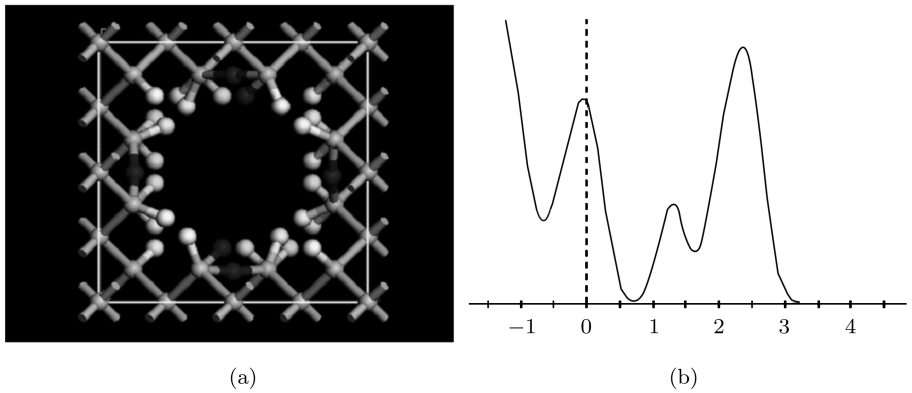


Fig.3. Optimized supercells containing Si–O–Si bonds (a) and their DOS (b).

4. Results and discussion

When nanocrystalline Si is oxidized, the Si–Si or Si–O–Si bonds are likely to weaken or break because of the large stress in the distortion surface. Figure 2(a) shows a structure that involves three unsaturated Si–O bonds (the remaining dangling bonds are saturated by hydrogen atoms) whose DOS is shown in Fig.2(d). 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 excess element, while the localized states are formed in gap obviously. Figures 2(b) and 2(e) show the structure and the DOS in the pore supercell saturated by two Si=O bonds (the remaining one is the unsaturated Si–O–bond). Figures 2(c) and 2(f) show the structure and the DOS in the pore supercell saturated by three Si=O bonds. On the other hand, the Si–O– Si bonds formed on nanocrystalline Si can also produce the localized states in gap as shown in Fig.3.

According to the results from Fourier transform infrared spectroscopy (FTIR),[4] the oxide layer on porous Si nanocrystal involves the Si = O bonds and the Si–O–Si bonds. In our model, if the Si nanocrystallite is passivated by oxygen, the localized trap states of electrons (or even the trapped exciton) may be formed in the Si = O bonds or Si–O–Si bonds. As shown in Fig.4, the model includes two systems: the left system that is a trap state system in the oxidation layer in which the Si = O bonds or the Si–O–Si bonds determine the trapped electron state energy that is size independent almost, and the right system that is a photon pump system in the Si nanocrystal in which the level of the valence band valley depends on nanocrystal size due to the quantum confinement. The positions of the trap states are in a region of 1.5–2.1 eV after considering the underestimation of the band gap in the LDA and the GGA calculations.

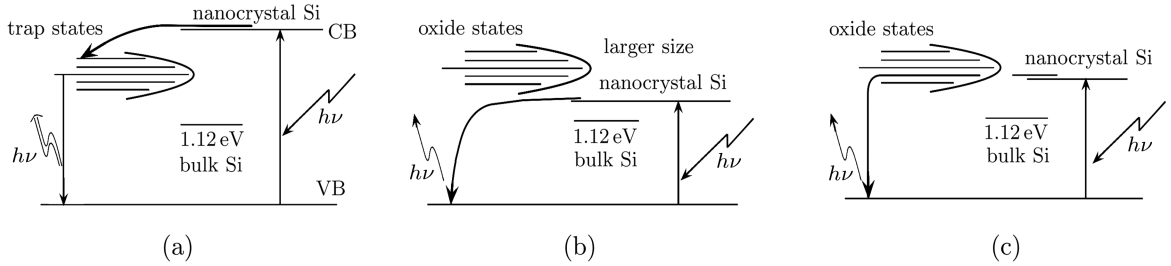


Fig.4. A model of three-level system associated with the crystal-oxide trap states, showing the PL pinning and enhancing model in which nanocrystal Si energy is higher than that of trap states (a), (b) the oxide states in the model for the case of extinct pinning and enhancing, and they cannot capture the electrons from valence band (b), and the conversion model of PL reducing (c).

In the model, the critical size of 3 nm is not important, and the most important factor for PL pinning and enhancing is the level position of trap states that is lower than that of electronic states of the photoexcitation in the nanocrystal after oxygen passivity. Figure 4(a) shows the obvious effects of the PL pinning and the PL enhancing in which the electrons from the valley of the conductor band opened are rapidly caught by the trap states in gap, then the population inversion between the top of the valence band and the trap states is thus possible due to the longer lifetime of the trapped electrons.[4] But as shown in Fig.4(b), the PL pinning and the PL enhancing effects disappear at all when the level position of trap states is higher than that of electronic states of the photoexcitation in the nanocrystal. Figure 4(c) shows a conversion situation of PL pinning and enhancing in which only a bottom party of oxide states can capture the electrons in conductor band.

After oxidation, the energy of oxide states increases slowly with the decrease of nanocrystal size because of surface distortion which is different from the quantum confinement.[4] For example, for a 5 nm nanocrystal after oxygen passivation, the energy of the oxide states is about 1.5 eV, while for a smaller nanocrystal (< 2 nm) the energy of the oxide states is about 2.1 eV. The results can explain the PL pinning and enhancing effects in smaller nanocrystals and a little shift of PL wavelength in larger nanocrystals.

In Fig.1(c), the range of the PL band of the nanocrystal passivated with oxygen is from 600 to 830 nm, which shows the good agreement between experiments and theory.

We could make the trap states distribute into a sharp region by controlling oxidation in irradiation and annealing as shown in Fig.5(a), where the laser with a three-level or four-level system has been realized.[9] Figure 5(b) shows the sharp emission stimulated on porous Si whose threshold transitions at 694(-■-) and 692 nm (-●-) are shown in Fig.5(c) as observed by using a conventional semiconductor laser. The PL peak has a Lorentzian shape with a full width at half maximum (FWHM) of 0.5–0.6 nm. The twin peaks belong to the kind of stimulated emission which could be demonstrated by its threshold behaviour and transition from sub-threshold to linear evolution in light emission. Figure 5(d) shows the emission spectra with excitation under threshold.

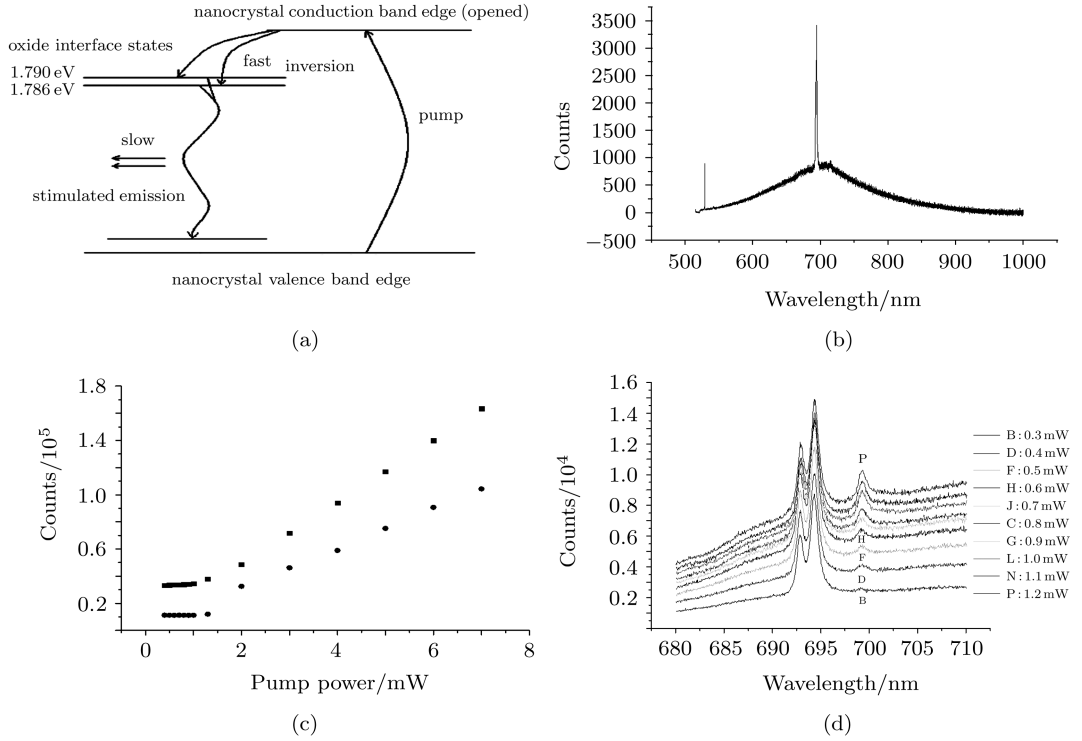


Fig.5. A sharp distribution model for trap states by controlling oxidation on porous Si in which the population inversion occur probably (a); laser on Porous Si (b); threshold transition at 694(-■-) and 692 nm(-●-) (c); emission spectra with excitation under threshold (d).

5. Conclusions

The results from calculation and experiment in the paper indicate the following points: (1) when the nanocrystalline Si is oxidized, the Si–O–Si bonds or Si = O bonds can produce trap states in gap; (2) when the band gap of Si nanocrystals opened by quantum confinement is wider than the gap between the trap state and the valence band, the recombination of the electron trapped in oxygen-related localized states and the hole on the valence band (or even trapped exciton) generates the PL pinning and the PL enhancing effects; (3) the sharp distribution of the trap states formed by controlling oxidation in irradiation and annealing could produce a laser on porous Si.

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