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Doping effect in Si Nanocrystals/SiO_2 multilayers

Dongke Li, Peng Lu, Minqing Qian, Jun Xu*, Wei Li, Kunji Chen
School of Electronic Science and Engineering, National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing, 210093, China.

*E-mail: junxu@nju.edu.cn

Abstract. Doping in Si nano-crystals (Si NCs) is currently a great challenge to develop the high-performance nano-devices. Here, we fabricated P-doped Si NCs by PECVD in Si/SiO_2 multilayered structures after annealing at high temperature. It is demonstrated experimentally that P dopants can be incorporated into Si NCs substitutionally. Furthermore, we found that the photoluminescence properties of Si NCs can be drastically modified by P doping in Si NCs/SiO_2 multilayers with the ultra-small size. A subband light emission centred at 1200nm is observed, which can be ascribed to the radiative recombination via the P-induced deep level in the gap of the Si NCs. Interestingly, it is also found that the subband emission can be enhanced obviously by B and P co-doping. Our results suggest that doping plays an important role in the electronic structures and optoelectronic characteristics of Si NCs, which provide a new route to realize the Si NCs-based optical and electronical devices.

1. Introduction

Doping in Si nano-crystals (Si NCs) is a fundamental issue in order to develop the next generation nano- and opto-electronic devices, such as nonvolatile memories[1], light emitting devices[2] and solar cells[3]. However, the theoretical calculation implies that doping in Si NCs is quite difficult since the formation energy related to the impurities is higher than that in mono-crystalline case. So the impurities tend to be expelled from the inner sites of Si NCs which is so-called self-purification effect[4]. In spite of these theoretical difficulties, several experimental studies have reported the doping effect in Si NCs[5-6]. It was reported that the dopant atoms location, the active doping concentration as well as the influences of dopants on the physical properties of Si NCs is quite different from the doping in bulk Si, and the doping mechanism is still unclear[7-8].

In the present work, doped Si QDs/SiO_2 multilayers were fabricated in conventional PECVD system after high temperature annealing. The doping behaviors in Si NCs with various doping concentrations were systematically studied by Raman, TEM and low temperature ESR techniques. It was found that photoluminescence properties of the ultra-small size Si NCs can be drastically modified by impurity doping and the subband emission was observed. Moreover, the subband emission can be improved by co-doping.

2. Experiment

The P-doped amorphous-Si/SiO_2 stacked multilayers were deposited on p-type Si wafers (1–3 Ω/cm) and quartz substrates by a PECVD system with the radio frequency of 13.56 MHz. The a-Si:H layer was deposited by using SiH_4 with a flow rate of 5 sccm. P doping or B/P co-doping was realized through adding PH_3 or PH_3+B_2H_6 into chamber during the a-Si layer deposition process. The actual content of

PH_3 and B_2H_6 are 1% by H_2 dilution. The deposition time and flow rate of PH_3 and B_2H_6 were varied to obtain different layer thickness and doping concentrations. Subsequently, the in-situ plasma oxidation was performed in oxygen ambient for 90s with a fixed O_2 flow rate. The deposition and oxidation process was alternatively repeated for times to get stacked multilayered structures. During the whole deposition process, the RF power was set at 50W and the substrate temperature was fixed at 250 ℃. Following, the as-deposited samples were first dehydrogenated at 450 ℃ and then annealed at various high temperatures (800-1000 ℃) for 1h under N_2 protection to form doped Si NCs.

The microstructure was revealed by HRTEM using a Tecnai G2 F20 electron microscope operating at 200 kV. The low temperature X-band ESR spectra were obtained by Bruker EMX 10/12+. The photoluminescence spectra were obtained by using liquid N_2 cooled InGaAs detector and the excitation source is a 325 nm He-Cd laser with 30 mW power.

3. Results and discussion

3.1. The microstructure of HRTEM. The cross-sectional TEM image of the Si NCs/SiO_2 multilayers after 1000 °C high temperature annealing is shown in Fig.1, and the inset is the magnified image of a single Si NC. The thickness of Si layer and SiO_2 layer are about 7.2 nm and 3.7 nm, respectively. In the Si layer, the dot-shaped Si NCs are formed after 1000 °C annealing, and they are uniformly dispersed in the Si layer. As shown in the inset, the crystalline structure can be identified and the diameter of the NCs is about 6.8 nm, which is consistent with the thickness of the initial a-Si layer. The lattice fringes of the single Si QDs is about 0.31 nm, which is corresponding to (111) plans of Si.

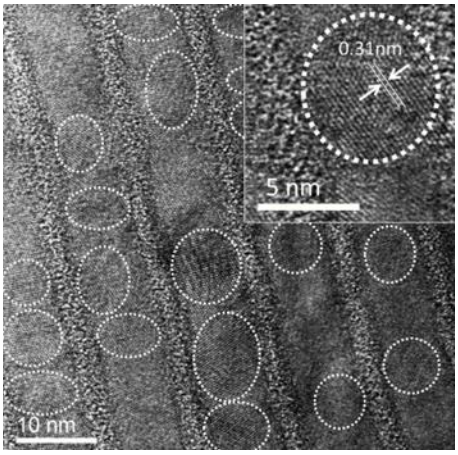

Figure 1. Cross-sectional HRTEM image of P doped Si NCs after 1000 ℃ annealing.

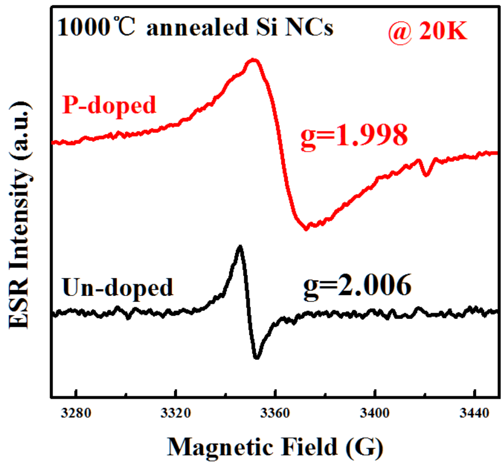

Figure 2. 20K low temperature X-band ESR spectra for un-doped and P doped Si NCs/SiO_2 multilayers with different P concentration after 1000 ℃ annealing.

3.2. The low temperature ESR for dopant location. The low temperature ESR can help us to explore the hyperfine microstructure of NCs and analyse the dopant location. Fig.2 is the X-band ESR spectra of Si/SiO_2 multilayers after 1000 °C annealing measured at 20 K with and without P doping. As shown in Fig.2, the ESR signal with g = 2.006 is detected for un-doped sample, which indicates the existence of dangling bonds in Si NCs-based films. However, when P atoms are introduced into Si NCs, the signal with g≈1.998 due to conduction electrons (CEs) is observed[9]. The CEs signal indicate some P dopants locate at the substitutional sites inside the Si NCs. When the P concentration is gradually increased, the g value remains at 1.998 for the CEs, and the linewidth of ESR spectra broadens, which prove more P atoms become the active atoms to provide free electrons.

3.3. The subband PL for doped Si NCs. For the ultra-small sized Si NCs, a radiative deep level will be induced in the bandgap by P impurities[10]. It is found that the 2 nm sized P-doped Si NCs/SiO_2 multilayers exhibit a broad subband emission band centered at 1.03 eV (1200 nm) after high temperature annealing. More interesting, we find the enhanced emission intensity with the similar PL spectra for B/P co-doped Si NCs. The mechanism for B/P co-doping luminescence behaviors is unclear at the present stage and the further studied is needed.

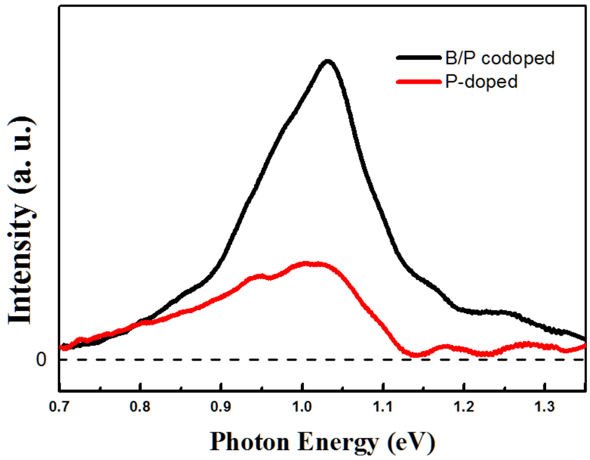

Figure 3. PL spectra for the P doped and B/P co-doped Si NCs/SiO2 multilayers

4. Conclusion

We have fabricated the a-Si/SiO_2 multilayers by PECVD and obtained the P doped and B/P co-doped Si NCs/SiO_2 multilayers after high temperature annealing. The ESR measurements reveal that P atoms can enter the Si NCs at the substitutional sites. For the 2nm ultra-small size Si NCs, P doping can induce a deep energy level and result in a subband light emission centred at 1.03 eV. The subband emission intensity can be enhanced in B/P co-doped Si NCs. Our results suggest that doping plays an important role in the electronic structures and optoelectronic characteristics of Si NCs, which provide a new route to realize the Si NCs-based devices.

Acknowledgments
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