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Threshold energy reduction for carrier multiplication in Si-QDs by phosphorus doping

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ABSTRACT

The Si-QDs/SiO2 multilayer films with phosphorus (P) doping have been prepared, and carrier multiplication effect of the films with and without P doping was investigated by relative quantum yield of photoluminescence (PL). The relative quantum yield of PL shows a step like increase when the excitation energy is larger than 2*Eg* of Si-QDs, and the carrier multiplication is caused by space-separated quantum cutting in adjacent QDs. The PL peak shifts toward high energy region after P-doping, and the PL intensity is enhanced, however, the threshold energy for carrier multiplication is decreased from 2.97 to 2.89 eV. The results suggest that non-radiative recombination at the surface of Si-QDs is suppressed by P passivation, and radiative recombination from conduction band to surface defect level is possible. Energy transfer from hot electron-hole pair to surface defect level leads to the optical excitation of defect level, which generates an extra electron-hole pair, and carrier multiplication effect is observed in the P-doped multilayer film with lower excitation energy.

1. Introduction

Silicon is one of the most important semiconductor materials in photovoltaic industry, and more than 90% of the commercialized solar panels are made of Si based materials [1]. The Shockley–Queisser efficiency limit has shown that 47% of solar energy is converted to heat in single junction crystalline silicon solar cells, and hot carrier cooling via phonon emission of high energy photons is a critical factor for energy loss [2]. A possible solution for enhancing the utilization ratio of solar energy is carrier-multiplication (CM, and it is also termed multiple exciton generation), in which multiple electron-hole pairs are generated by absorbing high-energy photons [3]. The power conversion efficiency in quantum dot solar cell exhibiting CM can greatly exceed that of bulk counter parts [4], and Si quantum dots (Si-QDs) have been prepared and characterized for over decades with regard to photovoltaic applications [5]. M. C. Beard et al. have shown that CM can be obtained in colloidal Si nanocrystals when the photon energy is 2.4 times larger than band gap, and the lifetime of multi-excitons in nanocrystal is 50–100 ps [6,7]. The high threshold energy and low generation efficiency limit the application of CM effect in the field of photovoltaics, and further research is needed for practical application. D. Timmerman et al. have shown that step-like increase of quantum yield can be observed in closely spaced Si nanocrystals when the excitation energy is close to energy conservation limit ($2E_g$) [8]. Further, space-separated quantum cutting (SSQC) has been adopted to explain the CM effect in dense Si nanocrystals, in which long-lived Auger-unaffected electron-hole pairs among interacting QDs were generated by Coulomb-driven energy transfer processes [9]. In addition, G. Allan et al. indicated that surface defects of semiconductor nanocrystals have a strong influence on the dynamics of hot carriers cooling, and impact ionization of defects can also induce single-carrier multiplication [10]. Therefore, the defect states at the surface of Si-QDs may be used for CM process, and the threshold energy can be further decreased.

In this letter, CM effect in Si-QDs was investigated by excitation energy dependence of relative PL quantum yields. The results show that step-like increase of quantum yield was observed in dense Si-QD films, and the energy threshold is close to 2*Eg* of Si-QDs. Furthermore, a P-doped multilayer film was prepared, and the threshold energy for CM in the P-doped multilayer film is lower than 2 *Eg* of the Si-QDs, which suggests that CM effect takes place between Si-QDs and the surface defect states.

2. Experimental details

The Si-QDs/SiO2 multilayer films were deposited on p-type Si and

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quartz substrates by a PECVD system [11–13]. SiH4, H2 and N2O were used as precursor gases, and the flow rates of SiH4 and H2 were 1 and 100 sccm, respectively. The flow ratio of N2O was kept at 25 sccm for the SiO2 layers, and 0.1 sccm for the Si-QDs layers. H2 diluted PH3 (100 times) was used as doping gas for the P-doped multilayer film, and its flow rate is 0.75 sccm during the Si-QDs layer deposition. Deposition pressure, substrate temperature and RF-power were kept at 120 Pa, 220 °C and 40 W, respectively. Multilayer films consisting of 30 Si-rich-silicon-oxide/SiO2 bi-layers were fabricated. After deposition, the multilayer films were annealed at 1100 °C in N2 for 60 min.

The Raman spectra were measured by a Horiba Jobin-Yvon LabRAM HR800 Raman spectrometer, and the excitation source was a 532 Ar^+ laser. The transmission electron microscopy (TEM) images were obtained from a F20 FEI microscope operating at 200 keV. Optical absorption spectra were measured by a Zolix 300 UV–VIS transmittance-reflectance spectrometer. The cw and time-resolved PL spectra were detected by a FLS920 fluorescence spectrometer (Edinburgh Instruments), and the excitation source were 450 W cw Xe lamp and 100 W pulse Xe lamp. The excitation wavelength dependence of relative external quantum yields of PL were determined experimentally by comparing the emitted and absorbed photons in the investigated samples, and the samples were placed inside an integrating sphere during measurements. The external quantum yields of PL can be expressed as [14]:

$$QY = \frac{\sum_{\text{emband}}[I_{Si}^{em}(E_{em}) - I_{ref}^{em}(E_{em})]C(E_{em})/E_{em}}{\sum_{\text{exband}}[I_{ref}^{ex}(E_{ex}) - I_{Sif}^{ex}(E_{em})]C(E_{ex})/E_{ex}} \quad .(1)$$

where I_{em} and I_{ex} are the optical emission and excitation intensities of the multilayer films and references, C is the calibration factor, and E_{em} and E_{ex} are the photon energy of emission and excitation photons. In order to protect the detector, the slit width of monochromator for excitation intensity measurement is much smaller than that of emission, and the obtained PL quantum yields are relative values.

3. Results and discussion

3.1. Carrier multiplication effect in Si-QDs without P doping

Fig. 1 shows the micro-structural and optical properties of the un-doped Si-QDs/SiO2 multilayer film. As can been seen in Fig. 1a, the main Raman peak of the un-doped film is located at 516 cm^{-1}, and it corresponds to the transverse optical mode of Si-Si vibration in crystal phase. The red shift of Raman peak corresponding to bulk crystalline Si (520.5 cm^{-1}) suggests that Si-QDs are obtained in the film [15], and it is further confirmed by HRTEM images. Fig. 1b shows the room temperature PL spectrum of the film, and the PL peak is located at 1.39 eV. The intense PL has been investigated in detail in our previous publications, and it originates from quantum-confined band-to-band transitions [11,16]. The UV–VIS absorption property of the film is investigated in Fig. 1c. The optical band gap (Eg) of the film can be

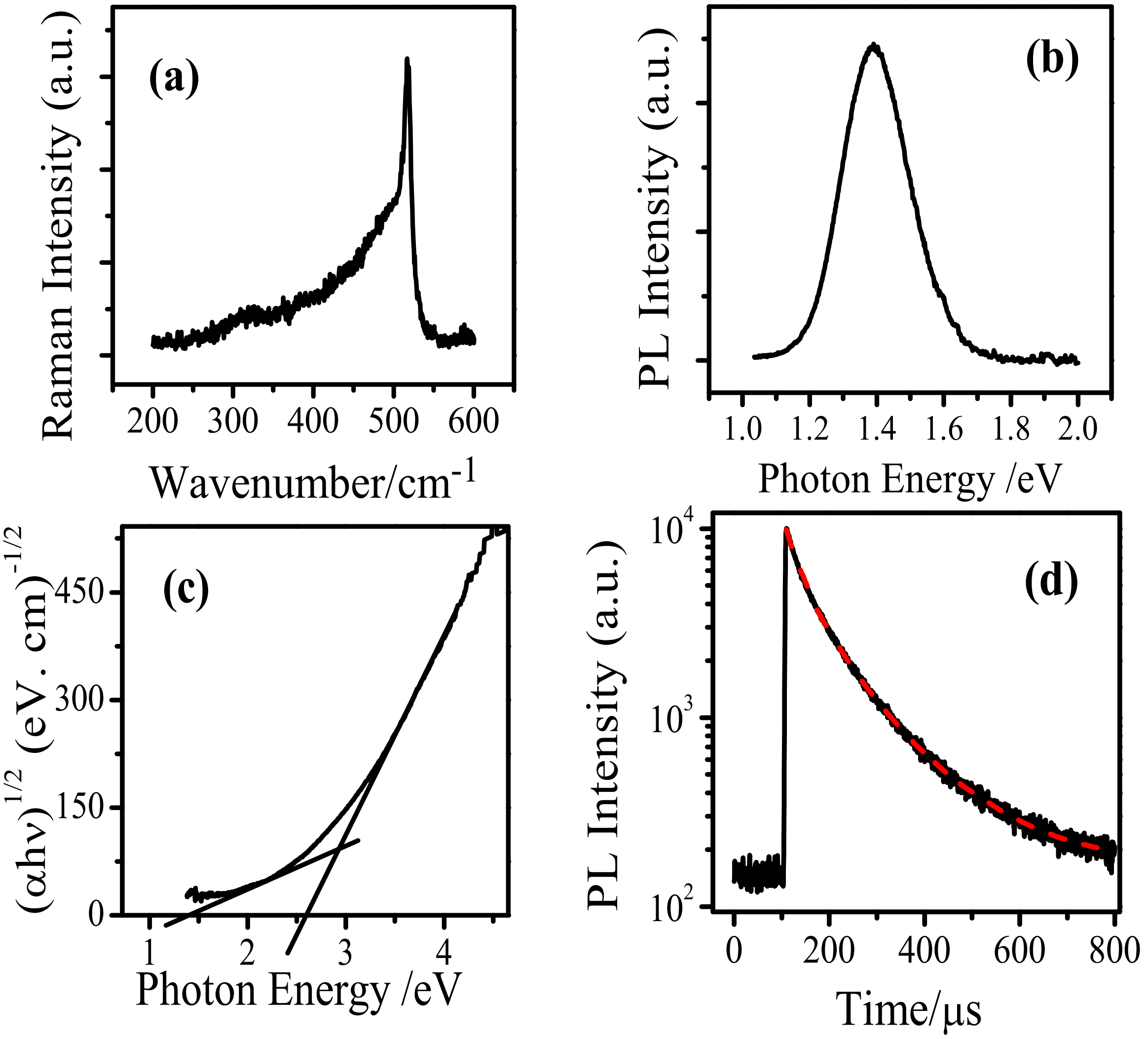

Fig. 1. Optical characteristic spectra of the Si-QDs/SiO2 film. (a) Raman spectrum; (b) Cw PL spectrum; (c) Absorption spectrum; (d) Time resolved PL spectrum and the fitting result.