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Short communication

Spectral characteristics of carrier transfer from Si cluster to nanocrystal in Si-rich-oxide/SiO_2 multilayer films

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ABSTRACT

Si-rich-oxide/SiO_2 multilayer composite films containing Si clusters and nanocrystals (NCs) have been synthesized by PECVD technique, and the carrier transfer processes from Si cluster to nanocrystal are studied by photoluminescence (PL) spectra. Compared with the references, intense PL is observed in the composite film, which is caused by the combined effect of Si clusters and NCs. Optical excitation is enhanced due to the dense Si clusters, while the carriers generated in the clusters are transferred to the Si–NCs due to their large carrier capture section. The PL excitation spectra shows that the resonance excitation energy is 3.58 eV, which corresponds to the excitation energy level of SiO_X shell covering the Si clusters. Double stretched-exponential decay model is used to demonstrate the PL decay processes in the composite film, and the results suggest that the carrier transfer time is about 35.8 μs.

Visible photoluminescence (PL) was observed in porous Si due to quantum confinement effect (QCE), and great potential applications in the fields of Si based light sources and solar cells have been suggested [1–3]. Various nano-scale Si structures have been prepared, and Si quantum dots (Si-QDs) embedding in oxide matrix is one of the most candidates due to the excellent confinement effect [4].

The absorption edge can be shifted from near-infrared to visible range by adjusting the size of Si-QDs, and all-Si tandem solar cells based on Si-QDs with different band gaps can utilize the sunlight efficiently [5]. Effective carrier transport among QDs is important for all-Si tandem solar cells, while it is limited to the high resistivity of embedding matrix [6]. Theoretically, carrier transport efficiency can be improved by the overlap of wavefunction in dense Si-QDs, and suitable surface modify can also improve the carrier transport property. Much effort has been made to fabricate dense Si-QDs, and the carrier transfer processes among Si–NCs have been investigated. O. B. Gusev and A. A. Prokofiev et al. have studied the energy migration between Si–NCs by time resolved PL spectra, and the excitation transfer time from small Si–NCs to large one is 38.5 μs [7]. D. Kovalev et al. have investigated the resonant energy transfer process from Si–NCs to molecular oxygen, and the surface structure and excitons radiative lifetime work together on energy transfer [8]. Although some progresses have been made, the carrier transfer probability among Si–NCs is still very low due to the small band gap difference in Si–NCs. The Si clusters are formed in the infancy of Si–NCs, and the band gap of which is much larger than Si–NCs due to their small size. While the carrier capture cross section of Si–NCs is larger than the clusters, and carrier transfer from Si clusters to NCs can be achieved easily if the density is high enough, which would dramatically influence the carrier transfer properties. In this work, Si-rich-oxide (SRO)/SiO_2 multilayer films containing Si clusters and NCs are obtained by plasma enhanced chemical vapor deposition (PECVD) technique followed by annealing treatment, and the carrier transfer processes from Si clusters to NCs are studied by the PL spectra.

The SRO/SiO_2 multilayer films were deposited on Si and quartz substrates by the PECVD technique, and the corresponding equipment has been described in detail previously [9]. In our previous work, we have shown that annealing temperature, annealing temperature and RF-power dramatically influence the structure and optical properties of Si QDs, and high-quality Si-QDs can be obtained when the deposition temperature, annealing temperature and RF-power were 200 °C, 1100 °C and 20 W, respectively [9–11]. However, the configuration and density of Si-QDs cannot be adjusted simultaneously by changing the above parameters. In this work, Si cluster and NCs were obtained in a composite film by changing the flow rate of N_2O during the SRO layer deposition. SiH_4,

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H_2 and N_2O were used as reactant gases, and the flow rates of SiH_4 and H_2 were set as 1 and 100 sccm, respectively. The flow rate of N_2O was increased from 1 to 4 sccm in 24 s during the SRO layer deposition, and then it was held at 25 sccm for 6 s during the SiO_2 layer deposition, and the composite film was defined as S_{14}. For comparison, two reference multilayer films were also fabricated, and the flow rates of N_2O were kept at 1 and 4 sccm during the growth of SRO layers, and they were defined as S_1 and S_4 respectively. All the multilayer films were consist of 30 SRO/SiO_2 bilayer sequences. Explosion occurs easily during the chemical reaction of silane and oxygen, and the SRO cannot be obtained in the oxygen enriched environment. In order to avoid the influence of oxygen, the deposition house was pumped to 2×10^{-4} Pa in 20 min before film deposition, and the deposition pressure was kept at 100 Pa during film deposition. After deposition, the samples were annealed at 1100 °C in N_2 for 60 min. In the end, hydrogen passivation is performed at 450 °C for 1 h, and the annealing chamber was pumped to 0.1 Pa before H_2 introducing.

The Raman spectra were performed at room temperature using a micro-Raman spectrometer (JY T6400), and the excitation laser was a 532 nm Ar^+ laser. The transmission electron microscopy (TEM) images were performed by a JEOL J2010F (S)TEM microscope operating at 200 keV. The steady and time resolved PL spectra were detected by a FLS920 fluorescence spectrometer (Edinburgh Instruments). The excitation sources were 450 W steady Xe lamp, 100 mW 532 nm Ar^+ laser, and 100 W pulse Xe lamp, respectively.

Fig. 1a shows the Raman spectra of the films. The main Raman peaks locate at 518 and 492 cm^{-1} for S_1 and S_4, respectively. The Raman peak locating at 518 cm^{-1} in S_1 is associated with Si—NCs, and the Raman peak at 492 cm^{-1} in S_4 corresponds to the Si clusters [12]. As shown in Fig. 1b, three Gaussian bands are obtained by curve fitting the Raman spectrum of S_{14}. The peak at 432 cm^{-1} is related to the LO mode of amorphous Si, and the peaks at 490 and 516 cm^{-1} correspond to the TO mode of Si clusters and NCs. The results suggest that Si clusters and NCs co-exist in S_{14}. Calculation shows that the integral Raman intensity ratio for Si clusters and NCs is 44.9, which indicates that the Si-QDs mainly exist in the form of Si clusters. The multilayer structure of S_{14} is shown in Fig. 1c, and one period of the multilayer structure is 17 nm with SiO_2 layer 4 nm. Fig. 1d shows that dense Si-QDs are observed in the HRTEM images, and lattice fringes can be seen only in few of them. The results further confirm that Si clusters are the dominant QDs in S_{14}. The density of Si clusters is estimated to be 2.5×10^{12} cm^2, and the mean size of which is about 2.6 nm. Only several Si—NCs are observed in the HRTEM images, and its mean size is about 3.5 nm. Typical Si cluster and NC are shown in the inset of Fig. 1d, which shows that the distance between them is close enough for carrier transfer.

Fig. 2 shows the PL spectra of the multilayer films. As can be seen, the PL peaks of S_1 and S_4 locate at 1.44 and 1.63 eV, and the PL peak intensity ratio of S_1 and S_4 is about 1: 2.5. The optical emissions of oxygen-terminated Si-QDs can be attributed to the interband transition caused by QCE or defect states transition at the surface of Si-QDs [13]. Our previous work has proved that QCE is the dominated PL mechanism of S_1, while interface defects recombination is the main origin of light emitting in Si clusters based system. The PL intensity is proportional to the number of light emitting centers and radiative recombination probability in the same excitation condition [14]. Due to the large structural disorder in Si clusters based system, the radiative recombination probability at

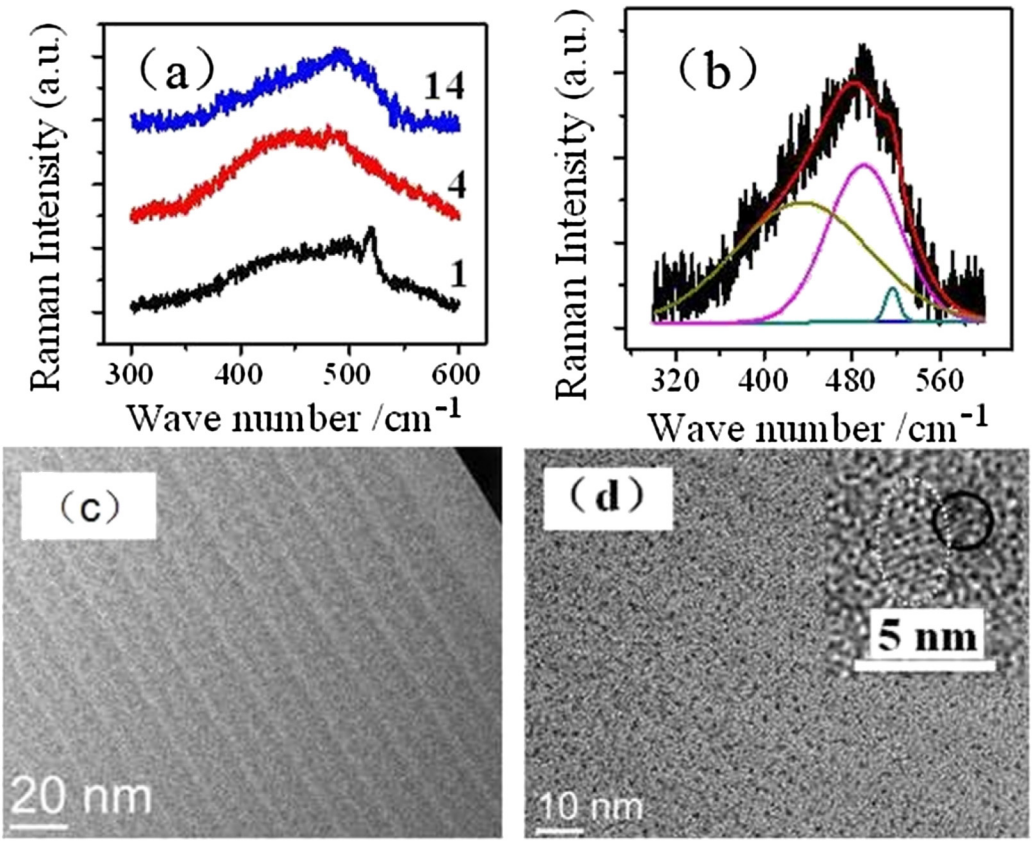

Fig. 1. (a) Raman spectra of t he films; (b) Curve fitting result of the Raman spectrum of S_{14}; (c) A TEM image of S_{14}; (d) A HRTEM image of S_{14}, and the inset shows a typical Si cluster and NC.