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The origin of blue photoluminescence from nc-Si/SiO_2 multilayers*

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Intensive blue photoluminescence (PL) was observed at room temperature from the nanocrystalline-Si/SiO_2 (nc-Si/SiO_2) multilayers (MLs) obtained by thermal annealing of SiO/SiO_2 MLs for the first time. By controlling the size of nc-Si formed in SiO sublayer from 3.5 to 1.5 nm, the PL peak blueshifts from 457 to 411 nm. Combining the analysis of TEM, Raman and absorption measurement, this paper attributes the blue PL to multiple luminescent centres at the interface of nc-Si and SiO_2.

Keywords: PL, nc-Si, Raman spectroscopy
PACC: 7360F, 6170A, 7855

1. Introduction

Si-based light-emitting materials have been of continuing interest for the purpose of developing full colour displays and integrated optoelectronics.[1−7] Since the discovery of porous Si with efficient room temperature visible photoluminescence (PL),[8] a large number of light-emitting materials have been explored.[9−12] Of all the materials, robust structures in various thermal and chemical environments are especially valued and required because of practical applications in various devices. As a simple and efficient structure for fabricating highly luminescent nanocrystalline-Si (nc-Si), SiO/SiO_2 multilayers (MLs) have attracted considerable interest in recent years owing to its possibility to control the size, size distribution, density of nc-Si. Thermal annealing of SiO/SiO_2 MLs prepared by reactive evaporation leads to phase separation and crystallization of the SiO layers and PL from this structure crystallized at 1000 °C was found from 960 to 810 nm as the SiO layer thickness was reduced from 4.1 to 2.0 nm.[9] However, up to now, SiO/SiO_2 MLs prepared by using plasma oxidation in plasma enhanced chemical vapour deposition (PECVD) system have never been reported. And the blue PL has also never been reported from crystallized SiO/SiO_2 MLs. From the viewpoint of optoelectric application, efficient blue light sources directly on silicon-integrated circuits is desirable and inspiring.

In this paper, we report the observation of blue PL at room temperature from nc-Si/SiO_2 MLs, which is obtained by thermal annealing of SiO/SiO_2 MLs fabricated by using well-controlled plasma oxidation in PECVD system. By controlling the size of nc-Si formed in the SiO sublayer, the PL peak moves from 457 to 411 nm. This is a very important advantage in the application of integrated optoelectrics.

2. Experiment

Amorphous SiO/SiO_2 MLs with 40 periods were fabricated on silicon and fused quartz substrate by capacitively coupled PECVD system. The SiO and SiO_2 sublayers were obtained by plasma oxidation of a-Si:H layer with different radiofrequency (RF) power. The a-Si:H layers were deposited by discomposing silane mixed with Ar gas at a pressure of 35.62 Pa under RF power of 30 W. The plasma oxidation was realized by using pure oxygen gas at a pressure of 37.21 Pa with RF power of 30 and 50 W, respectively. The substrate temperature is 250 °C. The stoichiometry of SiO and SiO_2 sublayers was monitored by the measurement of Fourier transform infrared (FTIR). The thickness of SiO_2 sublayer is 5.5 nm. By controlling the thickness

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of a-Si:H and plasma oxidation time, the thickness of SiO layers varies from 3.5 to 1.5 nm. After fabrication the samples were post-treated by thermal annealing at 1100 °C for 1h under N_2 atmosphere. The microstructure of the annealed samples was revealed by transmission electron microscopy (TEM) with a JEM 2010 electron microscope working at 200 kV. Raman scattering experiments were performed by Jobin Yvon Horiba HR 800 Raman system with the 488 nm line of an Ar^+ laser as an excitation source. Absorption spectroscopy was employed to record the absorption properties in the annealed samples with different thickness of SiO sublayer. PL measurements were carried out at room temperature by using He–Cd laser with wavelength of 325 nm as an excitation source.

3. Results and discussion

Figure 1(a) displays the cross-section TEM of the sample annealed at 1100 °C. The dark and white regions in the graph correspond to SiO with a thickness of 2.5 nm and to SiO_2 with a thickness of 5.5 nm, respectively. The multilayered structure and the phase separation are clearly visible. Nearly perfect crystals with size near 2.5 nm were grown in the SiO sublayers as observed by high resolution transmission electron microscopy (HRTEM), which is shown in Fig.1(b). The (111) crystallographic orientation of nc-Si in the sublayer can be clearly observed. The image demonstrates that nc-Si has formed within initially SiO sublayer and the nc-Si size is constrained within the thickness of SiO sublayer. In addition the Raman spectra of the annealed samples were measured, the sharp peaks ascribed to transverse optical (TO) mode of nc-Si shifts from 511 to 517 cm^{-2} with the thickness of SiO increasing from 1.5 to 3.5 nm, which further confirms that nc-Si has formed in all samples. According to the formula,[13] the size of nc-Si in samples with different SiO sublayer can be estimated to be 3.5, 3.1, 2.4, 1.5 nm, which is in agreement with that observed in the cross-section TEM micrographs of the annealed samples.

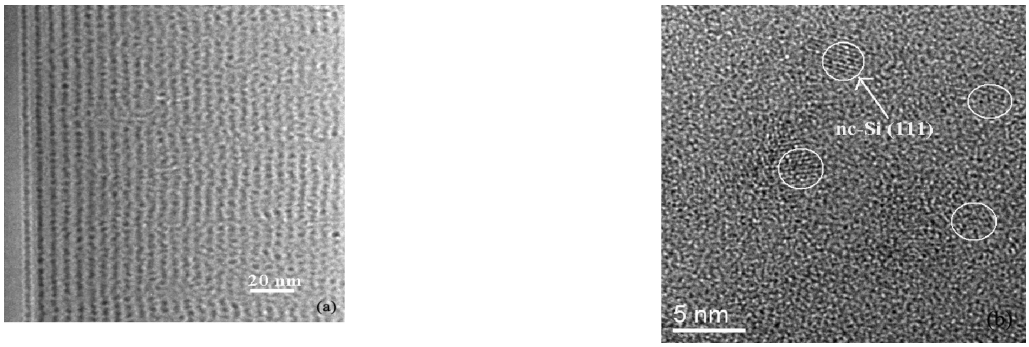


Fig.1. (a) Cross-section TEM photograph of nc-Si/SiO_2 MLs annealed at 1100 °C. (b) HRTEM photograph of nc-Si/SiO_2 MLs annealed at 1100 °C. The thickness of SiO and SiO_2 sublayer is 2.5 and 5.5 nm, respectively.

The room-temperature PL spectra of the nc-Si/SiO_2 MLs obtained by thermal annealing of SiO/SiO_2 with different thicknesses of the SiO sublayer are shown in Fig.2. The peak position of blue PL with a full width at half-maximum near 50 nm varies from 457 to 411 nm with decreasing nc-Si size from 3.5 to 1.5 nm. And the blue PL intensity increases with decreasing nc-Si size. In addition, a red PL peak at 750 nm is also observed. The red PL intensity is much lower than that of the blue one. It is noticed that the position of the red PL peak does not shift with the variation of nc-Si size.

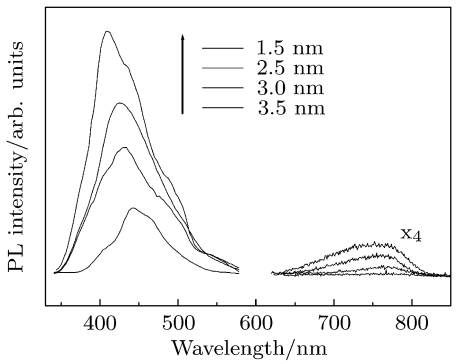


Fig.2. The room temperature PL spectra of nc-Si/SiO_2 MLs annealed at 1100 °C with different nc-Si size from 1.5 to 3.5 nm.

The PL of the annealed single SiO_2 sublayer obtained by plasma oxidation is also recorded. No PL peak is detected. In addition the x-ray photoelectron spec-

troscopy results confirm that the chemical composition of the oxide in the annealed sample is stoichiometric, which testify that the blueshift of PL peak cannot be influenced by SiO_2 or SiO. In addition the fixed charge density of the as-fabricated SiO_2 sublayers derived from C–V measurement is about $10^{11}\,cm^{-2}$, which means that the SiO_2 sublayer possesses good quality.[14] Thus it is also not related to the intrinsic luminescent centres in SiO_2.[15] In combination with the results of TEM and Raman, we find that it is obviously associated with the nc-Si formed in the samples.

In order to further clarify the origin of blue PL from the crystallize samples, we measured the absorption spectra of the annealed samples with different thickness of the SiO layers grown on fused silica substrate, as shown in Fig.3(a). It is obvious that the absorption edge of the sample moves to short wavelength when the size of nc-Si decreases.

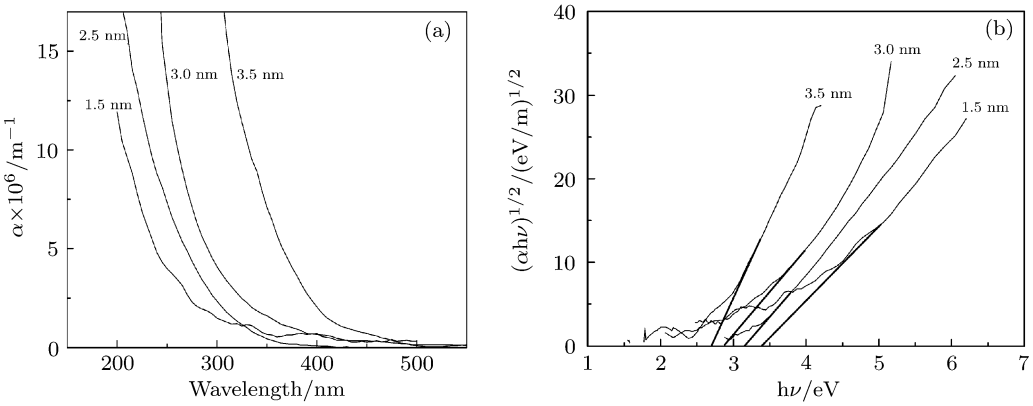


Fig.3. (a) The absorption spectra of nc-Si/SiO_2 MLs annealed at 1100 °Cwith various nc-Si size from 1.5 to 3.5 nm. (b) The absorption spectra [represented by $(\alpha h\nu)^{1/2} - h\nu$] obtained from Fig.3(a) showing that the band gap of the samples with 3.5, 3, 2.5 and 1.5 nm nc-Si are 3.43, 3.18, 2.90, 2.72 eV which are indicated by the intersecting points of bold line and horizontal axis.

As is well known, the optical band gap of the samples, i.e., the constant form, c, of the Tauc law: $(\alpha h\upsilon)^{1/2} = c(h\upsilon - E_g)$[16] can be obtained using the extrapolation of $(\alpha h\upsilon)^{1/2} - h\upsilon$ curve to zero ordinate. The curves are shown in Fig.3(b). The optical band gap is 2.72 eV for the sample with 3.5 nm, 2.89 eV for the sample with 3.0 nm, 3.18 eV for the sample with 2.5 nm and 3.43 eV for the sample with 1.5 nm nc-Si, respectively. It is evident that the band gap blueshifts from 2.72 to 3.43 eV with the decrease of the nc-Si size from 3.5 to 1.5 nm. The Stokes shift between the PL energy and band gap is shown in Table 1. It was found with the reduction of nc-Si size from 3.5 to 1.5 nm, the Stokes shift increases from 0.01 to 0.41 eV. The change trend of Stokes shift is different from that induced by quantum confinement effect of nc-Si. According to the calculation of Delerue *et al*,[17] the shift of band gap for the nc-Si is around 1.5 eV when the size of nc-Si changes from 1.5 to 3.5 nm. However our experimental results show that the shift of band gap for our samples is 0.71 eV, which is smaller than that from theoretical calculations. Therefore it is difficult to ascribe the blue PL peak to quantum confinement effect of nc-Si.

Table 1. The PL energy, band gap from absorption spectra and Stokes shift of nc-Si/SiO_2 MLs annealed at 1100 °C with various size of nc-Si from 1.5 to 3.5 nm.

average diameter /nm	1.5	2.5	3.0	3.5
blue PL peak position /eV	3.02	2.91	2.88	2.71
band gap /eV	3.43	3.18	2.90	2.72
stokes shift /eV	0.41	0.27	0.02	0.01

Some information about the recombination can be drawn from the variation of the Stokes shift. The existence of Stokes shift and the photons above the band gap indicates that radiative combination can take place between shallow trap states of electrons and holes,[18] which means that some of the electrons within nc-Si absorb photons and relax to localized states by emitting phonons and then radiatively combine there with holes. It is also noticed that the PL peak at 410 nm is one of the subbands of the blue PL peak for the samples with the SiO thickness of 1.5, 3.0, and 3.5 nm. In addition the PL peak at 450 nm is one of the subbands of the blue PL peak for the samples with SiO thickness of 1.5 and 3.5 nm. As for the reason why the intensity of PL peak at 410 nm increases as the thickness of SiO decreases from 3.5 to 1.5 nm, we conjecture that there are multiple lumi-

nescent centres located at the interface of SiO_2 and nc-Si, which result in multiple subbands of PL peak. Among them, the intensity of the PL peak at 410 nm increases more rapidly than that of other PL peaks. In addition to the blue PL peak, a red PL peak at 750 nm is also observed. Wolkin *et al*[19] have studied 750 nm PL of porous silicon exposed in air. They ascribed this PL peak to Si=O passivated nc-Si. We also tend to believe that the PL peak at 750 nm of our samples is originated from the correlation of nc-Si and localized states of interfacial Si=O.

4. Conclusions

In conclusion we observed blue PL from nc-Si/SiO_2 MLs by thermal annealing of SiO/SiO_2 MLs. The blue PL peaks with the full width at half maximum near 50 nm can be tuned in a range from 457 to 411 nm by controlling the nc-Si size from 3.5 to 1.5 nm. Combining of the analysis of TEM, Raman and absorption measurement, we find that the blue PL is attributed to multiple luminescent centres at the interface of nc-Si and SiO_2. Our preparation of nc-Si/SiO_2 MLs is completely compatible with the modern Si technology, and supplies a possible candidate for silicon blue-light emission devices.

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