Vol 16 No 5, May 2007
1009-1963/2007/16(05)/1410-07

Chinese Physics

© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Pseudo nanocrystal silicon induced luminescence enhancement in a-Si /SiO_2 multilayers*

Han Pei-Gao(韩培高), Ma Zhong-Yuan(马忠元)†, Xia Zheng-Yue(夏正月), Chen De-Yuan(陈德媛), Xu Jun (徐 骏), Qian Bo(钱 波), Chen San(陈 三), Li Wei (李 伟), Huang Xin-Fan(黄信凡), Chen Kun-Ji(陈坤基), and Feng Duan(冯 端)

National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093*, China*

(Received 20 July 2006; revised manuscript received 21 November 2006)

Enhanced photoluminescence (PL) at room temperature from thermally annealed a-Si:H/SiO_2 multilayers is observed through the step-by-step thermal post-treatment. The correlation between the PL and the crystallization process is studied using temperature-dependent PL, Raman, cross section high-resolution transmission electron microscopy (X-HRTEM) and x-ray diffraction (XRD) techniques. An intensified PL band around 820 nm is discovered from the sample annealed near the crystallization onset temperature, which is composed of two peaks centred at 773 nm and 863 nm, respectively. It is found that the PL band centred at 863 nm is related to the pseudo nanocrystal (p-nc-Si) silicon, and the PL band centred at 773 nm is attributed to Si = O bonds stabilized in the p-nc-Si surface.

Keywords: nanometre Si, photoluminescence, Raman spectroscopy
PACC: 6170A, 7360F, 7855

1. Introduction

Since the visible light emission was observed from porous silicon at room temperature for the first time in 1990,[1] enormous researches have been focused on the light-emitting properties of various silicon-based materials.[2−7] In the last decade, many kinds of low-dimensional Si/SiO_2 nanostructures, such as porous silicon, Si/SiO_2 superlattice,[2] and nc-Si embedded in SiO_2[3] have been fabricated and their light-emitting behaviours have been reported. Their compatibility with common microelectronic technology makes them attractive for their potential applications in integrated optoelectronic devices. Various theoretical models about the photoluminescence (PL) have been developed and computational work has been followed as well.[8,9] Besides quantum confinement effects,[2] radiative recombination at the Si/SiO_2 interface[3,10] or oxygen-related defects[11,12] are also suggested as the origin of PL. Although a great effort has been made to elucidate the physical insight of the PL process in a Si/SiO_2 system, the picture of the PL mechanism is not fully revealed, especially the origin that is responsible for the enhancement of PL from thermally annealed a-Si:H/SiO_2 multilayers near the crystallization onset temperature has been less reported.

In our previous work,[13] we have performed a detailed investigation to monitor the evolution of structure and PL from a-Si/SiO_2 multilayers to nc-Si/SiO_2 multilayers by thermal post-treatment. It is suggested that there exist various luminescence centres at different annealing temperatures, such as nonbridging oxygen hole centres (NBOHCs), thermal donors (TDs) and localized states of interfacial Si = O. In this paper, we concentrate on the enhancement of PL from the annealed Si/SiO_2 multilayers near the crystallization onset temperature. Raman scattering and X-HRTEM studies show that there is an intermediate phase of silicon between the amorphous and crystallized phases for the annealed sample near the crystallization onset temperature. The relationship between PL and the microstructure of the samples is carefully analysed.

2. Experiment

Two series of a-Si:H/SiO_2 multilayers were fabricated on the substrates located on an earthed electrode, at a temperature of 250 °C, in a computer-controlled rf plasma enhanced chemical vapour depo-

*Project supported by the Natural Science Foundation of Jiangsu Province, China (Grant No BK 2004410), the National Natural Science Foundation of China (Grant Nos 60508009, 90301009, 60471021 and 60571008), and the State Key Program for Basic Research of China (Grant No 2006CB0N0202).

† E-mail: zyma@nju.edu.cn

sition (PECVD) system. The a-Si:H layers were deposited in a mixture of SiH_4 and Ar at a pressure of 26.66 Pa. Subsequently, an in situ plasma oxidation was carried out in pure oxygen at 39.99 Pa. The rf power for both processes was kept at 30 W. The processes were repeated alternatively for 30 periods. The thickness of a-Si:H sublayer was designed to be 4 nm for sample A and 5 nm for sample B, and the SiO_2 sublayer was kept at 7 nm in thickness for both samples.

A series of post-treatments of these samples was performed by their annealing in N_2 atmosphere in a conventional furnace. The thermal treatment technique that we used was the step-by-step quasi-equilibrium annealing, which can simulate the temperature increasing process and time accumulating process as well. The annealing temperature increased step by step from 750 °C to 1100 °C. Each step lasted 60 min and subsequent Raman and PL measurements were employed to characterize the microstructure and luminescence properties of samples.

The PL and Raman measurements were carried out with a Jobin Yvon Horiba HR800 Raman Spectrometer with 600 g/mm grating and the detector was a charge-coupled camera. The 488 nm light of Ar^+ laser was used as an excitation light source. The X-HRTEM measurements were performed on a JEOL-4000EX HRTEM. XRD measurements were carried out for structure analysis of p-nc-Si using a D/Max-RA operated at 50 kV and 150 mA. Cu Kα_1 (λ = 0.154 nm) line was used.

3. Results

Figure 1(a) shows the room temperature PL spectra of sample A at different annealing stages. The step-by-step annealing causes the PL spectra to change significantly. A weak and broad PL peak at about 760 nm is observed at an annealing temperature of 750 °C. For annealing at 850 °C, the PL peak experiences a blue shift to 670 nm and its intensity remains weak. For further annealing at 900 °C, the PL peak suffers a red shift to 820 nm and its intensity abruptly increases by a factor of 4.5. However, after a higher temperature annealing (at 950 °C), the PL intensity reduces by a factor of 2.1 and the peak position has a slight blue shift to 770 nm. Figure 1(b) shows the room temperature PL spectra of sample B at different annealing stages. A weak and broad PL peak at about 700 nm is observed at an annealing temperature of 750 °C. For annealing at 850 °C the PL peak position has a red shift to 820 nm and its intensity increases by a factor of 10.7. However, for further annealing at 900 °C, the PL intensity reduces by a factor of 6.6 and the PL peak position has a blue shift to 710 nm. After further annealing at a higher temperature of 950 °C, the PL intensity remains weak and the peak position has a blue shift to 670 nm.

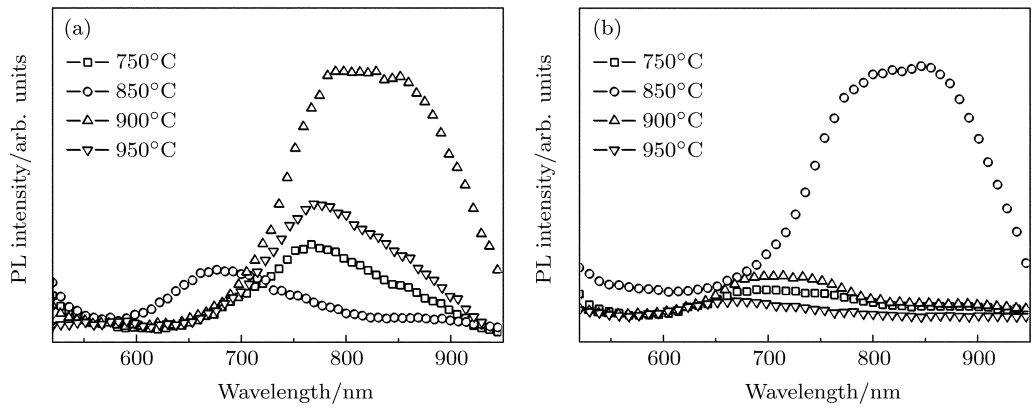


Fig.1. Room temperature PL spectra of sample A (a) and sample B (b) annealed, separately, at 750, 850, 900 and 950 °C.

In order to ascertain the PL mechanism for the enhancement of optical transition, the temperature-dependent PL spectra in a temperature range of 83–288 K for sample A have been investigated (Fig.2). It can be seen that the PL band intensity increases very fast with temperature decreasing, while the PL band position does not seem to change much with temperature varying.

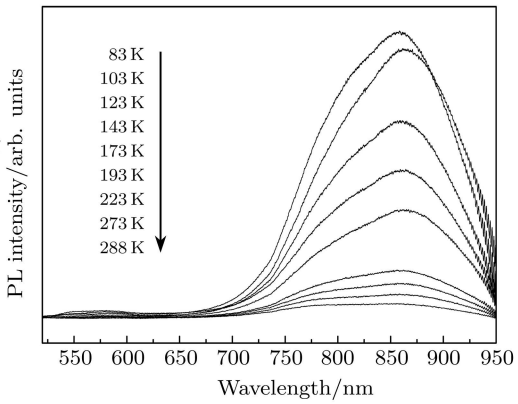


Fig.2. PL spectra at different temperatures ranging from 83 to 288 K for sample A after annealing at 900 °C.

Figure 3(a) shows Raman spectra of sample A at different annealing temperatures. The strong emission at 520 cm^{-1} corresponds to the silicon substrate signal. The results clearly show the presence of an amorphous silicon phase in the samples as shown by the strong band located at 480 cm^{-1}. For annealing at temperatures higher than 950 °C, a shoulder clearly appears at the band located at 520 cm^{-1} as shown with an arrow in Fig.3(a), which indicates the formation of nc-Si in the amorphous silicon sublayers, therefore, the crystallization onset temperature is between 900 and 950 °C for sample A. Figure 3(b) shows the Raman scattering results of sample B at different annealing temperatures. The shoulder corresponding to nc-Si can be clearly seen in sample B under annealing at 900 and 950 °C, which means the crystallization onset temperature of sample B is between 850 and 900°C. The difference in crystallization onset temperature between samples A and B is due to the difference in a-Si sublayer thickness.

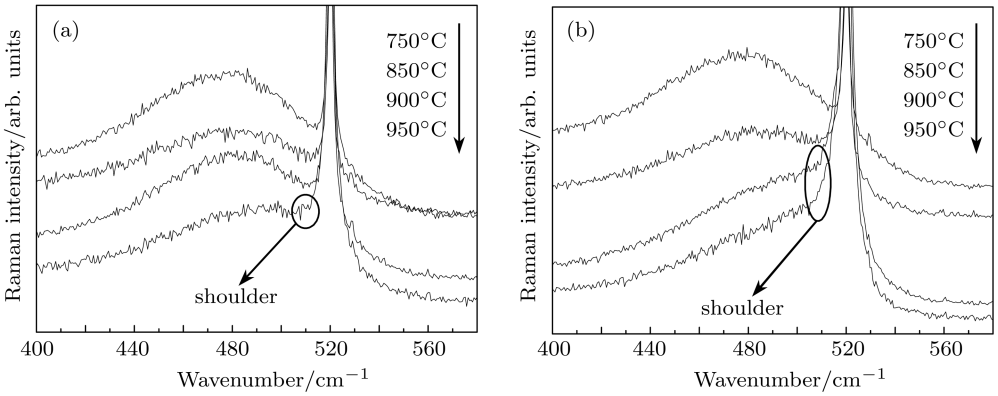


Fig.3. Raman spectra for samples A (a) and B (b) annealed at different temperatures.

Figure 4(a) shows the TEM image of sample A after annealing at 900 °C, the white and dark regions in the image correspond to Si and SiO_2 sublayers, respectively. The silicon sublayer contains some stick-like objects, and the X-HRTEM is shown in Fig.4(b), where no nc-Si is found, and the electron diffraction pattern in the insert of Fig.4(b) proves them to be amorphous, coincident with the Raman result. Figure 4(c) shows the TEM image of sample A after annealing at 950 °C, silicon dots with diameters around 4 nm can be clearly found in the silicon sublayer. Figure 4(d) shows the X-HRTEM of sample A after annealing at 950 °C, indicating that nearly perfect crystals of around 4 nm in diameter are grown in the multilayered structures. The inset of Fig.4(d) shows the HRTEM image of an individual nc-Si dot with a lattice constant of 0.31 nm corresponding to the Si(111) planes of the nanocrystallite. The result is coincident with that from the Raman spectra.

Figure 5 shows the XRD pattern of sample B after annealing at 850 °C. Only one diffraction peak centred at 33° corresponding to the (200) axis can be observed.

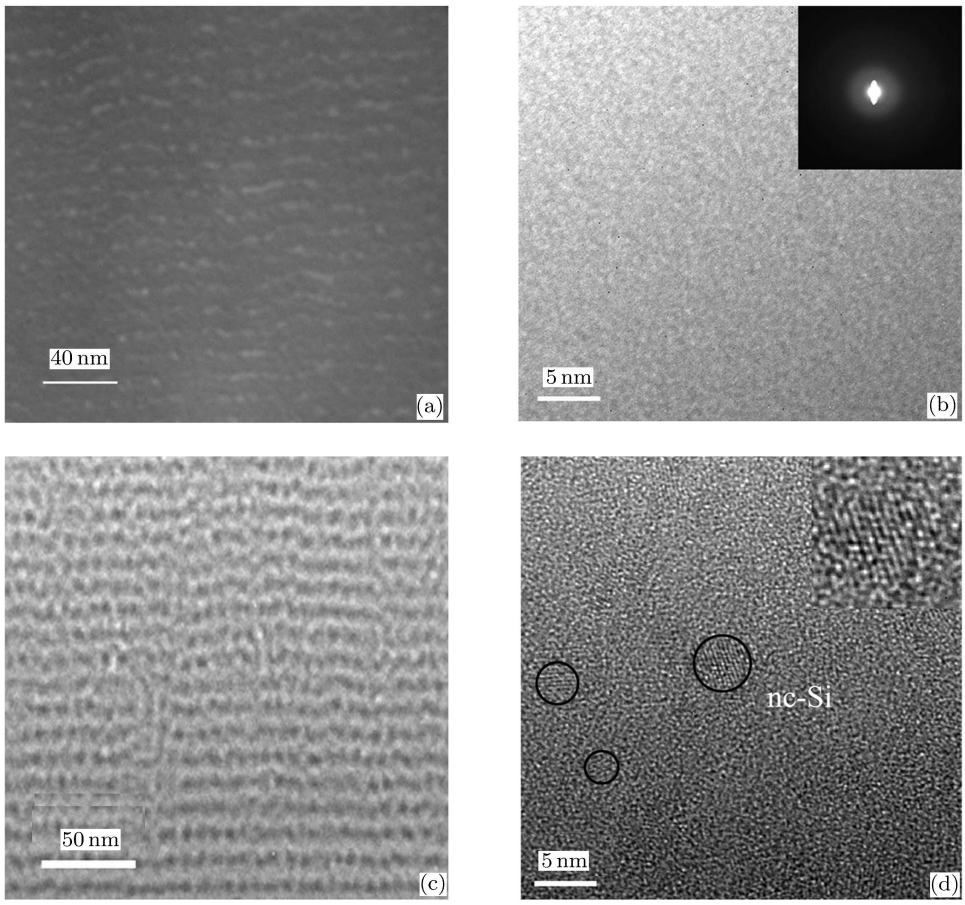


Fig.4. (a) TEM image of sample A after annealing at 900 °C. (b) X-HRTEM of sample A after annealing at 900 °C. (The inset shows the electron diffraction pattern.) (c) TEM image of sample A annealed at 950 °C. (d) X-HRTEM of sample A after annealing at 950 °C. (The inset shows the lattice structure of an nc-Si grain.).

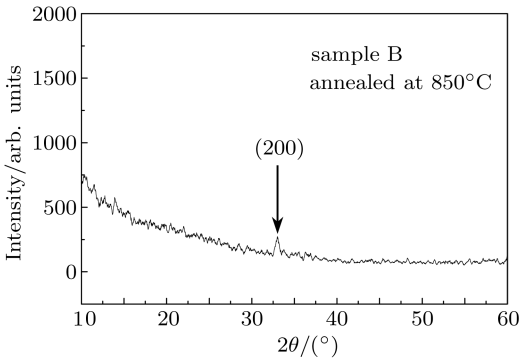


Fig.5. XRD spectra of sample B after annealing at 850 °C.

4. Discussion

The Raman scattering is an efficient way to determine whether the silicon occurs in its crystalline or amorphous phase. Owing to the difference in crystalline temperature between multilayers on silicon and quartz substrates,[14] we have performed the Raman scattering experiments directly on the samples with silicon substrate. The results are shown in Fig.3(a), where we can clearly find the presence of a crystalline silicon phase in the samples annealing at 950 °C. Below the crystallization threshold value, the structures of a-Si embedded in the annealed samples become more ordered, which is confirmed by the TO (transverse optical) mode of a-Si shifting towards the higher wavenumbers. The Gaussian deconvolution of the Raman data for sample A annealing at 900 °C is performed with three Gaussian functions, one Gaussian is used to represent the longitudinal optical (LO) band centred at 400 cm^{-1}, and the other two Gaussians are used to represent the TO band, of which one is centred at 475 cm^{-1} for amorphous silicon and the other band is found to be centred at 490 cm^{-1} (The TO band at 520 cm^{-1} of the silicon substrate is subtracted before the deconvolution). The Gaussian band centred at 490 cm^{-1} indicates that some kind of silicon object has a more ordered structure than the standard amorphous silicon emerging, but its phase is not so ordered as crystalline phase. The ratio of 490 cm^{-1}

band area to the 475 cm^{-1} band area is 0.2, which indicates that a high density of this kind of object emerges in the amorphous silicon sublayer before the onset of crystallization. The same Gaussian band centred at 490 cm^{-1} has been also observed in the Raman deconvolution results of H diluted amorphous silicon by Tsu *et al*,[15] and they ascribed it to an intermediate phase of silicon. This further confirms that the intermediate phase of the objects emerges before the onset of crystallization of our Si/SiO_2 multilayers.

It can be seen from Fig.4(a) that the amorphous silicon sublayer is no more homogeneous in structure, some stick-like objects in the amorphous silicon sublayers are observed, while no nc-Si is found from the X-HRTEM in Fig.4(b), and the film remains amorphous, which is revealed by the electron diffraction pattern in the insert of Fig.4(b). After annealing at 950 °C, sample A begins to crystallize, and dotted silicon nanocrystals emerge as shown in Fig.4(c). Nc-Si with clear lattice structure is demonstrated in the X-HRTEM in Fig.4(d). The TEM results are consistent with the observations of Raman scattering.

To further analyse the structure of the amorphous Si sublayers before the onset of crystallization, XRD measurement was carried out on sample B after annealing at 850 °C. As shown in Fig.5, a weak peak is shown to be centred at 33°, which indicates that the silicon structures in an intermediate phase emerging before the onset of crystallization begin to expose some preferred crystallographic orientation as nc-Si of (200).

Based on the analyses of the Raman, TEM and XRD results, we can determine that these objects emerge in the amorphous silicon sublayers before the onset of crystallization with an ordered intermediate state between random net-work amorphous phase and crystalline phase as p-nc-Si.

Generally, as the annealing temperature increases, bonded hydrogen effuses out of the a-Si:H/a-SiO_2 multilayers, some previously passivated defects, such as dangling bonds (Pbs), are depassivated. Accompanying with the formation of Pbs in Si/SiO_2 interfacial areas, some interstitial oxygen atoms could react with these Pbs to form some radiative centres, such as nonbridging oxygen hole centres (NBOHCs)[16] and thermal donors (TDs),[11] It has been reported that their emitting bands are around 650 and 750 nm, and these two emitting centres can coexist and contribute to the PL spectrum simultaneously. The PL band centred at 760 nm for sample A annealed at 750 °C, which is close to 750 nm observed in Ref.[11], is mainly ascribed to TDs. The PL band centred at 670 nm with a typical full width at half maximum of 0.33 eV after annealing it at 850 °C can be attributed to NBOHCs.[12]

Figure 6 shows the integral intensities of PL spectra of sample A and sample B, from which it can be seen that there appear an abrupt increase in intensity for both samples annealed near the crystallization onset temperature, or rather, at 850 °C and 900 °C respectively, and an abrupt decrease after crystallization (the difference in temperature comes from the difference in amorphous silicon sublayer thickness). This phenomenon is very attractive and has never been reported before. Our Raman and TEM results show that there exists a high density of p-nc-Si in our Si/SiO_2 multilayers annealed near the crystallization onset temperature, and the p-nc-Si plays an important role in abruptly increasing the PL intensity.

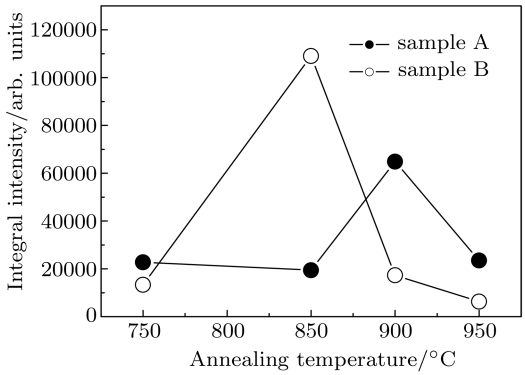


Fig.6. Integral intensity of the PL spectra. The line is a guide for eyes.

In order to further analyse the abrupt enhancement of the PL before the onset of crystallization and its abrupt decrease after crystallization, the PLs for sample A annealed, separately, at 900 °C and 950 °C are investigated (Fig.7(a)). Considering the line shape of the PL spectra, two Gaussian bands are used to fit the spectra for annealing at 900 °C and 950 °C respectively. It is found that both spectra have the same Gaussian band peak positions as shown by the dotted lines in Fig.7(a). One Gaussian band (band A) is centred at 773 nm, the other Gaussian band is centred at 863 nm (band B), indicating that the same PL mechanism occurs in sample A for annealing at 900 °C and 950 °C. For the further investigation of the PL mechanisms of band A and band B, the temperature-dependent PL for sample A annealed at 900 °C is mea-

sured at the temperatures ranging from 83 to 273 K (Fig.2). It is found that PL intensity increases with the testing temperature decreasing. The Gaussian deconvolution results show that the positions of band A and band B remain unchanged at 773 nm and 863 nm respectively when the temperature decreases from 273 to 83 K as shown in Fig.7(b). Based on the analyses of the Raman, TEM and PL results, the intense luminescence band B centred at 863 nm which emerges before the onset of crystallization and can be greatly suppressed after crystallization may be ascribed to originating from the p-nc-Si, and after sufficient crystallization at 1000 °C, band B totally disappears. The origin of band A, which emerges before the onset of crystallization and remains unchanged during the variation of temperature, is discussed latter.

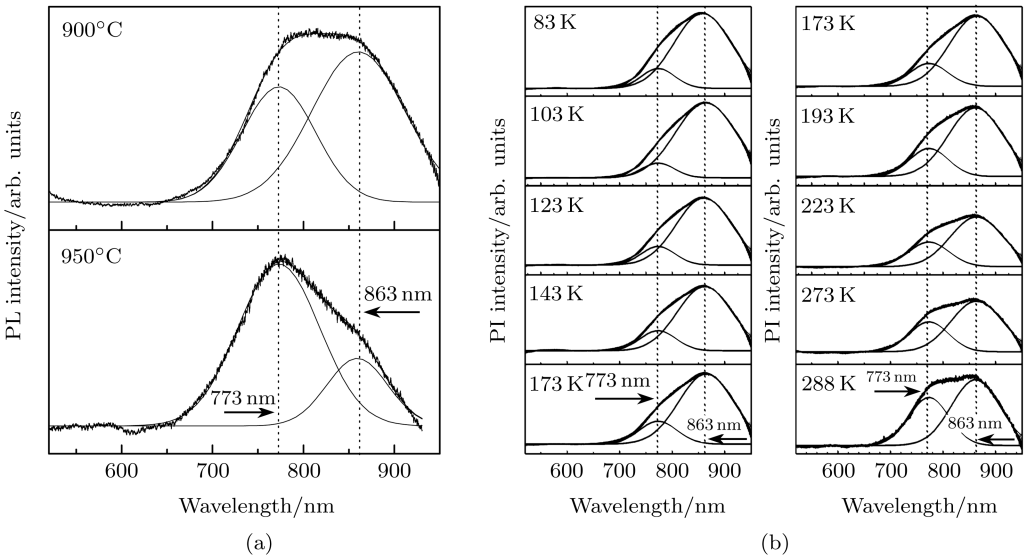


Fig.7. (a) Gaussian deconvolutions of the PL spectra of sample A near the crystallization onset temperature and after crystallization. (b) Gaussian deconvolutions of the PL spectra of sample A annealed at 900 °C for different temperatures.

It is worth noting that the luminescence character of p-nc-Si is quite different from that of nc-Si. According to Vashni's relation between band gap energy and temperature, $E = E_0 - \alpha T^2/(\beta + T)$,[17] the PL peak position should have a blue shift with the decrease of temperature in the case of nc-Si, while the PL peak position of p-nc-Si remains unchanged with respect to temperature, which indicates that the enhanced PL tends to stem from some luminescence structure defects which are abundant in p-nc-Si, and the PL from these defects is insensitive to temperature, more detailed work about the defects in p-nc-Si is in progress. In addition, in a Si/SiO_2 system, nc-Si is usually combined with Si = O, which gives rise to a band peaked around 750 nm,[13,18] and band A centred at 770 nm, which has a red shift compared with the PL of Si = O at the nc-Si surface, is attributed to originating from Si = O at the interface of the p-nc-Si, and its peak position shifts to 750 nm after annealing at 1000 °C (not shown here).

After annealing at 950 °C, the p-nc-Si in sample A partially turns into nc-Si as shown by the Raman results in Fig.3(a). It can be seen from Fig.1(a) that the PL band B corresponding to p-nc-Si decreases drastically due to the decrease in the density of p-nc-Si, and that the intensity of band A also suffers a decrease, but the intensity of the luminescence from Si = O at the surface of p-nc-Si still overwhelms that of Si = O at the nc-Si surface. After sufficient crystallization, the position of band A peak shifts to 750 nm and the Si = O at the nc-Si surface dominates, which shows a peak at 750 nm in our Si/SiO_2 multilayers.[13] As to sample B, due to the difference in amorphous silicon sublayer thickness, the PLs before and after crystallization show some difference from that of sample A, which is caused by the contributions of different luminescence centres such as NBOHCs, TDs and Si = O, and together with some non-luminescence centres such as Pbs, of which some may co-exist in some range of temperature and contribute to the PL spectrum simultaneously, which complicates the PL. But near the crystallization onset temperature, sample B shows an

enhanced PL line shape the same as that of sample A, which supports our p-nc-Si theory.

5. Conclusions

We have fabricated two series of a-Si:H/SiO_2 multilayers with different amorphous silicon sublayer thicknesses by means of PECVD. The step-by-step thermal annealing is performed on the samples. A high density of p-nc-Si which is in an intermediate state between the random amorphous silicon and the ordered nc-Si is found in the samples annealed near the crystallization onset temperature, and the enhanced PL induced by p-nc-Si is observed, and it can be soon removed by annealing after crystallization.

References

[1] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046

[2] Lu Z H, Lockwood D J and Baribeau J M 1995 *Nature* **378** 258

[3] Pavesi L, Negro L Dal, Mazzoleni C, Franzò G and Priolo F 2000 *Nature* **408** 440

[4] Park N M, Choi C J, Seong T Y and Park S J 2001 *Phys. Rev. Lett.* **86** 1355

[5] Yi L X, Heitmann J, Scholz R and Zacharias M 2002 *Appl. Phys. Lett.* **81** 4248

[6] Ma S Y, Qin G G, You L P and Wang Y Y 2001 *Chin. Phys.* **50** 1580

[7] Ji A L, Ma L B, Liu C and Wang Y Q 2004 *Acta Phys. Sin.* **53** 3818

[8] Luo X, Zhang S B and Wei S H 2002 *Phys. Rev. Lett.* **89** 76802

[9] Zhou Z, Brus L and Friesner R 2003 *Nano Lett.* **3** 163

[10] Wu X, Bek A, Bittner A M, Eggs C, Ossadnik C and Veprek S 2003 *Thin Solid Films* **425** 175

[11] Wu X C, Bittner A M, Kern K, Eggs C and Veprek S 2000 *Appl. Phys. Lett.* **77** 645

[12] Prokes S M and Glembocki O J 1994 *Phys. Rev.* B **49** 2238

[13] Mei J X, Rui Y J, Ma Z Y, Xu J, Zhu D, Yang L, Li X, Li W, Huang X F and Chen K J 2004 *Solid State Commun.* **131** 701

[14] Khriachtchev L, KilpeläO, Karirinne S, Keränen J and Lepistö T 2001 *Appl. Phys. Lett.* **78** 323

[15] Tsu D V, Chao B S, Ovshinsky S R, Guha S and Yang J 1997 *Appl. Phys. Lett.* **71** 1317

[16] Averboukh B, Huber R, Cheah K W, Shen Y R, Qin G G, Ma Z C and Zong W H 2002 *J. Appl. Phys.* **92** 3564

[17] Vivas Hernandez A, Torchynaska T V, Matsumoto Y, Jimenez Sandoval S, Dybiec M, Ostapenko S and Shcherbina L V 2005 *Microelectronics Journal* **36** 510

[18] Wolkin M V, Jorne J, Fauchet P M, Allan G and Delerue C 1999 *Phys. Rev. Lett.* **82** 197