Mechanism and enhancement of photoluminescence from silicon nanocrystals implanted in SiO_2 matrix

Wu Zhi-Yong(吴志永)†, Liu Ke-Xin(刘克新), and Ren Xiao-Tang(任晓堂)

State Key Laboratory of Nuclear Physics and Technology, Institute of Heavy Ion Physics, Peking University, Beijing 100871, *China*

(Received 4 January 2010; revised manuscript received 26 April 2010)

Photoluminescence (PL) spectra of Si nanocrystals (NCs) prepared by 130 keV Si ions implantation onto SiO_2 matrix were investigated as a function of annealing temperature and implanted ion dose. PL spectra consist of two PL peaks, originated from smaller Si NCs due to quantum confinement effect (QCE) and the interface states located at the surface of larger Si NCs. The evolution of number of dangling bonds (DBs) on Si NCs was also investigated. For hydrogen-passivated samples, a monotonic increase in PL peak intensity with the dose of implanted Si ions up to 3×10^{17} ions /cm^2 is observed. The number of DBs on individual Si NC, the interaction between DBs at the surface of neighbouring Si NCs and their effects on the efficiency of PL are discussed.

Keywords: ion implantation, nanocrystals, photoluminescence, dangling bond

PACC: 7865

1. Introduction

The discovery of photoluminescence (PL) from porous Si[1,2] has stimulated extensive research in the development of nanoscale Si material and the luminescence mechanism due to the promising applications in optoelectronic and photonic devices.[3] Si nanocrystals (NCs) were suggested as an alternative material with similar PL character to the porous Si and the advantages of stability as well as compatibility to microelectronics technology. The primal materials of Si-rich oxide matrix are prepared by different techniques.[4−7] Among these techniques, Si ion implantation can build up controllable and reproducible excess Si at selected locations in a matrix. Subsequently, thermal annealing at temperatures higher than 1000 °C induces nucleation of Si NCs due to phase separation.[8] It is clear that the presence of Si NCs causes the light emission, but the mechanism of PL in detail is still under discussion.

Quantum confinement effect (QCE) and the interface state recombination are both suggested as the main factors resulting in PL.[9−12] According to QCE, the PL peaks red shift with the increase in size of Si NCs, however, the interfacial radiative states are also considered to be related to the size of Si NCs.[13] Changing the surface structures of Si NCs seems to be feasible to reveal the mechanism of PL. As one of the methods, annealing in forming gas ambient (6% H_2 and 94% N_2) has been performed to passivate the interface states, such as the dangling bonds (DBs). The DBs act as nonradiative recombination centres[14] which reduce the efficiency of PL emission. However, with the increase in density of Si NCs in SiO_2 matrix, the DBs at the surface of neighbouring Si NCs become closer, and have influence on PL from Si NCs. This influence and its interpretation have less been addressed.

In this context, we investigate at first the annealing temperature dependence of PL behaviour for samples with lower doses of implanted Si ions. The origin of PL is discussed according to the size of Si NCs observed by transmission electron microscope (TEM). The relative enhancement of PL intensity (I_R) is used to analyse the role played by DBs on individual Si NC in PL emission process. The influence of the dose of implanted Si ions on the PL intensity is finally investigated under the optimal thermal treatment condition. The interaction between DBs at the surface of neighbouring Si NCs as an additional factor influencing the efficiency of PL is also discussed.

2. Experiment

The samples used in our experiments had a 1200 nm thick SiO_2 layer thermally grown on p-type Si (100) wafers with resistivity of 5–15 $\Omega\cdot$cm.

†Corresponding author. E-mail: zywu75@pku.edu.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

They were implanted with 130 keV Si ions at doses from 1×10^{16} ions /cm^2 to 3×10^{17} ions /cm^2 at room temperature at Institute of Semiconductor, Chinese Academy of Sciences. The expected depth profiles of the implanted Si atoms in the SiO_2 layers on the Si wafers were estimated using SRIM 2003 and found to be distributed in a nearly Gaussian profile peaked at a depth around 240 nm from the surface of SiO_2 matrix.

To investigate the influence of annealing temperature on the PL, the annealing temperatures for samples with a dose of 4×10^{16} ions/cm^2 ranged from 850 °C to 1150 °C. As for the influence of dose of implanted Si ions on PL, samples with different doses of implanted Si ions were annealed at 1050 °C. Ultrapure N_2 was used as ambient atmosphere in normal tube furnace for the thermal treatment. Some of the samples were additionally passivated with hydrogen by annealing samples in forming gas (6% H_2 and 94% N_2) at 500 °C for 1 h.

PL measurements were performed at room temperature for all annealed samples by using 514-line of an Ar^+ laser as the excitation source. The emitted light was detected with thermoelectrically-cooled charge coupled device (CCD) array. Tecnai F30 TEM was used to observe the size and distribution of Si NCs.

3. Results and discussion

3.1. Origin of PL from Si NCs

In order to investigate the origin of PL from Si NC, samples with lower dose of implanted Si ions (4×10^{16} ions /cm^2) were used to avoid the interaction between Si NCs.[6] The PL spectra of the as-annealed samples are shown in Fig. 1. The obvious increase in PL intensity when annealing temperature is higher than 950 °C indicates a critical temperature related to the formation of Si NCs due to phase separation.[8] An expected red-shift of PL peak from 710 to 780 nm with increasing annealing temperature from 1000 °C to 1150 °C is observed, presumably due to QCE. The PL intensity achieves its maximum value at 1050 °C. It suggests the optimal thermal treatment condition for this PL peak. With further increasing the annealing temperature, the increase in intensity of PL peak at about 860 nm occurs. The inset of Fig. 1 shows the deconvolution of PL spectra of sample annealed at 1150 °C. In a temperature-dependent PL investigation in Ref. [13], PL peak at about 860 nm was confirmed to originate from the interface states on Si NCs.

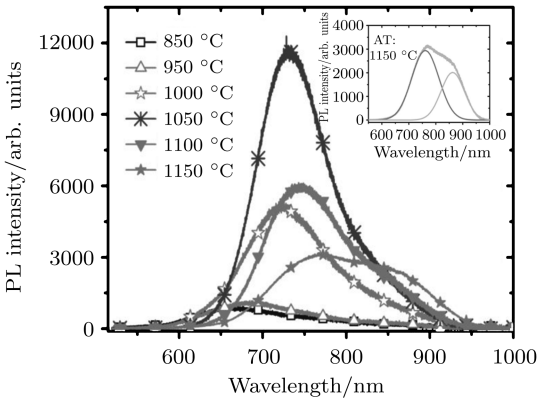


Fig. 1. PL spectra of passivated samples implanted with Si ion at 130 keV (4×10^{16} ions /cm^2) and subsequently annealed at various temperatures from 850 to 1150 °C.

TEM measurements were performed to explore the corresponding evolution of structure of Si NCs with PL spectra for the two samples above. Figure 2(a) shows the formation of Si NCs in the sample annealed at 1050 °C. It appears that nearly all the Si NCs observed are smaller than 3 nm. As for the sample annealed at 1150 °C, a distinctly broader distribution up to 5 nm of Si NCs is shown in Fig. 2(b), and the material is obviously composed of two groups of Si NCs, i.e., small Si NCs (< 3 nm) and large Si NCs (3–5 nm). The presence of double peaks in PL spectra for the same sample above assigns the larger Si NCs to the PL peak at longer wavelength. The results agree with the model proposed by Qin and Li,[11] that is, when the Si NCs are smaller, QCE dominates the PL mechanism, while the interface states dominate for larger Si NCs.

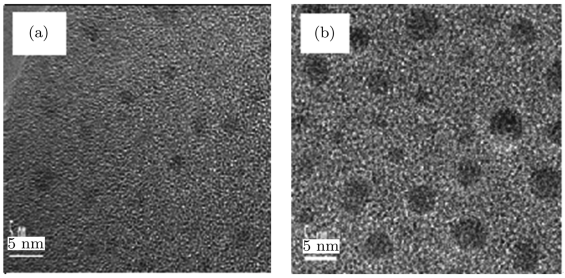


Fig. 2. TEM image of two samples implanted with Si ions at a dose of 4×10^{16} ions/cm^2 and annealed at 1050 °C (a) and 1150 °C (b). The scale bar is 5 nm.

3.2. Influence of DBs of individual Si NC on PL

Further investigation on PL behaviour is carried out by comparing the PL intensities of passivated and unpassivated samples. Figure 3 shows the relative enhancement of PL intensity ($I_{\rm R} = I_{\rm pas}/I_{\rm unpas}$) for three samples originally annealed at 1000, 1050, and 1100 °C respectively. It is well known that hydrogen merely passivates DBs without changing the size and distribution of Si NCs in SiO_2 matrix.[14] In the precondition that all the PL spectra are measured under the same conditions, $I_{\rm R}$ can reveal qualitatively the enhancement of PL efficiency of individual Si NCs. Moreover, DBs act as nonradiative recombination centres which quench the PL from Si NCs.[13] $I_{\rm R}$ indicates the number of DBs on individual Si NCs.

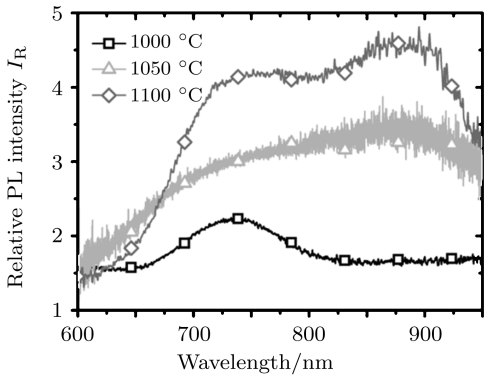


Fig. 3. The evolution of $I_{\rm R}$ with the wavelength for samples originally implanted at 4×10^{16} ions/cm^2 and then annealed at 1000, 1050, and 1100 °C.

For the samples annealed at 1000 °C, $I_{\rm R}$ changes obviously when wavelength ranges from 650 to 800 nm. The Si NCs smaller than 3 nm have been formed. In the case of annealing at 1050 °C, the $I_{\rm R}$ is larger than 3 at wavelengths from about 700 to 900 nm. This indicates a broadening size distribution of Si NCs even though the fraction of larger Si NCs is lower according to the result from TEM. The gradual increase of $I_{\rm R}$ with wavelength suggests that the number of DBs on individual Si NCs increases with the size of Si NCs. After hydrogen treatments, more DBs are passivated in larger Si NCs, leading to the expected broadening of PL on longer wavelength side for passivated samples. When the wavelength is longer than 900 nm, $I_{\rm R}$ decreases. This might result from the absence of even larger Si NCs (or too few to be detected) or the lower PL efficiency of even larger Si NCs.

Another result is that $I_{\rm R}$ increases with annealing temperature in the wavelength range from about 700 to 900 nm. Annealing at different temperatures might result in the formation of Si NCs in different equilibrium nucleation process,[15] leading to the variation of shape and internal structure of Si NCs. The surface tension of Si NCs in SiO_2 matrix then changes, which causes the change of number of DBs on a Si NC. Nevertheless, we know that PL measurements at room-temperature can induce broadening (result from phonon) of PL spectra.[16] It leads to the overlap of PL spectra of Si NCs with different sizes and adds ambiguity to $I_{\rm R}$. Therefore, further investigation on PL measured at low temperatures is needed.

3.3. Interactions between DBs on neighbouring Si NCs

The influence of the interaction between DBs on the efficiency of PL is studied. As is easily understood, such an interaction might occur in the case that the Si NCs lie close enough. Samples with various doses of implanted Si ions (from 1×10^{16} to 3×10^{17} ions /cm^2) are used. All samples are annealed at 1050 °C so as to decrease the fraction of larger Si NCs, as observed by the XTEM above. Figure 4(a) shows the PL spectra of all the passivated samples. A slight red-shift of PL peak with increasing dose of implanted Si ions is observed (guided by the dashed line). It is also in agreement with QCE, which indicates an increase in size of Si NCs with the dose of implanted Si ions. By TEM measurements, other researchers[17] have achieved the results that the size of Si NCs increases with the dose of implanted Si ions. However, in our work, nearly all Si NCs are smaller than 3 nm. It is quite difficult to detect the small difference of size due to the nominal resolution of our system.

In order to clarify the origin of enhancement in PL peak intensity, the values of PL peak intensity for all the samples are shown in Fig. 4(b). The dashed line shows the increase of PL peak intensity with the dose of implanted Si ions, presuming that the average size of Si NCs is the same as that of Si NCs in the sample with lowest density of Si NCs in our system (1×10^{16} ions/cm^2), and neglecting the influence of the interaction from DBs. The actual PL peak intensity for passivated samples is lower than the corresponding value of the dashed line due to the reduction of PL absorption cross-section caused by enlargement of Si NCs.[17]

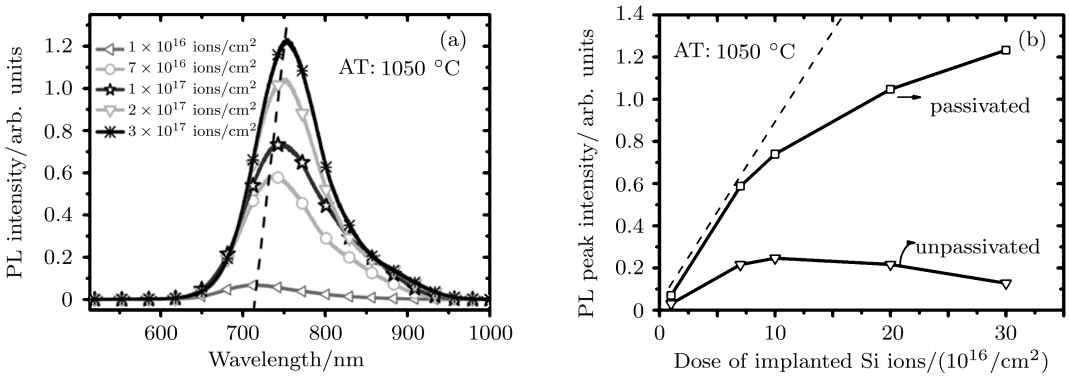


Fig. 4. (a) PL spectra of passivated samples implanted with doses from 1×10^{16} to 3×10^{17} ions/cm^2 and subsequently annealed at 1050 °C for 2 h; (b) the corresponding evolution of PL peak intensity for unpassivated and passivated samples.

As for the unpassivated samples, the maximum PL peak intensity achieves at the dose 1×10^{17} ions/cm^2. It is qualitatively consistent with the 'reactive nano-cluster model' by Iwayama and Kurumade,[6] which can explain the optimal dose for PL intensity. In this model, cluster–cluster interactions via a thin oxide interface are considered to be the essential factor in the luminescence process for the super-saturation of Si in SiO_2 matrix above 10%.

However, in the case of the passivation, a monotonic increase in PL peak intensity is observed as the dose of implanted Si ions increases (up to 3×10^{17} ions /cm^2). It indicates that H_2 passivation has more influence on samples implanted at higher dose of Si ions. We know that three major factors[6] affect the PL intensity of samples implauted with higher doses, namely, (i) the density of Si NCs, (ii) the average size of Si NCs, and (iii) the interaction between Si NCs. According to Ref. [6], interactions between Si NCs are also related to the density of Si NCs. Since hydrogen treatment hardly changes the size and distribution of Si NCs,[14] an additional factor that contributes to the monotonic increase in PL peak intensity is suggested. Hydrogen passivation might affect the interaction between DBs at the surface of neighbouring Si NC, and further enhances the PL intensity, especially for samples with higher dose of implanted Si ions.

4. Conclusions

Our investigation on the dependence of PL spectra behaviour and structure characters of Si NCs on the thermal annealing treatment reveals that smaller Si NCs result in a PL peak which red shifts with annealing temperature, and larger Si NCs are assigned to the PL peak at longer wavelength. The results are in agreement with the theoretical model proposed by Qin and Li.[11] With increasing size of Si NC, the number of DBs on it increases. The influence of dose of implanted Si ions on PL indicates that DBs play two roles in PL emission process: (i) DBs act as nonradiative recombination centres which reduce PL efficiency. (ii) The interaction between DBs on neighbouring Si NCs plays an additional role in PL emission process, especially for as-annealed samples implanted with a higher dose of Si ions.

Acknowledgments

The authors would like to express their sincere thanks to Xu Jia-Dong for his help in ion implantation and Dr. Wang Peng-Wei and Dr. Liu Cui for their kind help in PL measurements. Special thanks to Prof. Wang Yu-Gang for his helpful suggestions. The XTEM experiment was performed in Institute of Condensed Matter and Material Physics in Peking University, and Mrs. Zhang Xiao-Ping is also gratefully acknowledged.

References

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

[2] Lehmann V and Gösele U 1991 *Appl. Phys. Lett.* **58** 856

[3] Irrera A, Franzo G, Iacona F, Canino A, Stefano G Di, Sanfilippo D, Piana A, Fallica P G and Priolo F 2007

Physica E **38** 181

[4] Dal Negro L, Cazzanelli M, Daldosso N, Gaburro Z, Pavesi L, Priolo F, Pacifici D, Franzo G and Iacona F 2003 *Physica* E **16** 297

[5] Beaumont A and Souifi A 2009 *Solid-State Electron.* **53** 42

[6] Iwayama T S and Kurumado N 1998 *J. Appl. Phys.* **83** 11

[7] Tong S, Liu X N, Wang L C, Yan F and Bao X M 1997 *Acta Phys. Sin.* **46** 1217 (in Chinese)

[8] Gautam D, Koyanag E and Uchino T 2009 *J. Appl. Phys.* **105** 073517

[9] Ding L, Chen T P, Liu Y, Yang M and Wong J I 2007 *J. Appl. Phys.* **101** 103525

[10] Wolkin M V, Jorne J, Fauchet P M, Allan G and Delerue C 1999 *Phys. Rev. Lett.* **82** 1

[11] Qin G G and Li Y J 2003 *Phys. Rev.* B **68** 085309

[12] Eleonora L, Federico I, Rita M, Olivia P, Stefano O, Elena D and Valerio O 2007 *Phys. Rev.* B **75** 033303

[13] Wang X X, Zhang J G, Ding L, Cheng B W, Ge W K, Yu J Z and Wang Q M 2005 *Phys. Rev.* B **72** 195313

[14] Jung Y J and Yoon J H 2008 *J. Korean Phys. Soc.* **53** 5

[15] Rizza G C, Strobel M, Heinig K H and Bernas H 2001 *Nucl. Instr. and Meth.* B **178** 78

[16] Sychugov I, Juhasz R, Valenta J and Linnros J 2005 *Phys. Rev. Lett.* **94** 087405

[17] Garrido B, Lopez M, Gonzalez O, Perez-Rodríguez A, Morante J R and Bonafos C 2000 *Appl. Phys. Lett.* **77** 3143