Relative enhancement of photoluminescence intensity of passivated silicon nanocrystals in silicon dioxide matrix*

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Photoluminescence (PL) intensity of passivated silicon nanocrystals (Si NCs) embeded in an SiO_2 matrix is compared with that of unpassivated ones. We investigate the relative enhancement of PL intensity (I_R) as a function of annealing temperature and implanted Si ion dose. The I_R increases simultaneously with the annealing temperature. This demonstrates an increase in the number of dangling bonds (DBs) with the degree of Si crystallization via varying the annealing temperature. The increase in I_R with implanted Si ion dose is also observed. We believe that the near-field interaction between DBs and neighboring Si NCs is an additional factor that reduces the PL efficiency of unpassivated Si NCs.

Keywords: ion implantation, nanocrystals, photoluminescence, dangling bond

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1. Introduction

The discovery of photoluminescence (PL) from porous Si[1,2] has stimulated extensive research in the development of the nanoscale Si material and into the luminescence mechanism due to the promising applications in the optoelectronic and photonic devices.[3,4] Si nanocrystals (NCs) have been suggested to be an alternative material with similar PL characteristics to achieve the porous Si, and the advantages of stability and compatibility for microelectronics technology. The primal materials of Si-rich oxide matrix are prepared by different techniques.[5−7] Among these techniques, Si ion implantation can build up controllable and reproducible excess Si at selected locations in a matrix. Subsequently, thermal treatments at temperatures higher than 1000 °C induce the nucleation of Si NCs due to phase separation.[8]

The recent consensus on the luminescence mechanism is that both the quantum confinement effect (QCE)[9] and the interface state recombination[10] play important roles. However, the details are still controversial. In Ref. [11], it is considered that the QCE dominates NCs with larger sizes, while for NCs with smaller sizes the interface state effect plays a key role. Contrarily, Qin and Li[12] demonstrated that there is a critical NC size, below which the quantum confinement effect dominates, and above which the interface state effect prevails. It is difficult to disentangle the effects of such competing optoelectronic phenomena due to the substantial size inhomogeneity of these materials. In addition, much work on enhancing PL efficiency has been carried out.[13−15] The optimally implanted Si ion dose for PL intensity of as-annealed SiO_2 matrix was achieved, and the interaction between neighboring Si NCs was attributed to the decrease in PL intensity for samples with high Si ion dose.[16] Actually, many factors affect the PL process, such as defects, degree of Si crystalliztion, phonons, dangling bonds (DBs), etc. Especially, DBs were determined as nonradiative centers which quench PL,[17] but the role of DBs in the PL process has seldom been investigated in detail. In our previous work,[18] the PL intensity ratio (I_R) of passivated and unpassivated Si NCs which suggests the number of DBs on individual unpassivated Si NC was introduced to study the roles of DBs in the PL process. However, the investigation neglected the influence of the temperature-induced PL spectrum overlapping on I_R.

In this paper, we have studied primarily the de-

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pendence of I_R on environmental temperature. Based on the PL measurements at 10 K, the I_R is investigated as a function of the annealing temperature and the dose of implanted Si ions. Based on the TEM results, we discuss the roles that DBs play in the PL process.

2. Experimental setup

The samples used in our experiments have a 1200-nm SiO_2 layer thermally grown on p-type Si (100) wafers with the resistivity of 5–15 Ω·cm. They were implanted with 130-keV Si ions at dose from 4×10^{16} to 3×10^{17} cm^{-2} at room temperature. The expected depth profiles of the implanted Si atoms in the SiO_2 layers on the Si wafers were estimated by SRIM 2003 and found a nearly Gaussian profile distribution peak at a depth of around 240 nm from the surface of SiO_2 matrix.

To investigate the influence of enviremental temperature and annealing temperature on I_R, we used the samples with low ion dose (4×10^{16} cm^{-2}). Under this condition, the speculated interactions between neighboring Si NCs[16] can be ignored. The samples were annealed at temperature ranging from 1000 to 1100 °C. As for the investigation of the influence of implanted Si ions dose, samples at ion doses from 4×10^{16} to 3×10^{17} cm^{-2} were pre-annealed at 1050 °C for two hours.

The annealing treatments were performed with tube furnace under N_2 atmosphere. Some of the samples were additionally passivated in forming gas (6% H_2 and 94% N_2). The PL measurements for most of the samples were performed at low temperature using 514-line of an Ar+ laser as the excitation source. The light emission was detected by thermoelectrically-cooled CCD array. Tecnai F30 TEM was used to detect the size and distribution of Si NCs.

3. Results and discussion

3.1. Influence of environmental temperature on I_R

In this section, the influence of environmental temperature on I_R is studied. The PL measurements were performed respectively at room temperature and 10 K. The I_R was obtained by comparing the PL intensity for passivated sample with that for the corresponding unpassivated one.

The meaning of I_R should be emphasized at first. Since hydrogen passivating merely eliminates DBs without changing the Si NCs,[17] the I_R is related to the PL spectrum overlapping of Si NCs with different sizes, the size distribution of Si NCs, and the number of DBs. However, the PL spectrum overlapping of Si NCs with different sizes can expectably be ignored since the width of PL spectrum of individual Si NC is far smaller than the wavelength scale concerned, especially when measured at low temperature.[19] As for the size distribution of Si NCs, it keeps roughly unchanged for samples at same does when annealed under the same enviremental condition. Its effect is also excluded from I_R. Consequently, the I_R corresponds to the number of DBs on individual Si NC.

Figure 1 shows the I_R measured at 10 K and room temperature, respectively. Three main results are obtained. First, the I_R at room temperature increases slowly in a wavelength scale of about 100 nm in the short-wavelength end, while the I_R at 10 K shows a steep change in a narrower scale (20 nm). Such discrpency in I_R reveals the effect of PL spectrum overlapping on I_R. The width of PL spectrum increases with the enviremental temperature due to the influence of phonons. Then, the experimental value of I_R involves the contribution of Si NCs with different sizes, especially when measured at room temperature. It is clear that I_R at 10 K represents more accurately the number of DBs on individual unpassivated Si NC than it does at room temperature.

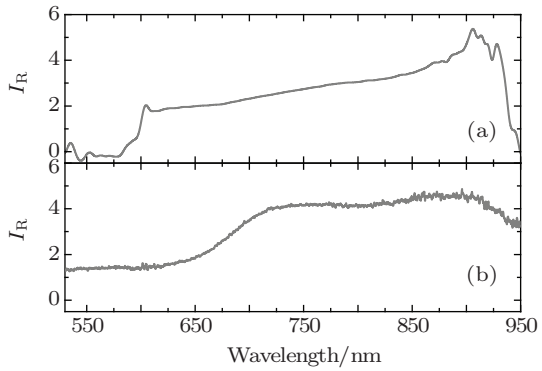


Fig. 1. PL intensity ratio (I_R) of passivated and unpassivated Si NCs for samples originally implanted at 4×10^{16} cm^{-2} and then annealed at 1050 °C. The I_R is measured at (a) 10 K and (b) room temperature. The lines are smoothed.

The second result is that I_R at 10 K shows a linear increase in the wavelength range from 600 to 930 nm. Since the band gap of Si NC decreases inversely with its size (according to the theory of QCE), the wavelength of excited photon is consistent with the size

of Si NCs. It was testified by the size-induced redshift of PL peak for Si NCs.[11] The I_R then indicates the existence of Si NCs in the given wavelength scale. Therefore, the linear increase of I_R demonstrates that the number of DBs increases with the size of unpassivated Si NC.

The last result is about the I_R at both sides of wavelength. The value of I_R almost keeps constant at wavelength smaller than 600 nm where Si clusters (< 1 nm) are amorphous. Point defects or other similar structures dominate the PL process.[20] The variation of I_R does not reveal the correlation between DBs and Si NCs. Likewise, the steep change in I_R at wavelength above 930 nm can also be explained by the absence of such correlation. When the size of Si NC reaches a critical value, the energy of photon is too small to be absorbed by DBs. Consequently, the influence of DBs on I_R is excluded, even though DBs exist on the surface of Si NCs. In short, the steep change in I_R here confirms that the DB-related PL spectra range from about 600 to 930 nm.

3.2. Influence of annealing temperature on I_R

Now, we focus on the dependence of I_R on annealing temperature. The values of I_R at 10 K for samples annealed at 1000, 1050, and 1100 °C were obtained, respectively, as shown in Fig. 2. For samples annealed at 1000 °C, the I_R varies obviously in a wavelength range from about 600 to 780 nm. This demonstrates the occurrence of small Si NCs according to the above discussion. Contrastively, the corresponding scale of wavelength increases up to 900 nm for samples annealed at 1050 °C. It can be explained by the occurrence of larger Si NCs, even though the fractoin of such large Si NCs is small according to the TEM images shown in Fig. 3(a). As for samples annealed at 1100 °C, the evolution tendency of I_R is similar to that for samples annealed at 1050 °C. However, as shown in Fig. 2, the I_R increases with the annealing temperature. As is well known, different annealing temperature gives rise to the formation of Si NCs in different equilibrium nucleation processes.[9] The degree of crystallization can contribute to such an increase in I_R. That is, increasing the annealing temperature changes the degree of crystallization, leading to an increase in the number of DBs on individual unpassivated Si NC.

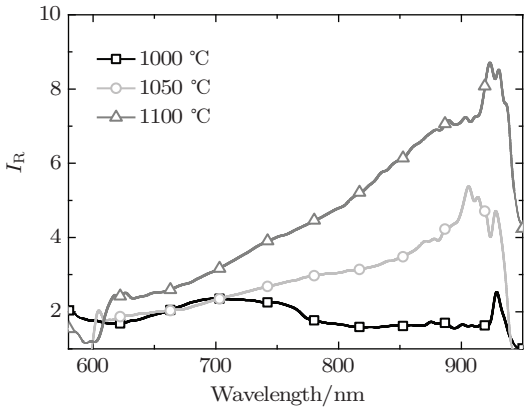


Fig. 2. PL intensity ratio of passivated and unpassivated Si NCs for samples originally implanted at 4×10^{16} cm^{-2} and then annealed at 1000, 1050, and 1100 °C, respectively. The I_R is measured at 10 K and the lines are smoothed.

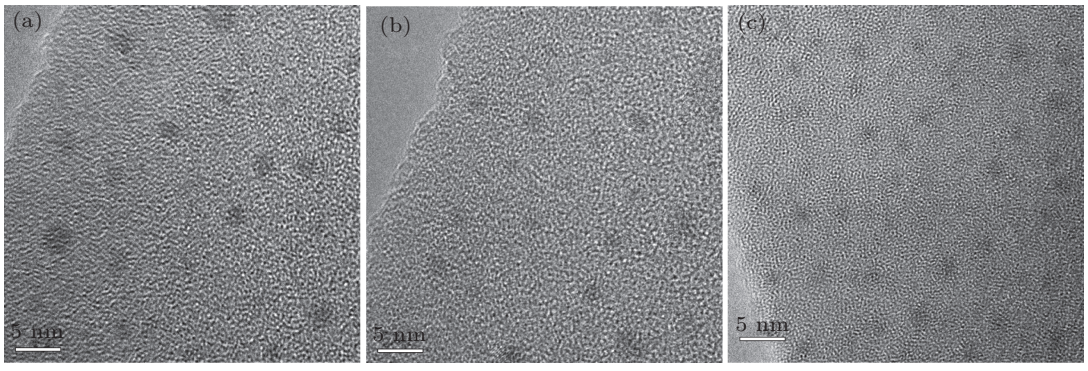


Fig. 3. TEM images of samples with dose of (a) 4×10^{16}, (b) 10^{17}, and (c) 3×10^{17} cm^{-2}, respectively. All the samples were originally annealed at 1050 °C.

3.3. Influence of implanted Si ions dose on I_R

The influence of implanted Si ions dose on I_R is investigated in this section. Samples with different doses were primarily annealed at 1050 °C to keep a narrow size distribution of Si NCs. TEM meauresments were performed to detect the evolution of Si NCs' size. From the TEM images shown in Fig. 3, we conclude that nearly all the formed Si NCs are smaller than about 3 nm. Therefore, it suggests that the distance of neighboring Si NCs decreases roughly due to the dose-induced increase in the Si NCs density.

Before investigatng I_R, we study the PL spectra at 10 K for passivated samples. Figure 4(a) shows that the PL peak red shifts slightly as the implanted Si ion dose increases. This can be attributed to the undetectable increase in the average size of Si NCs in our current work. Additionally, the PL peak intensity increases simultaneously with ion dose up to 3×10^{17} cm^{-2}. As is well known, hydrogen treatments do not change the distance between neighboring Si NCs. Such increase in the PL peak intensity then excludes the factor of the cluster–cluster interactions which is related directly to the distance between neighboring Si NCs. Therefore, the existence of DBs on unpassivated Si NCs should be taken into account.

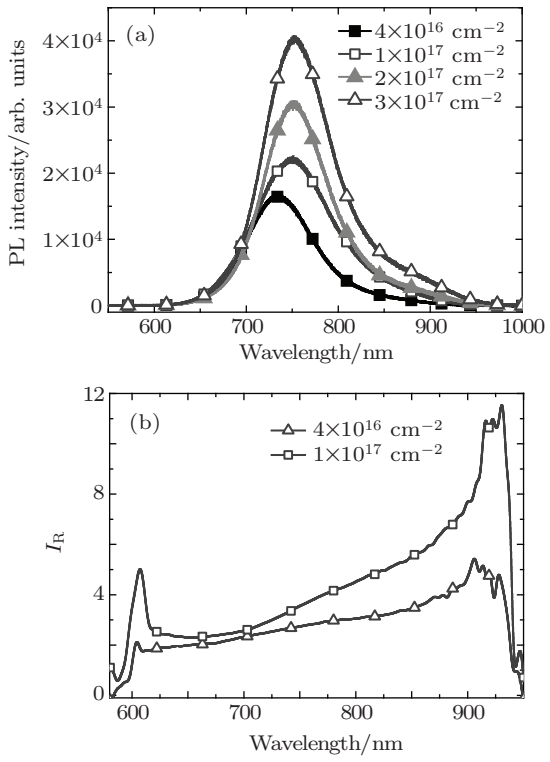


Fig. 4. (a) Low-temperature (10 K) PL spectra of passivated samples at different doses of implanted Si ions; (b) the corresponding I_R for samples at 4×10^{16} and 1×10^{17} cm^{-2}, respectively. All the samples were originally annealed at 1050 °C.

Next, we measured experimentally the I_R of samples at 4×10^{16} and 1×10^{17} cm^{-2}, respectively. The results were shown in Fig. 4(b). Noting that all the samples were annealed under the same temperature condition, we can expect the similar Si crystalization process and surface tension of Si NCs with the same size. This results in the nearly uniform number of DBs on the same size Si NCs, leading to the roughly fixed I_R. However, as shown in Fig. 4(b), the I_R increases with the implanted dose of Si ions, especially in the long-wavelength limit. The decrease in the distance between separated Si NCs obviously results in such an additional increase in I_R. We believe that the near-field interaction between DBs and neighboring Si NCs affects the PL process when the Si NCs are close enough. As a result, the DBs absorb the PL energy from neighboring Si NCs. This leads to a further decrease in the PL efficiency of unpassivated Si NCs, and offers potential pathways to further enhancing PL intensity via hydrogen-passivating closely-packed Si NCs in such materials.

4. Conclusions

According to the temperature-induced shrink in the width of PL spectra, we demonstrate that I_R at low temperature represents more accurately the number of DBs on individual unpassivated Si NC than it does at room temperature. The steep change in I_R also determines the range of DB-related PL spectra of unpassivated Si NCs. As the annealing temperature changes, the degree of Si crystallization changes and affects the number of DBs. We consider the near-field interaction between DBs and neighboring Si NCs as an additional factor in the PL process. This offers potential pathways to further enhancing PL intensity via hydrogen-passivating closely-packed Si NCs in such materials.

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