

인의 도핑으로 인한 실리콘산화물 속 실리콘나노입자의 광-발광현상 증진 및 억제

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Enhancement and Quenching Effects of Photoluminescence in Si Nanocrystals Embedded in Silicon Dioxide by Phosphorus Doping

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요 약

지난 10년 동안 유전체 내부에 형성된 나노미터 크기의 규소알갱이는 발광센터로서 주목 받아왔다. 나노미터 크기 인 결정질 규소의 엑시토닉 전자-홀의 쌍들이 발광결합에 기여한다고 여겨진다. 그러나 규소결정에 존재하는 여러가지 결함들은 비발광 천이의 경로가 되어 나노규소결정립의 발광천이와 경쟁하여 발광효율을 저하시키는 요인이 된다. 이러한 결정결합들은 고온 열처리과정에서 대부분 소멸되나 1000 °C 이상의 공정에서도 나노규소와 유전체의 계면에 존재하는 결함들은 나노규소결정립의 발광을 억제하게 된다. 일반적으로 수소로서 규소결정립의 계면을 마감처리하게 되면 규소결정립의 발광효율이 획기적으로 향상되나 불행하게도 매질 내 수소의 높은 이동성으로 말미암아 후속 열처리 과정에서 수소마감효과는 쉽게 손실된다. 따라서 본 연구에서는 온도가역적인 수소 대신 인을 이온주입 방법으로 첨가하여 수소와 같은 계면 마감효과를 얻으며 또한 후속 고온공정에 대한 내구력을 증대시켰다. 모재인 산화규소 기판에 400 keV, 1×10^{17} Si/cm²와 그 주위에 균일한 함량을 도핑하기 위하여 다중에너지의 인을 주입하였다. 규소와 인을 이온주입 후 Ar 분위기에서 1100 °C, 두 시간의 후열처리를 통하여 규소결정립을 형성하였으며 향상된 내열효과를 시험하기 위하여 Ar 분위기에서 1000 °C 까지 열처리하였다. 인으로 마감된 나노미터 크기인 규소 결정립의 향상된 광-발광(PL) 효과와 감쇄시간, 그리고 발광파장의 변화에 대하여 논의하였다.

주제어 : 규소나노결정립, 인도핑, 이온주입, 광-발광

Abstract

Nanometric crystalline silicon (nc-Si) embedded in dielectric medium has been paid attention as an efficient light emitting center for more than a decade. In nc-Si, excitonic electron-hole pairs are considered to attribute to radiative recombination. However the surface defects surrounding nc-Si is one of non-radiative decay paths competing with the radiative band edge transition, ultimately which makes the emission efficiency of nc-Si very poor. In order to passivate those defects - dangling bonds in the Si:SiO₂ interface, hydrogen is usually utilized. The luminescence

yield from nc-Si is dramatically enhanced by defect termination. However due to relatively high mobility of hydrogen in a matrix, hydrogen-terminated nc-Si may no longer sustain the enhancement effect on subsequent thermal processes. Therefore instead of easily reversible hydrogen, phosphorus was introduced by ion implantation, expecting to have the same enhancement effect and to be more resistive against succeeding thermal treatments. Samples were prepared by 400 keV Si implantation with doses of 1×10^{17} Si/cm² and by multi-energy phosphorus implantation to make relatively uniform phosphorus concentration in the region where implanted Si ions are distributed. Crystalline silicon was precipitated by annealing at 1,100°C for 2 hours in Ar environment and subsequent annealing were performed for an hour in Ar at a few temperature stages up to 1,000°C to show improved thermal resistance. Experimental data such as enhancement effect of PL yield, decay time, peak shift for the phosphorus implanted nc-Si are shown, and the possible mechanisms are discussed as well.

Key Words : Nanometric crystalline silicon; Phosphorous doping; Ion Implantation; Photoluminescence

1. INTRODUCTION

Since early 90s, nanometric crystalline silicon has been paid attention by researchers as a silicon-based light emitting material [1]. As the size of crystalline Si is small compared to its exciton Bohr radius, 4.9 nm, bulk crystal Si of indirect band gap shows quasi-direct property and larger band gap energy [2,3] simultaneously. Although the luminescence efficiency of nc-Si is higher than that of bulk c-Si, it is much poorer when compared with usual opto-electronic materials like GaAs *etc.* The luminescence mechanism from nc-Si is still under debate. The emission efficiency of photoluminescence has been improved through the defect passivation by hydrogen. However, because hydrogen is thermally unstable in substrate, the intensity enhancement of photoluminescence is reversible even by relatively low temperature treatment, e.g., 400°C [4]. Adding phosphorus in dielectric medium with nc-Si definitely has a PL enhancement effect, but quenches PL intensity as well. In this study, we will show both the intensity enhancement and quenching effect of PL intensity as a function of phosphorus concentration, which are explained as a defect passivation and Auger recombination induced by phosphorus respectively.

2. EXPERIMENTAL

Samples were fabricated by ion implantation using a 1.7 MV tandem Pelletron at Korea Institute of Geoscience and Mineral Resources (KIGAM). Because the beam transport efficiency is poor at a low terminal voltage for the tandem machine, we compromised Si ion energy as low as 400 keV in order to get practical amount of beam current. The range of Si ion in silica (amorphous silicon dioxide, a-SiO₂) is approximately 670 nm and its FWHM is approximately 200 nm at this energy.

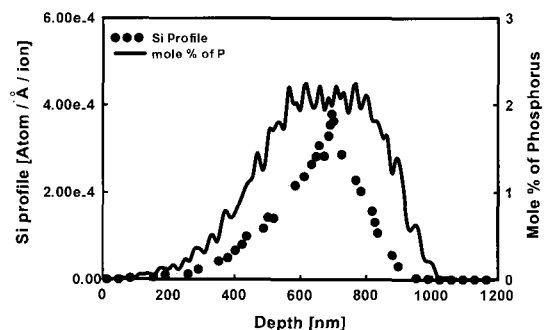


Figure 1. Profiles of Si (solid circle) and P (solid line). Silicon is implanted with 400 keV and 1×10^{17} /cm². Phosphorus is implanted by 350 keV, 0.75×10^{16} /cm² and 500 keV, 1.65×10^{17} /cm² yielding 2 mole % of uniform P concentration.

Silica substrates were implanted by multi-step ion energies with varying doses to make uniform phosphorus concentration from zero up to 2.4 mole %. Using the calculated result by SRIM-2000, 350 keV and 500 keV phosphorus ions were serially implanted with dose ratio of 1:2.2 after Si implantation as shown in Fig. 1. Implanted Si profile was inspected by RBS [7], and the formation of embedded nc-Si was confirmed by HR-TEM after 2 hour thermal annealing at 1100°C in Ar environment.

Improved thermal resistance against sequential processes is confirmed by PL after treating one of the phosphorus passivated sample at temperatures up to 1000°C for an hour in Ar. The PL spectra are produced by 488 nm Ar⁺ laser at a power of 200 mW. Visible spectra are measured by using a monochromator and GaAs PM tube as a detector. Detection efficiency is calibrated by tungsten lamp, considered as a virtual blackbody emitter within a range of interest. A mechanical rotating chopper of 200 Hz is used in the PL system to measure the decay time.

3. RESULT AND DISCUSSION

The distribution of implanted Si in silica is investigated by Rutherford backscattering spectrometry [7]. Measured range, R_p , is approximately 600 nm with a FWHM of 250 nm. These values can be compared with those predicted by SRIM-2000, but the range shortening is probably due to the charge buildup on sample surface during ion irradiation [5]. Because crystalline Si could not be observed by TEM for the sample of 1×10^{17} Si/cm² dose, we made TEM samples with doses of 2×10^{17} Si/cm² and 4×10^{17} Si/cm² respectively in order to observe crystalline size. The average size of nc-Si are 3.1 ± 0.7 nm and 5.2 ± 1.9 nm for these samples [7]. From this result, we can conjecture that the size of crystalline Si with a dose of

1×10^{17} Si/cm² would be less than 3 nm. XRD could be regarded as an alternative method for the size determination for smaller crystalline particles that can not be observed by TEM, however the well known Scherrer equation [6] predicts almost 4° wide Si (111) Bragg peak on the large scattering signals from a-Si with Cu K α . Therefore XRD is also found to be inappropriate as a method of size determination for the Si crystalline of a few nm.

The motivations of this experiment are to show the enhancement of PL intensity when phosphorus is doped in silica and to confirm the improved thermal resistance against sequential annealing that is to maintain enhanced light emission efficiency at certain phosphorous content. As reported by previous researchers [8-14], PL intensity is definitely enhanced at first and is diminished as well at a higher phosphorus concentration as shown in Fig. 2.

Luminescence spectra from these samples cover the emitting wavelengths from 700 nm to 1,000 nm. Peak positions of maximum intensity are about 830 nm and the corresponding crystalline size is approximately 4 nm by quantum confinement theory [15]. Such a crystalline size is somewhat larger than the size estimated by TEM. The effectiveness of intensity enhancement for a longer wavelength can be explained by the defect

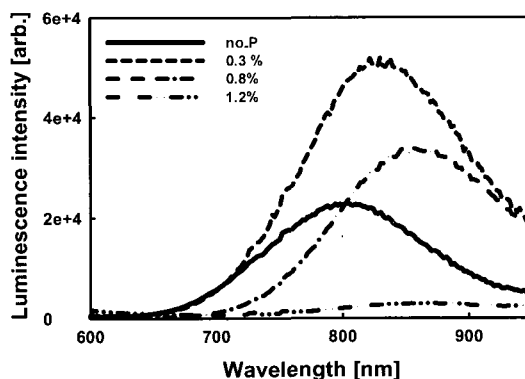


Figure 2. Photoluminescence spectra from nc-Si buried in P implanted silica substrate.

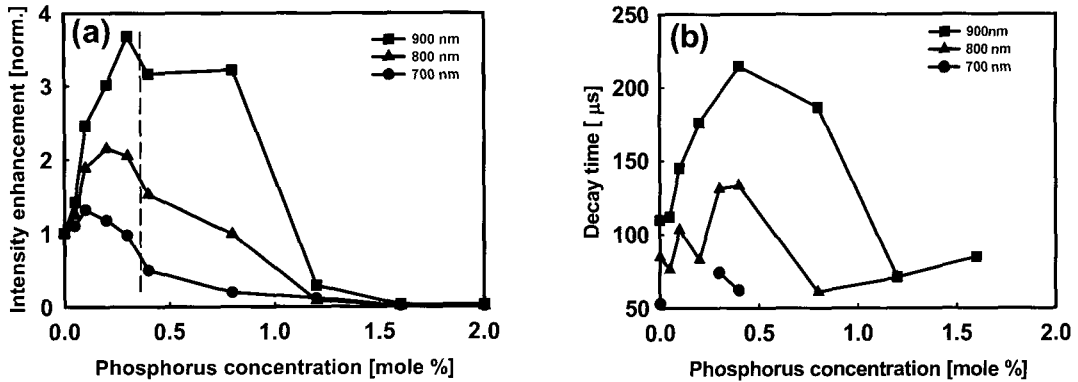


Figure 3. Intensity enhancement and decay time variation according to phosphorus concentration in silica substrate. (a) PL intensities are normalized by the no-phosphorus sample for each wavelength. Heavily phosphorus doing sample set (right side of vertical dashed line) was fabricated a month in advance (b) PL spectra are fitted using single exponential decay scheme, $I(t) = I_0 e^{-t/\tau}$.

passivation on the Si:SiO₂ interface. Among the defects which induce non-radiative recombination, P_b center is known as the only defect that survives under high temperature thermal annealing [16, 17] of 2 hours, 1,100°C in this work. Because defect density on the surface is proportional to the crystalline surface area, *i.e.* square of particle dimension, surface passivation might be more effective for large nc-Sis. Therefore intensity enhancement at longer wavelength can be easily anticipated shown in Fig. 3(a).

The PL intensity is no longer enhanced and rather quenched above at certain phosphorus concentration. It is attributed to Auger recombination which is one of non-radiative recombination paths when exciton electron-hole pair coexists with an excess charge [18]. While P_b center originated by dangling bond could be directly confirmed [14] by utilizing electron paramagnetic resonance (EPR), we have not an appropriate method to investigate Auger recombination except measuring its relatively short decay time [18]. The recombination rate of each non-radiative decay scheme mediated by neutral silicon dangling bond or Auger recombination is known at least 3 orders magnitude faster than that of radiative band edge

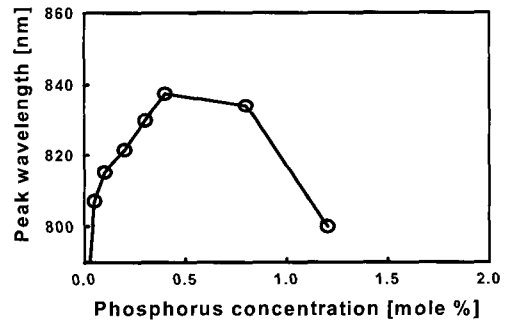


Figure 4. At low phosphorus concentration PL peak shows obviously red shift and then returns back toward short wavelength as doping level increases.

transition [18].

By fitting the PL decay spectra with a single-parameter exponential function, we got different characteristic decay times [Fig. 3 (b)] as a function of phosphorus concentration. Though we succeeded to measure the decay time variation that shows almost the same trend as that of intensity enhancement depending on P concentration, but we have failed to observe the evidences by EPR or low temperature PL in near IR region [14] which is known as the alternative method to measure the intensity of surface dangling bond. As shown in Fig. 4, both the intensity enhance-

ment and quenching effects are begun with the large size nc-Si corresponding to the long wavelength, *i.e.* peak position goes longer wavelength as PL intensity enhances and peak position comes back again as intensity quenching starts by Auger reaction.

Because samples are thermally treated at 1,100 °C to precipitate Si crystalline, it is reasonable to expect that those samples are highly resistive to succeeding thermal treatment at the temperature lower than the final treatment. One of the samples that exhibit maximum PL intensity enhancement, *i.e.* 0.3 mole % P, was underwent thermal treatment at several different temperatures in an inert gas for an hour. Unlike passivation using hydrogen, these samples preserve PL enhancement effect up to 1000°C as shown in Fig. 5.

4. CONCLUSION

By phosphorus implantation into the nc-Si embedded dielectric medium, PL intensity is enhanced due to defect passivation of especially

crystalline surface dangling bond, and quenched through activation of Auger process [10] by the phosphorus addition that works as an electron donor inside nc-Si. Assuming the non-radiative dangling bond is passivated by phosphorus in the Si:SiO₂ interface, initial red shift of emission spectra can be explained as follows. Because the number of surface defects is proportional to the crystalline size, enhancement might be effective for dangling bonds. With the same conjecture, Auger recombination would be anticipated to quench luminescence yield from the longer wavelength, *i.e.* from the large size nc-Si. Though we didn't find out a direct evidence to explain those phenomena, decay time variation can be a clue for the further investigation. In case of phosphorus doping, there is an optimum concentration of intensity enhancement before quenching overwhelms radiative recombination.

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REFERENCES

- [1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
- [2] C. Delerue, M. Lannoo, G. Allen, and E. Martin, Thin Solid Films **255**, 34 (1995).
- [3] M. V. Wolkin, J. Jorne, P.M. Fauchet, G. Allen, and C. Delerue, Phys. Rev. Lett. **82**, 197 (1998).
- [4] S. P. Withrow, C. W. White, A. Meldrum, J. D. Budai, D. M. Hembree, Jr. and J.C. Barbour, J. Appl. Phys. **86**, 396 (1999).
- [5] Joonkon Kim, W. Hong, H. J. Woo, and C. H. Eum, J. Korean Phys. Soc. **43**, 582 (2003).
- [6] A. Turkovič, M. Ivanda, S. Popovič, A.

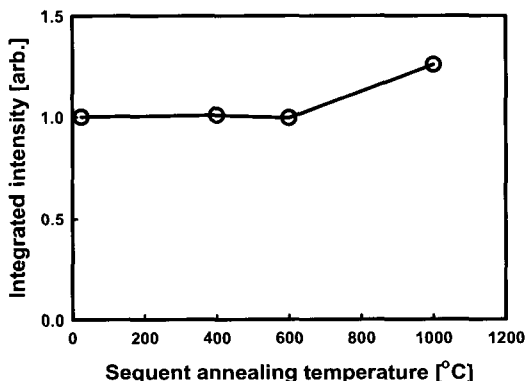


Figure 5. PL yield as a function of sequent anneal temperature by phosphorus passivated nc-Si precipitated in silica in Ar. Unlike hydrogen, improved PL efficiency by phosphorus passivation is kept up to temperature of 1000°C. Intensities are normalized by the RT sample that means no annealing.

- Tonecjc, M. Gotič, P. Dubček, and S. Musič, *J. Mole. Struct.* **410-411**, 271 (1997).
- [7] H. W. Choi, H. J. Woo, J. K. Kim, G. D. Kim, W. Hong, and Y. Y. Ji, *Bull. Korean Chem. Soc.* **25**, 525 (2004).
- [8] D. I. Teitelbaum, S. A. Trushin, V. A. Burdov, A. I. Golovanov, D. G. Revin, and D. M. Gaponova, *Nucl. Instr. and Meth. B* **174**, 123 (2001).
- [9] D. I. Teitelbaum, S. A. Trushin, A. N. Mikhaylov, V. K. Vasil'ev, G. A. Kachurin, S. G. Yanovskaya, and D. M. Gaponova, *Physica E* **16**, 410 (2003).
- [10] A. Mimura, M. Fujii, S. Hayashi, D. Kovaliev, and F. Koch, *Phys. Rev. B* **62**, 12625 (2001).
- [11] M. Fujii, A. Mimura, S. Hayashi, and K. Yamamoto, *Appl. Phys. Lett.* **75**, 184 (1999).
- [12] A. Mimura, M. Fujii, S. Hayashi, and K. Yamamoto, *Solid State Commun.* **109**, 561 (1999).
- [13] M. Fujii, A. Mimura, S. Hayashi, and K. Yamamoto, *J. of Luminescence* **87/89**, 429 (2000).
- [14] M. Fujii, A. Mimura, S. Hayashi, K. Yamamoto, C. Urakawa, and H. Ohta, *J. Appl. Phys.* **87**, 1855 (2000).
- [15] Y. Kanzawa, T. Kageyama, S. Takeoka, M. Fujii, S. Hayashi, and K. Yamamoto, *Solid State Commun.* **102**, 533 (1997).
- [16] S. Guha, M. D. Pace, D. N. Dunn, and I. L. Singer, *Appl. Phys. Lett.* **70**, 1207 (1997).
- [17] S. Guha, *J. Appl. Phys.* **84**, 5210 (1998).
- [18] M. Lannoo, C. Delerue, and G. Allen, *J. of Luminescence* **70**, 170 (1996).