J Mater Sci (2007) 42:6862–6865
DOI 10.1007/s10853-006-1306-y

Effects of hydrogenation and aging on the optical properties in porous Si layers

Do-Hyun Oh · Soojin Lee · Woon-Jo Cho · Tae Whan Kim

Received: 26 April 2006 / Accepted: 21 November 2006 / Published online: 26 April 2007

Abstract The effects of hydrogenation and aging on the optical properties in porous Si (PS) layers were investigated by using photoluminescence (PL) measurements. When the hydrogenated PS layers were aged in air, the intensity of the PL spectrum increased. The emission peak for the hydrogenated PS layers shifted to higher energy with decreasing H_2/N_2 ratio. The relation of the dehydrogenized states in the as-formed PS surface to the quantum states of Si nanoparticles with relatively small sizes is discussed. These results indicate that the optical properties of PS layers are significantly affected by hydrogenation and aging.

Introduction

The potential applications of optoelectronic devices utilizing porous Si (PS) layers consisting of Si nanoparticles have driven extensive and successful efforts to control precisely the sizes and the shapes of the nanostructures [1, 2]. Visible light emissions from PS layers have been particularly attractive because of interest in their promising applications in complete Si-based optoelectronic technologies [3]. Even though PS layers have emerged as promising candidates for potential applications in the fabrication of Si-based optoelectronic devices, there are still many inherent problems because the optical properties of the PS layer are not stable in ambient air, a problem that must be solved before this material can be used in industry. One of the most significant problems in obtaining high-quality PS layers has been the existence of large nonradiative defects in the PS layers [4]. Since hydrogen atoms can passivate dangling bonds or defective bonds, hydrogenation treatment is very important for improving the crystallinity of the epilayers [5–8]. The effects of hydrogenation on the optical properties of semiconductor thin films have been extensively investigated [9], and a significant increase in the photoluminescence (PL) intensity of the PS layer has been achieved by hydrogenation passivation of the nonradiative defects [10, 11]. Furthermore, since the structures of the PS layers can easily suffer from variations in the surface states during aging in air [12–16], investigations concerning aging of the PS layers are very important for luminescent devices. Therefore, systematic studies of the effects of hydrogenation and aging on the optical properties of PS layers are very necessary before they can be used in optoelectronic devices.

This paper reports data for the effects of hydrogenation and aging on the optical properties of PS layers formed by anodization. PL measurements were performed to investigate the optical properties of the as-grown, hydrogenated, and hydrogenated and aged PS layers. Dependence of the optical properties on the H_2/N_2 ratio and the aging time in PS layers was investigated.

Experimental details

The PS layers studied in this work were formed by using an electrochemical anodization in a HF-based electrolyte. The

D.-H. Oh · S. Lee · W.-J. Cho
Nano Device Research Center, Korea Institute of Science & Technology, Seoul 136-791, Korea

Present Address:
D.-H. Oh · T. W. Kim (✉)
Advanced Semiconductor Research Center, Division of Electronics and Computer Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea
e-mail: twk@hanyang.ac.kr

resistivities of the boron-doped p-type Si (100) substrates used in this experiment were 10 and 0.001 Ωcm, respectively. The Si substrates were alternately degreased in acetone and methanol solutions at 27 °C for 20 min, rinsed in de-ionized water, and etched in a mixture of HF and H_2O (1:10) at 27 °C for 2 min.

The anodization was carried out in a $HF:C_2H_5OH$ (1:2) solution at 300 K and at a constant current density of 10 mA/cm^2 for 5, 10, 30, or 120 min. The anodized samples were rinsed with methanol for 2 min and dried under a nitrogen gas blow. As soon as the anodization process was finished, the samples were mounted onto a susceptor in the chamber, and the surfaces of the PS layers were treated with a hydrogen plasma utilizing a plasma-enhanced chemical-vapor deposition. The samples were placed downstream in a hydrogen plasma with an rf power of 10 W for 10 min at 80 °C. The hydrogenated PS samples were put in polystyrene cases and aged in air. The PL spectra were measured using a 75-cm monochromator equipped with an GaAs photomultiplier tube. The excitation source was the 3,250-Å line of a He-Cd laser, and the sample temperature was kept at 300 K.

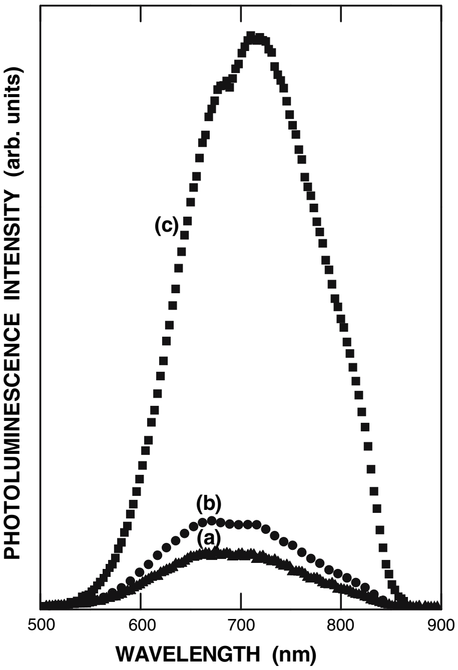

Fig. 2 Photoluminescence spectra for porous Si layers formed from p-type Si substrates immersed in a HF and ethanol solution for (**a**) 10, (**b**) 30, and (**c**) 120 min

Results and discussion

A top-view scanning electron microscopy image depicts that the PS layer formed by using the anodization method exhibits an irregular porous structure, as shown in Fig. 1. The typical thickness of the PS layer is approximately 20 μm. The shape, the size, and the depth of the pores in the PS layers are significantly affected by the current density and the time of anodization. The depth of the pores in the PS layer increases with increasing anodization time, resulting in an increase in the surface volume.

Figure 2 shows PL spectra at 300 K for the PS layers formed from the p-type Si substrate immersed in $HF:C_2H_5OH$ for (a) 10, (b) 30, and (c) 120 min. The dominant PL peak around 700 nm is attributed to emission bands due to the wide band-gap distribution of the Si nanocrystal assembly [1]. The broadness of the PL peaks might originate from the various sizes of the nanoparticles. While the PL intensity at 700 nm increases with increasing etching time, the PL peak position does not significantly change. The increase in the PL intensity with increasing etching time might be attributed to the nucleation and the formation of the pores in the PS layers, resulting in the increase in the number of Si nanocrystals [16]. Therefore, while the number of the Si nanocrystals in the PS layers increases with increasing etching time, the size of the nanocrystals dangling at the PS layer is independent of the etching time. When the etching time becomes 120 min, a dominant peak at 712 nm and a shoulder at 682 nm are observed. The peaks at 712 and 682 nm are related to the emission bands of large- and small-sized nanoparticles, respectively.

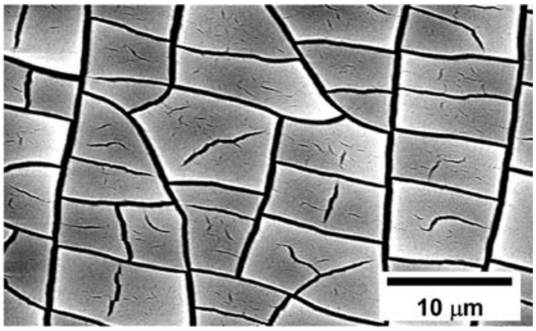

Fig. 1 Top-view scanning electron microscopy image for the porous Si layer formed on the p-type Si substrate

Figure 3 shows that PL spectra at 300 K for the (a) as-formed and the (b) hydrogenated PS layers. The etching time of the PS layers is 5 min, and the H_2/N_2 ratio is 0.03. One dominant peak appears at 650 nm with a Gaussian distribution for the as-formed PS layer, and a weak peak and a shoulder appears at 500 and 700 nm, respectively, together with a dominant peak around 650 nm, for the hydrogenated PS layer. After hydrogenation, the PL spectrum showed that new two exciton peaks appeared. The

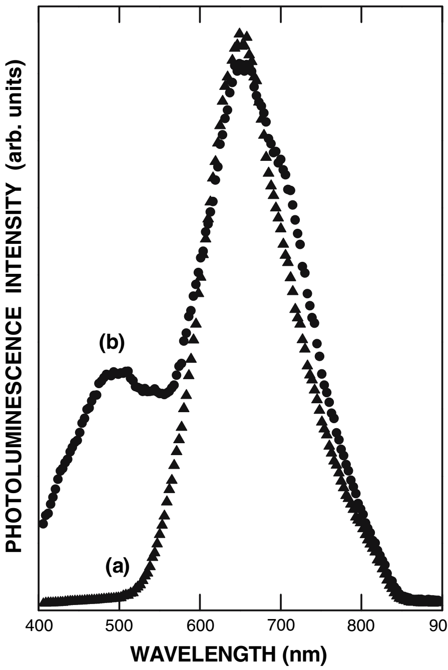

Fig. 3 Photoluminescence spectra at 300 K for the (**a**) as-formed and the (**b**) hydrogenated porous Si layers treated with H_2/N_2 ratio of 0.03

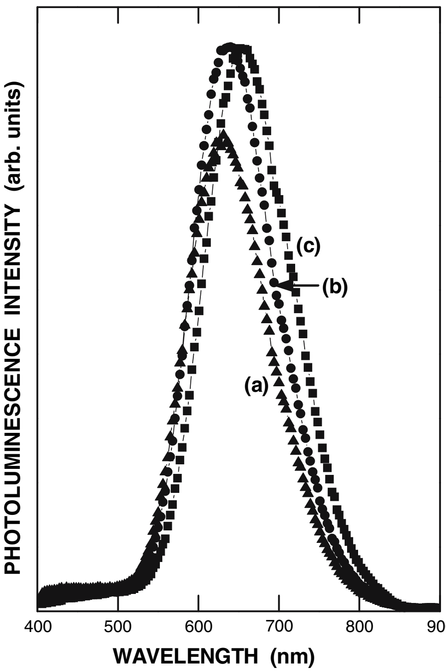

Fig. 4 Photoluminescence spectra at 300 K for the hydrogenated porous Si layers treated with H_2/N_2 ratios of (**a**) 0.33, (**b**) 1, and (**c**) 40

exciton peak at 500 nm might originate from passivation, due to hydrogenation, of the small-sized nanoparticles existing at the pores in the PS layers. The small-sized clusters are more sensitive to hydrogenation than the large-sized clusters [17]. The shoulder at 700 nm is attributed to an increase in the hydrogen concentration of the PS surface after hydrogenation [5].

Figure 4 shows that the PL spectra at 300 K for the hydrogenated PS layers treated with H_2/N_2 ratios of (a) 0.33, (b) 1, and (c) 40. The emission peak for the hydrogenated PS layers shifted to higher energy with decreasing H_2/N_2 ratio. Since the stability of the Si–N bond are higher than that of the Si–H bond [18], the blue-shift behavior with decreasing H_2/N_2 ratio might be attributed to an increase in the number of Si–N bonds on the PS surface, as shown in Fig. 4.

Figure 5 shows the PL spectra at 300 K for the (a) hydrogenated PS layer without aging and for the hydrogenated PS layers aged in air for (b) 5 days and (c) 10 days. When the hydrogenated PS layers were aged in air, while the PL peak position did not dramatically change after aging, the intensity of the PL spectrum was significantly increased. The significant increase in the PL intensity after aging might be attributed to the combined effects of quantum confinement of the nanoparticles in the PS layers and defects in the Si–O bonds covering the PS surface [12]. When the hydrogenated PS layers were aged for 5 or 10 days, the weak peak around 500 nm disappeared. These results indicate that the peak around 500 nm of the PL spectrum for the hydrogenated and aged PS layers might be related to the quantum states of the relatively small-sized Si nanoparticles.

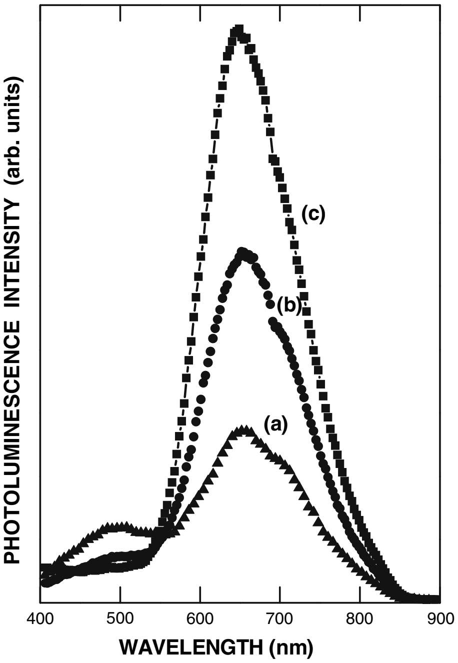

Fig. 5 Photoluminescence spectra at 300 K for the (**a**) hydrogenated Si layer without aging, and for the hydrogenated porous Si layers aged in air for (**b**) 5 days, and (**c**) 10 days

Summary and conclusions

The hydrogenation and the aging effects in PS layers formed with an anodization method were investigated by using PL measurements. After hydrogenation, the PL spectrum showed that the emission peak attributing to the passivation of the small-sized nanoparticles existing at the pores in the PS layers. The emission peak of the PL spectrum for the hydrogenated PS layers shifted to higher energy with decreasing H_2/N_2 ratio. When the hydrogenated PS layers were aged in air, the intensity of the PL spectrum significantly increased due to the combined effects of the quantum confinement of the nanoparticles in the PS layers and defects in the Si–O bonds covering the PS surface. These results can help improve understanding of the effects of hydrogenation and aging in PS layers.

Acknowledgements The work at KIST was supported by KIST contract 2E18540, and the work at Hanyang University was supported by the Korea Science and Engineering Foundation through the Quantum-functional Semiconductor Research Center at Dongguk University.

References

1. Kovalev D, Gross E, Diener J, Timoshenko VY, Fujii M (2004) Appl Phys Lett 85:3590
2. Jacobsohn LG, Bennett BL, Cooke DW, Muenchausen RE, Nastasi M (2005) J Appl Phys 97:033528
3. Hirschman KD, Tsyhcskov L, Duttagupta SP, Fauchet PM (1996) Nature 384:338
4. Martin-Palma RJ, Pascual L, Landa A, Herrero P, Martinez-Duart JM (2004) Appl Phys Lett 85:2517
5. Cheylan S, Elliman RG (2001) Appl Phys Lett 78:1225
6. Kim B-H, Cho C-H, Kim T-W, Park N-M, Sung GY, Park S-J (2005) Appl Phys Lett 86:091908
7. Kveder V, Badylevich M, Steinman E, Izotov A, Seibt M, Schroter W (2004) Appl Phys Lett 84:2106
8. Ke YY, Ya MH, Chen YF, Wang JS, Lin HH (2002) Appl Phys Lett 80:3539
9. Kang TW, Yuldashev ShU, Kim DY, Kim TW (2000) Jpn J Appl Phys 39:L25
10. Tsai C, Li K-H, Kinosky DS, Qian R-Z, Hsu T-C, Irby JT, Banerjee SK, Tasch AF, Campbell JC, Hance BK, White JM (1992) Appl Phys Lett 60:1700
11. Xiong ZH, Liao LS, Yuan S, Yang ZR, Ding XM, Hou XY (2001) Thin Solid Films 388:271
12. Fukuda Y, Furuya K, Ishikawa N, Saito T (1997) J Appl Phys 82:5718
13. Gelloz B, Sano H, Boukherroub R, Wayner DDM, Lockwood DJ, Koshida N (2003) Appl Phys Lett 83:2342
14. Sun J, Lu YW, Du XW, Kulinich SA (2005) Appl Phys Lett 86:171905
15. Gelloz B, Kojima A, Koshida N (2005) Appl Phys Lett 87:031107
16. Pascual A, Fernández JF, Sánchez CR (2002) J Appl Phys 92:866
17. Shin JH, Seo S-Y, Lee S-J (1998) Appl Phys Lett 73:3647
18. Daami A, Bremond G, Stalmans L, Poortmans J (1999) J Lumin 80:169