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Highly Efficient and Stable Photoluminescence of Nanocrystalline Porous Silicon with Fully Annealed and Passivated Surfaces

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1. Introduction

Getting efficient and stable Si-based visible luminescence, whether it is photoluminescence (PL) or electroluminescence (EL), is a key issue for monolithic optoelectronic integration as well as for other photonic applications where the compatibility with advanced silicon planar technology is crucial. So far, the best reported external quantum efficiencies and power efficiencies of EL from porous silicon (PS) devices are 1.1 % and 0.4 %, respectively [1-3]. Further work should be pursued to achieve efficiencies and sufficient long-term stability suitable for practical use (>1% in power efficiency).

As recently reported [4,5], the external quantum efficiency of the red PL of PS has been enhanced up to 23% using a treatment based on high-pressure water vapor annealing (HWA). At the same time, both the PL and EL are drastically stabilized [6]. Another useful method to stabilize PL and EL is surface chemical modification (CM) based on thermally induced hydrosylilation [7,8] by which residual Si-H bonds at nanocrystalline silicon surfaces are replaced with stable Si-C covalent bonds.

To enhance these achievements further, combined effect of HWA and CM on PL is presented in this paper.

2. Experimental

In this study, HWA and CM techniques have been combined to make the best use of their effects on the PL efficiency and stability. The HWA treatment was applied to both as-anodized PS and CM-treated PS (CM-PS).

The substrates used were (100)-oriented, B-doped p-type (4 Ωcm) silicon wafers. The PS layers were formed by conventional anodization in an ethanoic HF solution under galvanostatic condition in the dark.

Chemical derivatization of the PS surface was carried out by letting the samples in 1-decene at 100ºC for 3 h. The samples were then rinsed and dried under N_2 gas flow. For HWA treatment, PS samples were heated in water vapor at a temperature of 260 °C for 3 h in similar way to previous papers [4,5], and then cooled down to room temperature. The water vapor pressure in the container during annealing was 1.3 MPa.

The PL measurements were carried out in air by using a 325 nm He-Cd laser as an excitation source. The PL characteristics were evaluated in terms of the emission spectra and the time dependence of PL intensity in air under continuous excitation. To clarify the PL stabilization effect, the surface characterization was done by Fourier transform infra-red (FTIR) analyses.

3. Results and discussion

Figure 1 shows PL spectra of PS layers whose initial porosity was 68%. Both as-anodized PS and CM-PS exhibit no luminescence. After HWA, in contrast, they become highly luminescent. The enhancement of the PL of PS confirms our previous results [4,5]. For CM-PS, the PL intensity was even more enhanced. It should be noted that the PL emission band remains similar to that of conventional luminescent PS in which the luminescence originates from recombination of excitons concerted with surface states [9].

Associated with the emission enhancement, the PL is very much stabilized by HWA. **Figure 2** shows the PL intensity of a conventional PS layer (as-anodized, porosity of 80%) as well as that of a HWA-treated CM-PS layer during continuous irradiation by the HeCd laser. Since generation of nonradiative surface defects due to uv-induced oxidation is effectively suppressed, the PL of HWA-CM-PS is kept stable in comparison with that of conventional PS.

FTIR measurements have shown that the surfaces of PS and CM-PS are oxidized by HWA. **Figure 3** shows the absorption of CH_x (x=1,2,3) stretching mode vibrations in CM-PS before and after HWA. Clearly, the amount of carbon in CM-PS was decreased by HWA. This can be attributed to the partial oxidation of the surface of CM-PS upon HWA, which led to the formation of Si-O-Si bridges to the detriment of Si-C bonds. Nevertheless, a significant amount of carbon is still present after HWA. Therefore the surface of HWA-CM-PS consists partly of carbon-terminated Si and partly of Si oxide.

Thus, the enhancement of the PL intensity and stability of CM-PS after HWA is related to complementary surface passivation by both high-quality thin oxides with little interfacial defects and stable Si-C bonds.

These highly luminescent and stable PS layers would provide practical active layer for EL diodes and for related photonic devices.

4. Conclusions

Appropriate combination of HWA and CM for PS is very effective to produce highly efficient and stable PL emission. High-quality surface oxide network produced by HWA contribute to enhance and stabilize PL in conjunction with tight covalent bonds formed by CM. This technique is promising for development of PS-based luminescent, photonic, and possibly other functional devices.

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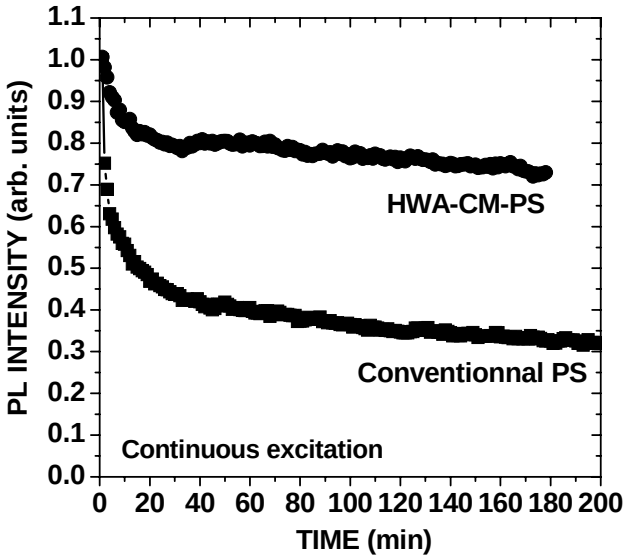

Fig. 2. PL intensities as a function of time for a conventional PS layer (as-anodized; 80% porosity) and a HWA-treated chemically modified PS layer. Both samples were continuously irradiated in air by a 325 nm HeCd laser.

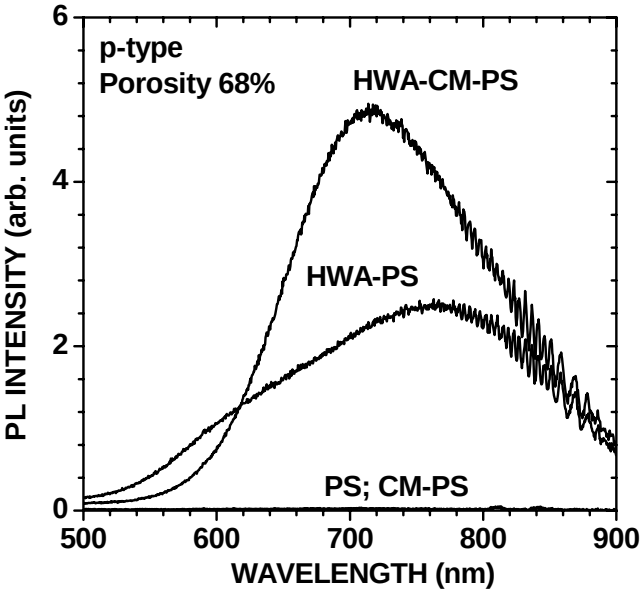

Fig. 1. Effect of HWA treatment on the PL spectra of as-anodized PS and chemically modified PS (CM-PS). The PL is significantly enhanced by HWA, although original PS and CM-PS show no luminescence.

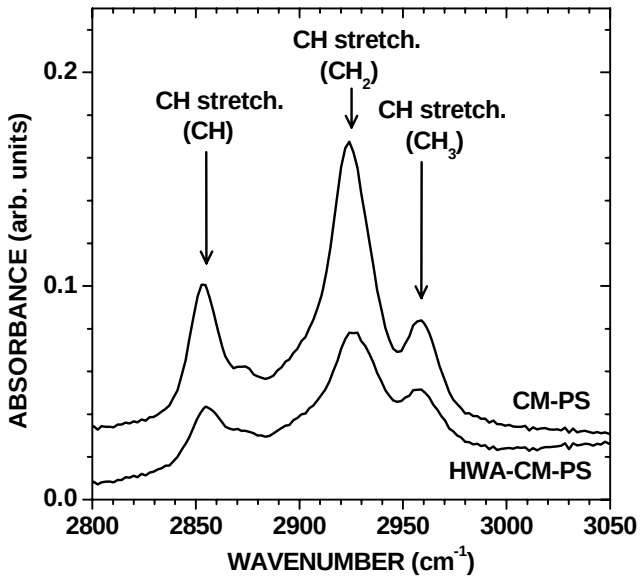

Fig. 3. FTIR spectra showing the absorption of CH_x (x=1,2,3) stretching mode vibrations for chemically modified PS (CM-PS) before and after HWA.