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Photosynthesis of Luminescent Porous Silicon

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A novel process to realize visible light emission from Si has been developed. Si wafers were immersed in an aqueous HF solution without any electrodes, and a He-Ne laser light was irradiated on the Si surface in the HF solution. This simple technique gives the luminescent porous layer of which thickness is controlled with the irradiation time and the laser power density. A visible photoluminescence (PL) peak has been observed around 670nm, which was similar to the spectra frequently observed in anodized porous Si.

1. Introduction

Observations of visible luminescence from anodized porous Si at room temperature have demonstrated the potential of Si for optoelectronics. We have recently examined the luminescent region in anodized porous Si with transmission electron microscopy and PL imaging [1]. In the total 20~50μm-thick porous layers, the luminescent region was restricted only to the 1~1.5μm thick topmost surface layer as shown in Fig. 1 (photo-excitation on the cleaved facet). For realizing efficient electroluminescence devices, how to remove the thick highly-resistive porous layer underneath the luminescent layer is important. In this paper, preliminary results on photosynthesis of the luminescent porous layer is reported for the first time. Our result will promote the basic understanding of the formation mechanism of the luminescent layer as well as the practical advantage discussed above. The luminescence mechanism will be also discussed.

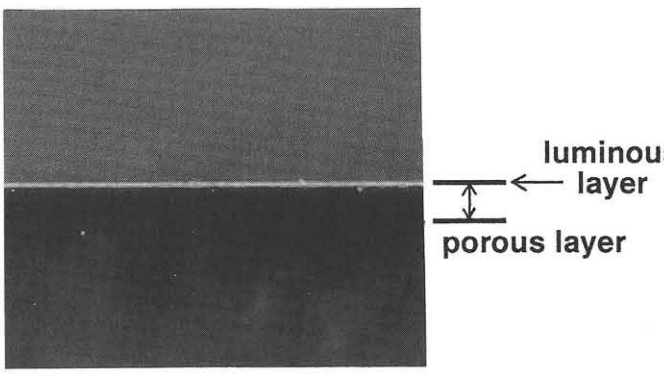

Fig. 1 Cross-sectional PL image of (111)Si anodized for 1h in 25%HF solution. Porous layer is 26μm thick in this example.

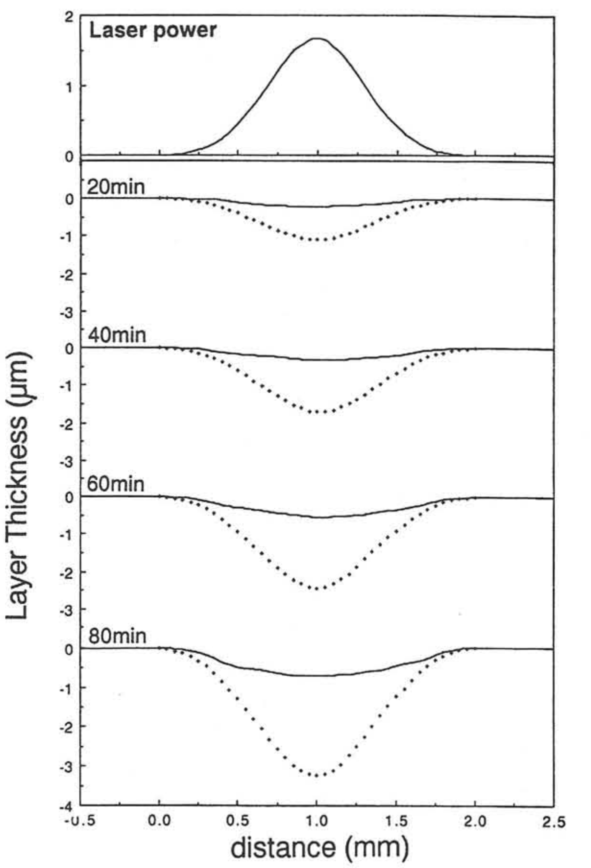

Fig. 2 Time evolution of photosynthesized porous layer.

2. Experimental Procedure

Silicon substrates used were p-(boron doped) and n-(phosphorus doped) type (100) and (111) silicon wafers with the resistivities of 0.01Ωcm and 15Ωcm. After cleaning with organic solvents, the silicon wafers were immersed in an aqueous HF (50%) solution, and a He-Ne laser (1mW) light was irradiated on the silicon surfaces in the HF solution for 20~80 minutes. In this process, we need neither electrodes nor DC power supply for anodization.

3. Results and Discussion

Figure 2 shows the irradiation time dependence of the depth profile of the photosynthesized porous layer and the incident laser beam profile. The thickness of the porous layer linearly increased with the irradiation time as shown in Fig. 3. The thickness of the porous layer was not dependent on the crystalline axes of (100) and (111), but it was dependent on the resistivity of the silicon wafers. It is noted that the porous layers were formed on the n-type Si, but it was not formed on the p-type Si.

These results indicate that the depletion layer at the semiconductor surface plays a prominent role for the formation of the porous layer. Photo-generated holes in the surface depletion layer in n-type Si are effectively supplied to the surface by the internal field as shown in Fig. 4(a), which assist the pore formation [2]. On the other hand, holes generated in the depletion layer of p-type Si drift toward the reverse direction and are not supplied for the surface reactions.

It was also found that the formation of the photosynthesized porous layer depends on the wavelength of the irradiated light as shown in Table 1.

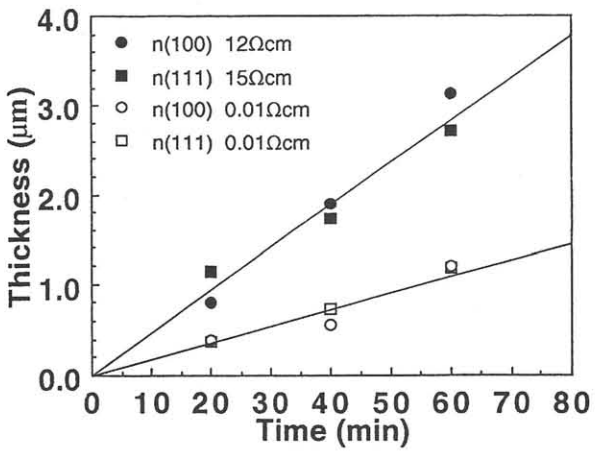

Fig. 3 Porous layer thickness increases linearly with the photo-irradiation time.

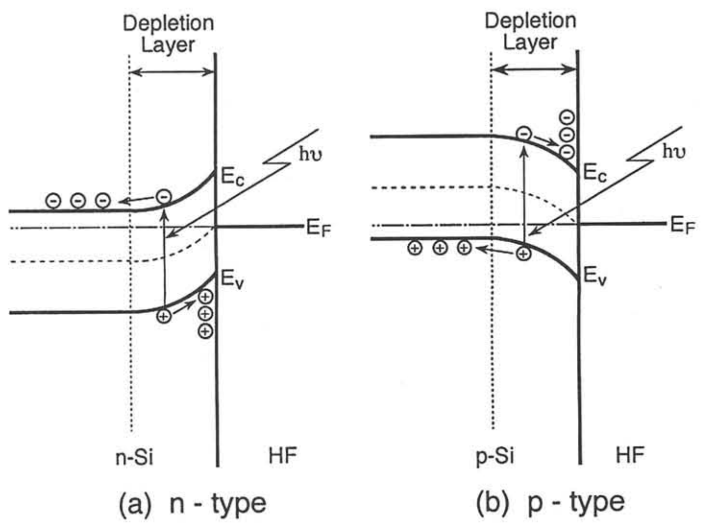

Fig.4 Behavior of Photo-generated holes in the surface depletion layer.

Light Source	Formation	Phenomena
1mW He-Ne Laser (632.8nm) <175mW/cm²>	○	The luminous layer was formed on the irradiated area.
Xe Lamp + >590nm low pass filter <117mW/cm²>	○	The luminous layer was formed on the irradiated area. (sensitive to surface condition)
Xe Lamp + >690nm low pass filter <112mW/cm²>	○	
Xe Lamp + 300~400nm band pass filter <3.1mW/cm²>	×	No change.
Xe Lamp (all wavelength) <127mW/cm²>	×	Only etching occurred.

(n-Si, 50%HF solution, for 60 minutes, in Dark)

Table 1 The wavelength dependence of the porous layer formation.

From these results, it is probable that the light irradiation with the photon energy higher than the absorption edge of the porous layer generates holes in the porous layer and that this makes the porous layer dissolve during the surface reactions.

Observation of the PL image on the cleaved facet showed that the whole porous layer with the maximum thickness of about 3μm was luminescent. The PL spectra were measured using the 325nm He-Cd laser (13mW/cm^2) excitation. The n^--Si samples photosynthesized for 60-minutes exhibited orange color. The PL peak wavelength was around 670nm. During the PL measurements, the PL intensity was decreased with the He-Cd laser irradiation, which was attributed to oxidation in the porous layer [3]. The PL spectra were slightly modified during this PL intensity change and were finally stabilized as shown in Fig. 5. The PL peak wavelength remained almost unchanged.

The n^+-Si samples exhibited yellow color just after the photosynthesis. The decrease of the PL intensity with the He-Cd laser irradiation similar to the one for the n^--Si samples was also observed for the n^+-Si samples. In this case, especially the shorter wavelength side of the PL spectra decreased and the PL spectra finally approached that of n^--Si shown in Fig. 5.

Similar intensity and spectral changes were also observed for anodized porous silicons during PL measurements, and the PL spectra approached to the one shown in Fig. 5 [3]. These results indicate that the luminescence properties of the porous layers prepared with anodization and photosynthesis are very similar to each other.

Figure 6 shows the micrograph observed with a scanning electron microscope. The surface of the photosynthesized porous layer was composed of the microparticles as shown in Fig. 6, which is the same structure as that of the anodized luminescent layer [1]. Therefore, the quantum box model proposed in Ref. [3] as the luminescence mechanism may be also applied to this photosynthesized porous layers.

4. Conclusions

We have demonstrated the photosynthesis of porous layers that show luminesce in the visible region. This novel process is very simple, and the whole porous layer was luminescent. Therefore the photosynthesized porous layers may be applied to highly efficient silicon optical devices. The photosynthesized porous layers were formed only on n-type silicon wafers and had the dependence upon the wavelength of the incident light. These results indicated that the photo-generated holes play an important role to form the luminescent layer. The structure and the PL spectra were very similar to the anodized porous layers.

Reference

[1] N.Noguchi etal, Jpn. J. Appl. Phys. 31 (1992) L490.

[2] V.Lehmann etal, Appl. Phys. Lett. 58 (1992) 856.

[3] I.Suemune etal, Jpn. J. Appl. Phys. 31 (1992) L494.

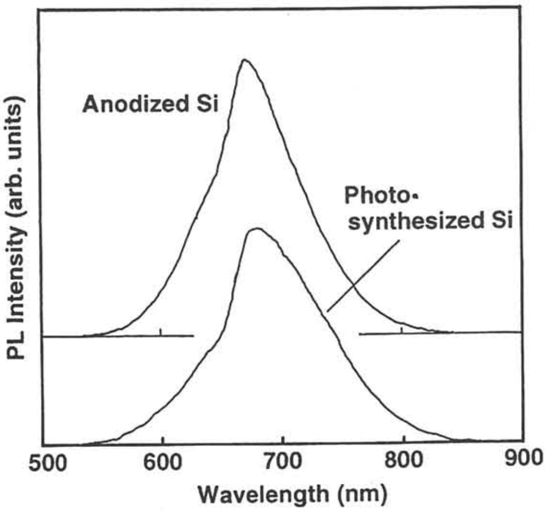

Fig. 5 Comparison of PL spectra between anodization and photosynthesis.

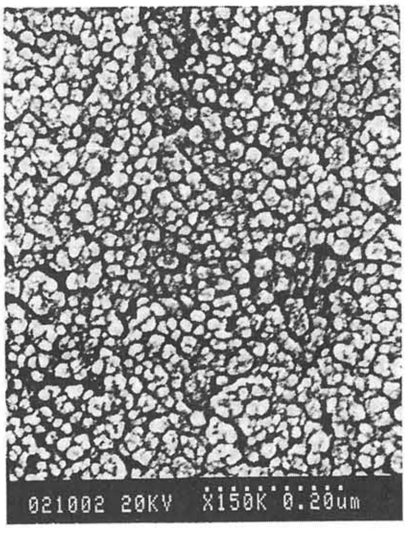

Fig. 6 Surface of the photosynthesized porous layer on n^+-Si.