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Chemical Treatment after Annealing Enhances Photoluminescence from Porous Silicon

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Abstract

A silicon wafer was anodized to form porous silicon and then annealed followed by a chemical treatment. Annealed porous silicon has little efficiency of photoluminescence. The chemical treatments yielded photoluminescence at around 850 nm. The IR and ESR spectra showed that annealing forms silicon oxide with Pb-center and a-center levels, which results in the suppression of photoluminescence. After the chemical treatment, silicon oxide was removed and the two kinds of centers are disappeared. It possibly enhanced the photoluminescent efficiency. Further chemical treatment showed a blue shift of the photoluminescence. These results well support a quantum effect and suggest that the two kinds of centers in oxide are a factor of suppressing photoluminescence.

Keywords

Porous Silicon, Thermal Annealing, Chemical Treatment, ESR Spectra, IR Spectra

1. Introduction

Porous silicon is formed by the anodization of silicon wafer with a relatively low current density in HF acid solution. It was known from a long ago to have a sponge-like peculiar structure. Followingly, it was found to have the ability of photoluminescence in 1990 [1]. Vast amount of studies have been devoted to light-emitting characteristics so far [2]. Silicon is basically categorized as an indirect semiconductor, so the efficiency of light emission is too low for a light emitting device. It is because a hetero junction of silicon with direct semiconductor is even now an attractive issue in spite of its difficulty.

The forming conditions are the resistivity of the silicon wafer, the type of it, concentration of the solution, current density and anodization time. On the analytical aspects, x-ray diffraction, electron microscopy, infrared absorption, electron-spin resonance and several kinds of luminescence have been widely performed.

The downside of the porous silicon is a poor reproducibility, but the low-cost of the formation is incredibly attractive. Even the dream to realize opt-electronic hybrid chips has been discussed at countless times.

The phenomenon of photoluminescence from porous silicon is not only interesting from the engineering aspect, but from physical fundamentals. A quantum size effect may be involved in light emission from silicon. Actually, the microstructure of porous silicon stands between crystalline and amorphous silicon. It is a region of nano-scale science as a matter of fact [3].

In order to investigate this attractive material, the annealing of the porous silicon and following chemical treatments are studied in this article. The infrared absorption and the electron-spin resonance measurements have been utilized.

2. Experiment

A p-type silicon wafer doped with boron whose resistivity was between 1 and 10 Ω cm was installed at the bottom of a container of the solution of HF acid:ethanol = 1:1 in volume. The anodization was performed for half an hour in dark, with the current density of 20 mA/cm^2. The obtained porous silicon sample (a) was then annealed in an electric furnace for 5 minutes at 900˚C (b). And then a chemical treatment was done once by soaking in the solution of HF acid:pure water:ethanol = 1:1:2 for 2 minutes (c). The same chemical treatments were performed successively one more time (d).

The four samples were analyzed by means of Fourier-transformed infrared absorption (FTIR) and electron-spin resonance (ESR) measurements. FTIR spectra were obtained with the System 2000 by Perkin Elmer Co. ESR spectra were obtained with ES-10 by Nikkiso Co. PL spectra were taken with a conventional apparatus with the help of Hg lamp excitation.

3. Results and Discussion

Figure 1 shows successive FTIR spectra from (a) initial porous silicon, (b) annealed, (c) chemically treated once and (d) chemically treated once more. These spectra tell us the chemical surface states of the samples clearly. A doublet around 2100 cm^{-1} arises from the stretching modes of the SiH and SiH_2 species [4], and three structures at 1105, 907 and 500 cm^{-1} arise from the bulk Si-O-Si asymmetric stretching mode, the scissor mode of the SiH_2 species and the Si-O-Si rocking mode with a shoulder for the Si-Si stretching mode, respectively [4] [5]. The spectra suggest the as-formed porous silicon has Si-H_x species on the surface and oxidized parts at the same time. It is because the anodization is performed in HF acid which results in a chemically active surface.

After annealing, two main broad structures at 3300 and 1250 cm^{-1} appeared instead of sharp peaks observed before annealing. These broad structures are featured by a glass or amorphous state; silicon oxide was formed to a great extent. After the chemical treatments, both structures disappeared. It is considered that oxide parts are solved in HF acid solution during the chemical treatment.

Figure 2 shows the photoluminescence spectra from Sample b-d. Sample a did not give any PL intensity similar to Sample b. Only after chemical treatment, photoluminescence was observed. Sample d shows a slight blue shift from Sample c.

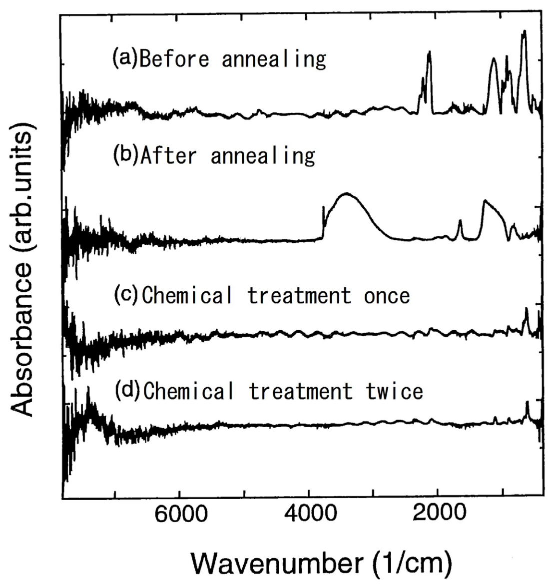

Figure 1. FTIR spectra from the successive sample: (a) initial porous silicon, (b) annealed, (c) chemical treated once and (d) chemical treated once more.

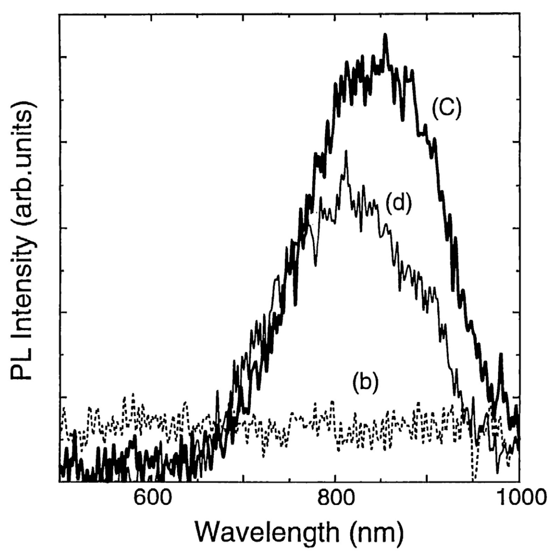

Figure 2. Photoluminescent spectra from the samples. The index of (b)-(d) stands for the same as in Figure 1. Sample a did not show photoluminescence and then is omitted here.

Figure 3 shows the ESR spectrum from Sample a. The two strong signals at 3350 and 3440 gauss are a beacon signal from MnO_2 as a standard. The signal was not observed enough in the center area. On the other hand, Figure 4 shows the ESR spectrum from Sample b. In this figure, two strong signals, even stronger than the beacon signal, were observed in the center area. They are assigned to be two kinds of defects (g = 2.0029 and 2.0057) observed in silicon and Silicon oxide interface [6]. Successive chemical treatments eliminated the two structures as shown in Figure 5. Sample c showed the similar spectra to Sample d. From these ESR spectra changes shows that Sample b (annealed) only includes quite amount of dangling bonds on the porous silicon surface.

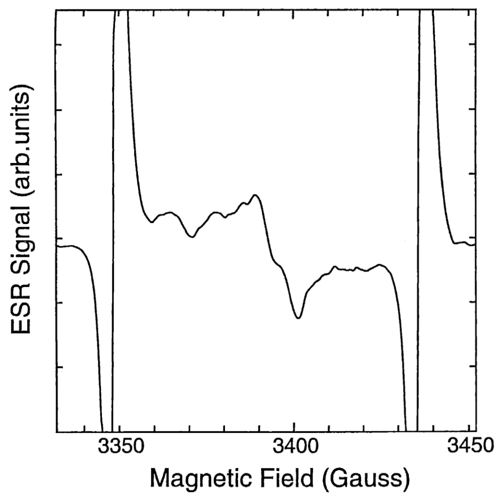

Figure 3. ESR spectrum from Sample a.

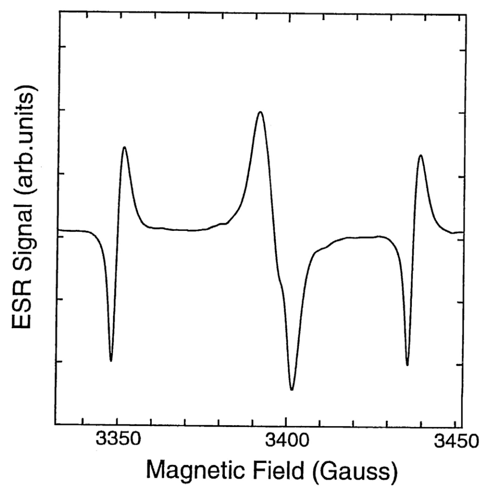

Figure 4. ESR spectrum from Sample b.

These dangling bonds surely suppress the photoluminescence efficiency. The existence of Si-H and Si-H_2 species also suppress the photoluminescence efficiency according to Sample b. From the fact that only chemically treated samples (Samples c and d), photoluminescence is thought to derive from the quantum size effect of silicon crystal.

Photoluminescence from silicon-related materials is attractive and the discovery of photoluminescence from porous silicon is a big breakthrough for light technology. It is also attractive if the photoluminescence from porous silicon is based on quantum size effect from the physical point of view, but the surface chemical state strongly affects the photoluminescence efficiency. The control of these surface conditions is of great importance for the future advancement of the new technology.

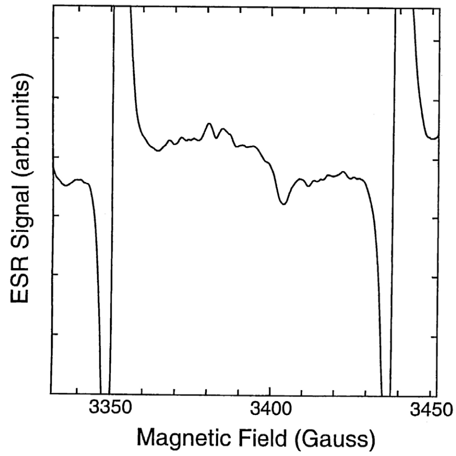

Figure 5. ESR spectrum from Sample d.

4. Conclusion

High resistivity p-type silicon wafers were anodized to form porous silicon. The porous silicon was annealed and then chemically treated. The samples after chemical treatments only showed photoluminescence. With the help of FTIR and ESR spectra, it is considered that Si-H_x species and silicon oxide suppress the photoluminescence from porous silicon. From the fact that successive chemical treatments showed the blue shift in photoluminescence, the light emission is suggested to be based on a quantum size effect.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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