High Resolution Patterning of Luminescent Porous Silicon with Photoirradiation

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High-resolution patterning of luminescent porous silicon was achieved by a photosynthesis method. Porous silicon was selectively formed on Boron doped p⁺ regions with uniform photo-irradiation. 7μ m stripe porous regions exhibited clear visible photoluminescence. The mechanism of the selective formation is discussed from the viewpoint of how photo-generated holes are accumulated. The resolution limit in the present method will be given by the widths of depletion layers at p-n junctions, and the formation of sub-micron patterns of luminescent porous silicon will be possible.

1. Introduction

Visible photoluminescent porous silicons have been intensively investigated from the viewpoint of physics, and the luminescence mechanisms have been actively discussed from various viewpoint.[1] At the same time, possible applications to optoelectronic devices have also been studied.[2] In a previous report, we proposed a photosynthesis method.[3] This technique will be much more easily incorporated into LSI technologies compared with conventional anodization techniques.

For the future applications, selective formation of luminescent porous areas will be desirable to realize silicon optical devices integrated on silicon electronic circuits. In this paper, we report on a new selective formation method of luminescent porous silicon by photoirradiation on a Si surface with a built-in p-n potential distribution. The mechanism of the selective formation and the limit of the spatial resolution will be discussed.

2. Experimental Procedure

Silicon wafers examined were n-(111) silicons with resistivities of $0.01\Omega \text{cm}(n^+)$ and $15\Omega \text{cm}(n^-)$ and p-(111) silicons with those of $15\Omega \text{cm}(p^-)$ and $0.1\Omega \text{cm}(p^+)$. After cleaning with organic solvents, a SiO₂ mask of about 3000Å thickness was formed on the silicon wafers. The SiO₂ mask was etched in stripes of $5 \sim 320 \mu m$ width by optical lithography. Then Boron was diffused on the Si surface covered with the SiO₂ mask for 120 minutes at 1050°C. The depth of the p-n junction thus prepared was about $2.2 \mu m$ for n⁺ silicon wafers.

These wafers were immersed in a 50wt.% hydrofluoric (HF) acid aqueous solution. The sample surfaces were photoirradiated with a xenon lamp through a low-pass optical filter of 590nm to have the pore formation.[3] The incident optical power was about 55mW/cm².

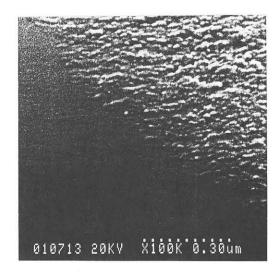
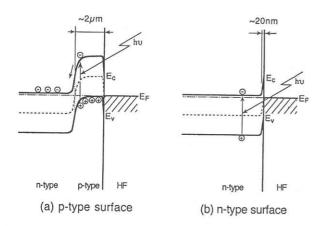


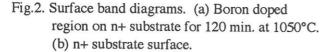
Fig.1. Cross-sectional view observed with SEM. Porous layer was selectively formed with photosynthesis for 30 min. The boundary was coincided with the p-n junction.

3. Results and Discussion

Figure 1 shows the cross-section of the porous layer observed with a secondary-electron microscope (SEM). The sample was n-(111) silicon with the resistivities of 0.01 Ω cm and was photoirradiated for 30 minutes in a HF solution. Porous silicon layer was formed selectively on the Boron doped surface that was located on the right hand of Fig. 1. Its microscopic structure viewed with further magnification was the same as the one observed with anodization,[4] i.e., microparticle structures with the size of \leq 20nm. The boundary between the porous region and the single-crystalline Si coincides with the location of the p-n junction observed with stain etch.

Figure 2 shows the band diagram of a p+ surface on a n+ substrate and that of a n+ substrate surface. The





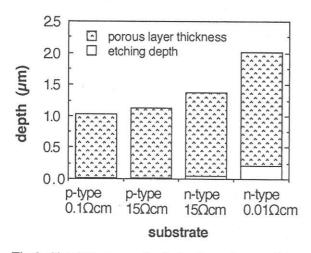


Fig.3. Si substrate conductivity dependence of the depth of the porous layer and surface etching depth prepared with 60 min. photoirradiation in HF solution.

potential distribution suggests that the surface p+ layer works as the effective potential well for holes. Therefore photo-generated holes will be accumulated in this p+ region. Since Boron was heavily doped on the surface of the p+ region, the depletion layer near the liquid-solid interface will be thin enough for holes to be supplied to the surface chemical reactions by tunneling or via interface energy levels.

In our previous reports on the photosynthesis of porous silicon on uniform surfaces, the porous layers were formed on n-Si surfaces, not on p-Si surfaces.[3] This was interpreted to be due to the bending of surface potentials as shown in Fig. 2(b) for a n-Si surface. Therefore, the dependence of the porous layer formation on the substrate conductivity was examined. P+ stripe regions were formed on other Si surfaces with different conductivities by the same diffusion method. The porous layer thickness prepared with the same photosynthesis conditions was dependent on the substrate conductivities as shown in Fig. 3. The fastest porous layer formation was observed on the n+ substrate, and it was the slowest on the p+ substrate. The depth chemically etched from the surface during the photosynthesis also showed the same tendency.

Following the mechanism discussed above, the observed conductivity dependence was examined from

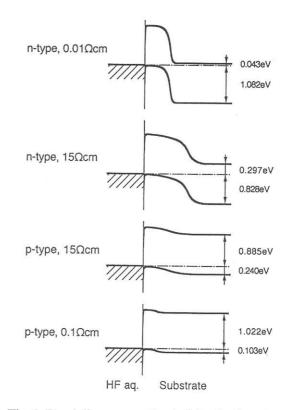
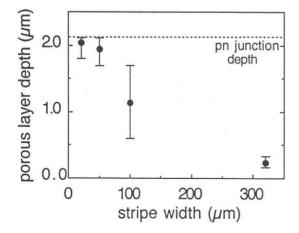


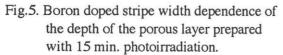
Fig.4. Band diagrams estimated for the four types of the silicon substrate in Fig. 3, where Boron is doped on the surface. the potential profiles shown in Fig. 4. Clear correlation between the enhancement of the porous layer formation and the Fermi level in the substrates was observed, i.e., the formation was enhanced when the Fermi level in the substrates approached the conduction band. This suggests that the deeper surface potential well leads to the more effective hole accumulation and therefore to the enhanced surface reactions.

The reason why porous layers on patterned n-type surfaces are not formed are not yet well-understood. However, the interval of the stripes was $200 \sim 550 \mu m$ and was comparable to the diffusion length of holes in n+ silicon. Therefore it is probable that holes photogenerated on n-type surfaces diffuse along the surfaces toward p+ regions before they take part in surface reactions on n-type surfaces. Figure 5 shows p+ stripe width dependence. The formation enhancement was observed in narrower stripes. This result indicates that holes generated in the region between stripes were accumulated in the p+ regions.

We examined the possibility of fine pattern formations of luminescent porous silicon. A sample that has various widths of Boron doped stripes on the n^+ surface was prepared. Figure 6 shows the photoluminescence image observed with weak ultraviolet light irradiation. Every stripe showed high contrast red luminescence. The narrowest luminous stripe obtained was about 7μ m, the width of which was almost similar to that of porous layer.

The spatial resolution of the luminescent region is essentially limited by the width of the depletion layer at the p-n junction from the above-discussed formation mechanism. The depletion layer in the case of the p^+-n^+ junction is less than 0.1μ m, and the high spatial resolution is expected. From a practical viewpoint, the





spatial resolution of the luminous region will be limited by the spatial resolution during the formation of p^+ regions. Therefore the resolution up to sub μm should be possible employing the recent VLSI technologies.

4. Conclusions

The capabilities of the selective formation of the porous silicon layer was demonstrated with the photosynthesis method. The mechanism of the selective formation was discussed considering the potential profiles near the surface. The narrowest stripe width examined was about 7μ m and visible photoluminescence was observed from the selectively-formed porous area. The essential spatial resolution is determined by the width of the depletion layer at the p-n junction. This new photosynthesis method will offer a fundamental technique for the selective formations of optical devices on silicon substrates. This work was supported in part by the Kurata Research Grant.

Reference

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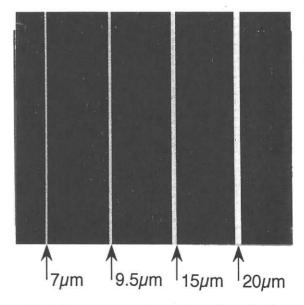


Fig.6. Luminescence image from the selectively formed porous stripe regions.