Inhibition Effect of a Laser on Thickness Increase of p-Type Porous Silicon in Electrochemical Anodizing

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We demonstrate that the thickness increase of the porous layer on p-type (1–10 ohm-cm) silicon can be inhibited from hundreds to several nm/min in regular anodizing by exposure to He–Ne laser irradiation. During 2.0 mW laser irradiation, the growth in thickness was reduced to 5–6 nm/minute by anodizing with a current density of 10 mA/cm². The inhibition effect on the thickness increase of porous silicon depends significantly on the laser power during a fixed anodizing time.

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Because the nanoscale structure of pores in porous silicon displays interesting electronic, photonic, chemical, and mechanical properties, owing to an extremely high surface area-to-volume ratio and quantum confinement effects,1 this material has been extensively studied for various applications, such as layer transfer,2 MEMS,3 optics,4 solar cells,5 and biomedical engineering.6,7

In anodizing operation in hydrofluoric acid (HF)-based electrolyte, the holes in silicon play a key role in the formation of porous silicon.8 Therefore, p-type silicon substrate is eligible for fabricating the porous silicon layer with high controllability and reproducibility. By contrast, for forming a porous layer on an n-type silicon, it is necessary to illuminate the specimen to excite holes for anodizing.9 The electrochemical etching of n-type silicon only in illuminated regions can designate porous regions to pattern silicon surfaces without applying a photoresist.10,11 In general, a higher anodic bias applied to the substrate increases porosity and decreases the diameter of the pore walls, producing porous silicon with a large bandgap through one- or two-dimensional quantum confinement.12,13 However, it is difficult simultaneously to restrict the thickness of porous silicon formation on a nanoscale in the anodizing conditions due to the high growth rate on the micron-scale. We found a strong inhibition effect of a He–Ne laser on the formation of p-type porous silicon in the anodizing process. During laser irradiation in the anodizing, the photoexcited electrons accumulate on the surface of the p-type silicon, forming a hole-depletion region,14–15 which inhibits the electrochemical etching and slows the formation of porous silicon.

Experimental

Figure 1 shows a schematic diagram of the experimental setup for preparing the porous silicon layer. The 5 × 5 cm² specimens, which were prepared by boron-doped (100-oriented) p-type silicon wafers with a resistivity of 1 to 10 Ω-cm following standard RCA cleaning procedures,13 were used as anodic electrodes. The surface of the specimen exposed to the electrolyte occupied an area of 9.62 cm², defined by the Teflon cell, and was face-up to allow the vertical laser beam to focus on the centre.

Electrochemical anodizing was performed at a constant current of 100 mA with a platinum cathode in the electrolyte (mixture of 49.5% HF and 99.5% ethanol at 1:1 volume ratio). During anodizing, we used a He–Ne laser system (632.8 nm, maximum 2 mW, Model HRP020-1, Thorlabs) to create a beam spot 1.0 mm in diameter on the specimens. The addition of ethanol was to improve the wettability of the electrolyte and the uniformity of the porous silicon layer by reducing the adsorption of hydrogen bubbles. After anodizing, the specimens were rinsed with deionized water and then dried by nitrogen purging. A field emission scanning electron microscope (FE-SEM, JEOL JSM-7000F) and a He–Cd laser (325 nm, 3.81 eV) were used to characterize the morphology and the photoluminescence (PL) spectrum of the porous silicon layers.

Results and Discussion

After anodizing, the electrolyte contact area other than the laser-irradiated region appeared in black owing to the formation of porous silicon. In the laser-irradiated region, the surface color was similar before and after anodizing. The FE-SEM image in Figure 2 shows the transition zone formed during the 30-minute anodizing between an irradiated region by a 2.0 mW He–Ne laser (thickness = 130 nm) and a non-irradiated region (thickness = 4,510 nm). The gradual change in thickness of the porous silicon in the transition zone exhibits a
Gaussian profile that implies the intensity of the laser beam, which indicates that a crucial influence factor on the inhibition effect, could be in the Gaussian distribution.\textsuperscript{10,15}

Figure 3 illustrates the FE-SEM images of the electrochemically etched surfaces. The intensity level of He–Ne laser changed the thickness of the porous layer formed at the anodizing condition of a current density of 10 mA/cm\textsuperscript{2} for 30 minutes. The thickness of the porous silicon was reduced from several micrometres (in the un-irradiated region) to 100 nanometres via a 2.0 mW laser irradiation. The surface morphology of porous silicon was severely roughened proportionally to the increase in intensity of the laser illumination. From the observation in the partially enlarged transmission electron microscope (TEM) image of the interface of porous silicon and silicon substrate in the 2.0 mW laser-irradiated region, several nanocrystals in the linkage of the network structure are embedded in an amorphous phase.\textsuperscript{16} The diameter of the nanocrystals is estimated to be in the range of 2.5–3.0 nm.

The degree of inhibition is defined as $\varepsilon = (r_o - r_i)/r_o$, where the formation rate is $r_o$, the thickness of the porous silicon divided by the anodizing time is in the absence of an inhibitor (photon), and the rate $r_i$ is in the presence of an inhibitor. The degree of inhibition of the porous

![Figure 2. FE-SEM image of a transition zone between the un-irradiated region (left) and the irradiated region (right) formed in anodizing with the irradiation by a 2.0 mW He–Ne laser.](image)

![Figure 3. The FE-SEM and AFM images of the porous silicon layer formed during the 30-minute anodizing display the outside and inside of the laser-irradiated region at various intensities (0.5–2.0 mW).](image)
Table I. The formation rate and the photoluminescence of porous silicon formed by anodizing at 10 mA/cm² under various output powers of a He–Ne laser.

| Laser Power (mW) | Formation Rate (nm/min) | Degree of Inhibition (%) | PL Peak Wavelength (nm) |
|------------------|--------------------------|--------------------------|-------------------------|
| 0.0              | 252.0                    | N/A                      | 637                     |
| 0.5              | 19.2                     | 91%                      | 638                     |
| 1.0              | 10.8                     | 96%                      | 636                     |
| 2.0              | 5.6                      | 98%                      | 638                     |

Silicon at various intensities of the He–Ne laser beam is summarized in Table I, suggesting a directly proportional relationship. Figures 4a and 4b illustrate that higher power laser irradiation on the specimens during anodizing results in less thickness and greater roughness of the surface of the porous silicon layer.

The PL spectra of the porous silicon layers were measured by excitation with a He–Cd laser lamp (325 nm), as shown in Figure 4c. Whether the anodizing of silicon specimens did or did not receive irradiation from He–Ne lasers at various powers, their PL luminescence peaks appeared in the range of 636–638 nm.

According to the model of porous silicon formation, there are electrochemical 1 and chemical 2 and 3 reactions on the anode electrode (silicon):

\[
\text{Si} + 2\text{HF} + (2 - n)h^+ \rightarrow \text{SiF}_2 + 2\text{H}^+ + ne^- \quad [1]
\]

\[
\text{SiF}_2 + 2\text{HF} \rightarrow \text{SiF}_4 + \text{H}_2 \quad [2]
\]

\[
\text{SiF}_4 + 2\text{HF} \rightarrow \text{SiF}_6^{2-} + 2\text{H}^+ \quad [3]
\]

Several potential intermediate etching reactions are skipped here because they are complex and vary with photoelectrochemical conditions. It is interesting to follow up this research further, but this is not our present concern. From the electrochemical reaction in

![Figure 4](image_url)

**Figure 4.** The relationship between the power of laser irradiation and the thickness (a) and the surface roughness of porous silicon (b) and the photoluminescence response under UV irradiation (c).
Equation 1, holes are the key charge carriers for the formation of porous silicon. Although holes are the majority carriers in p-type silicon, a downward band bending at the surface (i.e. the interface of silicon and electrolyte) impedes the hole flow to the surface from the valence band. However, by applying a forward bias, the valence band holes can accumulate at the interface and then cross to dissolve silicon in HF. On the other hand, laser irradiation on the surface of p-type silicon causes the opposite effect. The surface band bending of p-type silicon is downward, leading to an energy barrier repelling the holes from the separation of pairs of electrons and holes by photon-excitation toward the bulk region, establishing a layer of hole depletion (electron accumulation) at the surface. The presence of the hole depletion diminishes the oxidation process and inhibits the growth of a p-type porous silicon layer.

In Figure 3, in the porous silicon layer formed in the irradiation by a 2.0 mW He–Ne laser, it appears that grain structure and the energy gap are increased by 80% (from 1.12 eV to 1.94 eV) because of the PL peak wavelength of 638 nm. The PL intensity of porous silicon increases as the irradiating power of the laser increases, as shown in Figure 4c. The most likely reason is the increase in the number of silicon nanocrystals. Another possible reason may be the thickness of the porous silicon layer, as thinning down to nanoscale allows the excited light to penetrate but not to be absorbed by the underlying porous silicon layer, as in the case of the outside thick porous layer. This mechanism may explain why the peak wavelength of the PL spectra is still in the range 636–638 nm when the PL intensity is increased by an increase in the laser power (i.e. the decrease of thickness). The fluoride ions’ attraction results in a rough surface (electron accumulation) at the surface. The presence of the hole depletion diminishes the oxidation process and inhibits the growth of a p-type porous silicon layer.

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