Communication—Effect of Free-Carrier Absorption on an Anodized Silicon Surface for Producing Dense and Uniform Nanocrystals

Benjamin T.-H. Lee and C. C. Chiang

Department of Mechanical Engineering, National Central University, Taoyuan City, Taiwan

The present study disclosed that free-carrier absorption (FCA) activated by 1310-nm laser irradiation caused a distinct effect on the formation of nanocrystals in the porous layer of $p^{++}$ silicon with the anodization less than 10 minutes. Under ultraviolet excitation, the photoluminescence peak locations are quite different in the irradiated spot ($\sim$535 nm) and in the normal porous silicon ($\sim$640 nm). In the irradiated spot, the intensity of the photoluminescence is at least 10 times higher than that of the peripheral porous silicon layer. This shows that the FCA effect provides an alternative way to produce dense and uniform nanocrystals.

Obviously, holes play a dominant role in the dissolution of silicon, which allows us to modify the porous structure directly by adjusting the current density, dopant/electrolyte concentration, and processing time. Controlling the number of holes by applying an appropriate illumination, the silicon atoms that dissolved on the bulk surface immersed in electrolyte could create a three-dimensional coralline-like structure filled with nanocrystals during anodization. These nanocrystals display the characteristics of quantum confinement behavior of photoluminescence for detection. Here, we demonstrate that the free-carrier absorption (FCA) produced by irradiation with a long-wavelength laser (>1100 nm) can modify the formation of $p$-type porous silicon in anodization.

The materials used were boron-doped and phosphorus-doped (100) silicon prime wafers (cut into $5 \times 5$ cm$^2$) with two resistivities: 1 to 10 $\Omega$ cm ($p$- and $n$- specimens) and 0.001 to 0.005 $\Omega$ cm ($p^{++}$ and $n^{++}$ specimens). Prior to anodization, all silicon specimens were cleaned using solutions of NH$_4$OH:H$_2$O$_2$:H$_2$O = 1:1:5 and HCl:H$_2$O$_2$:H$_2$O = 1:1:6, and then dipped into 1% HF for several seconds to remove native surface oxide. Electrochemical anodization was performed at a constant current density of 10 mA/cm$^2$ with a platinum cathode in the electrolyte (a mixture of 49.5% HF and 99.5% ethanol at 1:1 volume ratio). During anodization, we used a laser system equipped with a 1310 nm laser drive (max power = 7.0 mW) to create a 1.0-mm diameter light spot on the surface of the specimens.

In the anodization of $n$-type silicon, illumination that produces photogenerated holes is a way to carry out electrochemical etching. However, for $p$-type silicon, the effect of illumination is the opposite: inhibiting the formation of porous silicon because of photogenerated electrons from interband absorption, which forms the outflow of electrons canceling the holes at the interface of the specimen/electrolyte.

With illuminating the anodized silicon, there are two types of photon-absorption modes on the surface: interband (bandgap) absorption and FCA. In comparison with the interband absorption, FCA is a process that does not produce electron–hole pairs, instead, transferring the existing free carriers into another unoccupied, higher energy state in the same band or sub-band. The FCA coefficient, $a_{FCA}$, can be expressed as follows:

$$a_{FCA} = 1.8 \times 10^{-9} N \lambda^2,$$

where $N$ is the concentration of free carriers and $\lambda$ is the wavelength.

As is well known, FCA usually activates phonon scattering and has an unfavorable effect on the performance of electronic or optical devices, such as alteration of the refractive index. However, we report that FCA has an impressive effect on the formation of silicon nanocrystals in electrochemical processing. In general, the wavelength of photons is shorter than 1100 nm to meet the requirement of interband absorption for generating electron–hole pairs modifying the formation rate of the porous silicon layer. Because the onset is at 1100 nm where interband absorption is weak enough to result in FCA contributing to the total absorption of silicon, we used a 1310 nm laser to achieve the FCA effect on a silicon substrate, as shown in the experiment schematic illustrated in Figure 1a. The anodization was performed in a darkroom to compare directly the etching results between the irradiated region and the dark region under the same conditions.

We individually performed the anodization of $p^{++}$, $n^{++}$, $p$, and $n$-type silicon specimens at a current density of 10 mA/cm$^2$. Nevertheless, only the $p^{++}$-type silicon specimen exhibited a significant difference in etching result when the anodization time was <10 min, thereby focusing on the photoelectrochemistry of $p^{++}$ silicon with the laser power at 1.0, 3.0, and 7.0 mW. As the intensity of the irradiating laser was increased, the pore-aperture radius was wider, resulting in a rougher surface, as listed in the Table I of roughness vs. laser power. The thickness of the anodized silicon layers was inhibited to 1.6 $\mu$m (irradiated region) from 26.1 $\mu$m (dark region). With anodization time less than 10 min, the color of the laser-irradiated region was almost the same as bare silicon, but the outside region appeared black—the natural color of porous silicon. We propose that the mechanism is that hot holes created by FCA diffused laterally from the irradiated region and then dispersed into the dark neighboring region (Figure 1b). This is because the resistivity of the diffusion path is low enough to prompt hot holes directly into the neighboring region rather than into the electrolyte, which needs to transfer over the Schottky barrier, i.e., a downward bending of the band edges occurring at the interface of the silicon/electrolyte. Besides, the number of hot electrons (minority carriers) is fairly low, we can neglect the possibility of tunneling. 

\[Si + 2HF + (2 - p)h^+ \rightarrow SiF_2 + 2H^+ + pe^-\]

\[SiF_2 + 2HF \rightarrow SiF_6^{2-} + 2H^+\]

\[SiF_4 + 2HF \rightarrow SiF_6^{2-} + 2H^+\]

\[n-E-mail: benlee@ncu.edu.tw\]
Figure 1. Schematic principle of photoabsorption, energy band, and experiment diagram. The experiment schematic (a) shows the 1310-nm laser irradiating the surface of the anodized silicon substrate. Schematic for the Schottky barrier (b), a downward bending energy band near the interface of the silicon in an electrolyte solution, which pushes hot holes into the neighboring region rather than into the electrolyte despite the electric field.

effect of electrons to cancel holes. Once anodization time > 10 min, the color of the irradiating region quickly changed to black, revealing the formation of porous silicon. We interpret this phenomenon in the following way: the surface resistivity of the silicon was rapidly increased (typically > 10$^5 \, \Omega \cdot \text{cm}$) due to the formation of numerous nanocrystals. The high surface resistivity retards the diffusion of the hot holes, thereby enhancing the in-situ growth of the porous silicon. Although the 1310-nm laser might be absorbed by boron at a bandgap of about 0.56–0.71 eV in silicon, defects, or via two-photon-absorption processing, the inhibition effect still vanished after 10-min anodization. The time-limited result suggested that FCA is the most likely dominant factor.

After anodizing at 10 mA/cm$^2$ under irradiation of a 1310-nm laser (7 mW, 10 min), coralloid mesoporous structures appeared with many nanocrystals distributed on the surface, as shown in Figure 2. In Figure 3a, the photoluminescence (PL) peak positions were in the range of 535–545 nm (2.32–2.27 eV) in 10-min anodization and then was shifted to 650 nm (1.91 eV) when the anodization time was 30 min, the same as that in the dark region. The intensity of the PL peak at 545 nm (irradiated at 7 mW) was 10 times that at 650 nm (anodized in the dark). The emitting light from the laser irradiated region is green under the inspection of a 15 W fluorescent microscope, as shown in Figure 3b. It evaluates the size of nanocrystal to be about 2.3 nm according to the energy of the PL peak location by employing the following equation:

$$E_{PL}^\text{corr} = E_0 + \frac{3.73}{d^{1.39}} + \frac{0.881}{d} - 0.245,$$

where $E_0 = 1.17$ eV, the bandgap of bulk silicon, and $d$ is the diameter of the nanocrystal.

Conclusions

The effect of FCA changed the size of nanocrystals causing the shift of PL peak location from 640–650 nm to 535–540 nm under the same anodization condition. The narrow PL full width at half maximum (FWHM) and high PL intensity (> 10 times than anodization in the dark) display the highly uniform nanocrystals produced on the anodized surface. The FCA effect demonstrates an effective and sim-
Figure 3. The PL measurement of the anodized silicon layer irradiated by a 1310-nm laser at various intensities at a current density of 10 mA/cm² for 10 min. The PL intensity of the anodized layer (PL peak wavelength = 540–545 nm) increased by up to 10 times with an increase in the intensity of the 1310-nm laser at 7 mW as compared with that obtained in the dark (PL peak wavelength = 640 nm). (a) Using a 15 W fluorescence microscope to examine the anodized layer irradiated with a 1310-nm laser at 7 mW. (b) The laser-irradiated region emitted bright green light.

ple way to form nanocrystals directly on a silicon surface, which emit green light under UV excitation.

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ORCID

Benjamin T.-H. Lee ⓒ https://orcid.org/0000-0002-2493-7602

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