Forming a Photoluminescent Layer on Another Surface in the Dark through Lasering of N-Type Silicon in an Electrolyte

Heng-Chun Tai, Chao-Ching Chiang, and Benjamin Tien-Hsi Lee*  

ABSTRACT: Photoetching of n-type silicon induces a photoluminescent (PL) layer containing nanocrystals on the irradiated surface, usually through band gap absorption (wavelength <1100 nm). Here, we demonstrate the formation of a PL layer restricted to the backside surface, not the irradiated surface, by using a 1064 nm Nd:YAG laser. A nanoscale structure of the PL layer is achieved by merely modifying the electrolyte concentration without adding oxidants. To illustrate the working principle, we submit the hypothesis of a quasi-pn structure based on the theory of a quasi-Fermi level. Because of the “injection current” effect due to the quasi-pn structure, the hole current promoted by free-carrier absorption flows toward the backside surface, leading to anodization. This result is remarkable because anodization of n-type silicon is very hard to achieve with just an etchant in the dark.

INTRODUCTION

The characteristics of quantum confinement due to the nanocrystals formed in porous silicon (PS), have inspired numerous studies, especially on the visible photoluminescence (PL) observed at room temperature, which has potential applications in Si-based optoelectronic devices. As generally recognized in academic publications, electro-chemical etching with an applied bias is an effective and simple method for fabricating a PS layer and creating a PL layer. In this method, holes are the key to silicon etching in a hydrofluoric acid (HF)-based electrolyte during anodization. Therefore, according to common sense, it is quite difficult to etch n-type silicon in HF-based electrolytes via a bias process unless holes are generated by strong light irradiation, the addition of strong oxidants, or the creation of a p−n junction structure.

An alternative method to applying a bias is photoetching processing. This method is applied to n-type silicon by using a Xe light or laser with a wavelength shorter than 600 nm, allowing band gap absorption. An interesting result occurs during photoetching processing in an HF-based electrolyte: PL layers appear on the surfaces of both sides, the irradiated front side and the back side. The addition of an oxidizing agent, for example, KIO₃ or FeCl₃ to HF solution can eliminate the occurrence of the etching region on the backside surface because the addition of oxidizing (reducing) agents may increase the standard reduction potential in the positive (negative) direction. From etching results, it is observed that the measured PL and electroluminescence peak energies of the PS layer are in the range of 1.7−2.3 eV, enabling the potential application of the photoetching technique in fabricating Si photonic devices with embedded circuitry. Because of the absence of electrodes, the photoetching approach can also be applied to silicon-on-insulator materials and micromachined silicon-based devices. Adachi et al. described the n-type PS formation mechanism in an HF/oxidizing agent electrolyte with the aid of a surface energy−band diagram.

Here, we demonstrate a method without the addition of oxidizing agents for forming a PL PS layer on one side of a substrate by merely adjusting the concentration. Furthermore, we suggest a quasi-pn structure model based on the concept of the quasi-Fermi level to assess the working principle of photoetching on the back side of a substrate. Figure 1 shows the effect of the quasi-Fermi level formed by laser irradiation with anodization. For example, in the anodization of p-type silicon, the appearance of an n-quasi-Fermi level due to laser irradiation (Figure 1a) inhibits etching of silicon and the formation of a green PL layer (Figure 1b). In contrast, the p-quasi-Fermi level that appears with laser irradiation (Figure 1c) promotes etching of the irradiated region on n-type silicon, forming a yellow PL spot (Figure 1d).

We believe that the free-carrier absorption has a profound effect on anodization in photoetching, therefore, we propose...
the quasi-pn structure model. To verify the effect of the quasi-pn structure model, not band gap absorption, on photoetching, we employed a Nd:YAG laser (wavelength = 1,064 nm; penetration depth >1,000 \( \mu \text{m} \) for silicon) as the light source. A specimen thickness of less than 700 \( \mu \text{m} \) means that a very small fraction of the Nd:YAG laser can generate electron−hole pairs via band gap absorption. Hence, free-carrier absorption may trigger the flow of hot carriers as the main driving force of etching. By adjusting the electrolyte concentration, a PS layer was formed only on the backside surface, which was opposite to the abovementioned results obtained using an oxidant. Therefore, considering the rectification behavior when anodizing n-type silicon, the quasi-pn structure model is suitable for explaining the formation mechanism of the PS layer. According to this model, some of the holes excited by band gap absorption (explaining photoetching on the back side in the case of Xe light) may be driven to the back side, that is, the holes are driven to the back side (n-type), thereby promoting electrochemical etching of silicon and eventually forming a PL porous layer on the backside surface. The experimental results provide a novel finding—the PL layer and the laser-irradiated region are not on the same side—based on which the quasi-Fermi-level mechanism can be applied in the field of photoetching processing to extend the electrochemistry applications.

## EXPERIMENT

The examined silicon wafers (Wafer Works Corp., Taiwan) were 6\( ^\circ \), 650−700 mm thick, phosphorus-doped n-type \( \langle 100 \rangle \) CZ-grown silicon with a resistivity of 1−10 \( \Omega \text{cm} \) (\([P]\) = 5 \( \times \) 10\(^{12}\) to 5 \( \times \) 10\(^{15}\)/\text{cm}³). All wafers were cut into approximately 15 \( \times \) 15 mm\(^2\) specimens. After cleaning with RCA solution (NH\(_4\)OH/H\(_2\)O\(_2\)/H\(_2\)O = 1:1:5 in volume), the silicon specimens were immersed in the electrolyte and positioned at the bottom with a clearance of a few millimeters. The processing times were set to 0.5, 1.0, 2.0, 3.0, 5.0, or 12.0 h. All chemical solutions were of CMOS grade.

The electrolytes were the solutions of HF (49 wt %) and C\(_2\)H\(_5\)OH (95%) mixed at ratios of 2:1, 1:1, or 1:2 in volume. We mounted a Nd:YAG laser (Gentec-EO) on the optical platform fixture and adjusted the output power to 20 mW through a polarizer, as shown in Figure 2. Figure 2b displays the observation of a red-orange PL region on the back side following photoetching in an electrolyte (HF/C\(_2\)H\(_5\)OH = 2:1)
by irradiating a 1064 nm laser on the front side for 5 h; an etched point appeared on the back side.

The experimental process was performed in a dark room to prevent any light other than the laser from affecting the numerical reading of the laser power, thereby ensuring the quality and accuracy of the experimental data. Finally, a high-intensity UV lamp (100 W, UVP, B-100AP), a field emission scanning electron microscope (JEOL, JSM-7600F), and a PL spectrum analyzer (HORIBA, T64000) were used to confirm the photoetching results.

**RESULTS AND DISCUSSION**

The front side of the specimen is defined as the surface irradiated by the laser beam (1 mm in diameter), and the back side is the surface not exposed to the laser. We summarize the results of PL measurements (10 mW, 325 nm He-Cd laser) in Table 1, including the data of the PL peak location and full width at half-maximum (fwhm) and the estimated energy gap and nanocrystal diameter for all specimens. The data show that the photoetching results are different from those in existing publications. To evaluate the size of nanocrystals obtained by photoetching, we employed the following equation based on the energy ($E_{PL}^{corr}$) of the PL peak location

$$E_{PL}^{corr} = E_0 + \frac{3.73}{d^{3.33}} + \frac{0.881}{d} - 0.245$$

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

The anodization mechanisms by which photoetching triggers the etching behavior on the frontside and backside interfaces are different. Electrochemical etching occurs at the frontside Si/HF interface because of band gap absorption, resulting in electron–hole generation due to the Nd:YAG laser irradiation despite the low absorptivity (absorption coefficient). At the backside Si/HF interface, the occurrence of electrochemical etching can be explained by the forward-bias action of the quasi-pn structure that we propose. The concept of the quasi-pn structure is similar to the configuration of a photoelectrochemical device for solar water splitting but without a metal counter electrode or an external bias. Figure 3a,b demonstrates the Schottky junctions formed on both sides.

### Table 1. PL Peak Location and fwhm and Estimated Energy Gap ($E_g$) and Nanocrystal Diameter after Irradiation with a 1064 nm Nd:YAG Laser Beam at Various Times and Electrolyte Concentrations

| HF/C$_2$H$_5$OH | time (h) | PL peak (nm) | fwhm (nm) | $E_g$ (eV) | diameter (nm) |
|-----------------|----------|--------------|-----------|------------|---------------|
| 2:1             | 0.5      | 655          | 114.8     | 1.89       | 3.1           |
|                 | 1        | 572.4        | 178.8     | 2.17       | 2.49          |
|                 | 2        | 646.8        | 119.8     | 1.92       | 3.03          |
|                 | 3        | 562.3        | 184.6     | 2.21       | 2.43          |
|                 | 5        | 641.6        | 147.2     | 1.93       | 2.99          |
|                 | 12       | 604.1        | 248.7     | 2.05       | 2.7           |
| 1:2 (front side)| 0.5      | 666          | 120.9     | 1.86       | 3.19          |
|                 | 1        | 681.3        | 168.6     | 1.82       | 3.33          |
|                 | 2        | 686.3        | 146.2     | 1.81       | 3.37          |
|                 | 3        | 677.2        | 166.6     | 1.83       | 3.29          |
|                 | 5        | 568.5        | 167       | 2.18       | 2.47          |
|                 | 12       | 664.9        | 198.9     | 1.87       | 3.18          |
| 1:2 (back side)| 0.5      | 613.3        | 231.5     | 2.02       | 2.77          |
|                 | 1        | 664.9        | 155.4     | 1.87       | 3.18          |
|                 | 2        | 663         | 151.3     | 1.87       | 3.16          |
|                 | 3        | 687.3        | 128       | 1.81       | 3.38          |
|                 | 5        | 676.1        | 125.8     | 1.84       | 3.28          |
|                 | 12       | 675.1        | 167.4     | 1.84       | 3.27          |
| 1:1 (front side)| 0.5      | 666         | 126.9     | 1.86       | 3.19          |
|                 | 1        | 686.3        | 165.5     | 1.81       | 3.37          |
|                 | 2        | 687.3        | 146.1     | 1.81       | 3.38          |
|                 | 3        | 679.2        | 149.1     | 1.83       | 3.31          |
|                 | 5        | 567.6        | 167.4     | 2.19       | 2.46          |
|                 | 12       | 668         | 208.1     | 1.86       | 3.21          |
| 1:1 (back side)| 0.5      | 666         | 120.8     | 1.86       | 3.19          |
|                 | 1        | 664         | 111.7     | 1.87       | 3.17          |
|                 | 2        | 698.5        | 137.2     | 1.78       | 3.49          |
|                 | 3        | 642.7        | 136       | 1.93       | 3.3           |
|                 | 5        | 678.1        | 129       | 1.83       | 3.3           |
|                 | 12       | 678.1        | 121.7     | 1.83       | 3.3           |
of the silicon specimen before and after the specimen was immersed in the electrolyte. Figure 3c shows that the formation of the quasi-Fermi level induces a “forward bias” due to the free-carrier absorption.

When the HF/C₂H₅OH ratio was 1:1 or 1:2, electrochemical etching occurred on the frontside and backside Si/HF interfaces and dark etching points were formed. However, when the ratio was changed to 2:1, electrochemical etching occurred only on the backside Si/HF interface. After photoetching in the HF/C₂H₅OH = 2:1 electrolyte, an etched point slightly larger in diameter than the beam appeared only on the back side. Upon inspection of the photoetched point by the naked eye under ultraviolet lamp irradiation, red-orange light emission could be clearly seen (Figure 2b). The brightness of the excitation changed depending on the photoetching time. The brightest PL was observed for the 5 h photoetched specimen.

In this case, electrochemical etching did not occur on the irradiated frontside surface, in contrast to the cases of HF/C₂H₅OH = 1:1 and 1:2. The most likely reason is that when the volume ratio of HF and ethanol is changed, the redox level is also changed. Hence, once the HF concentration exceeds a critical value, for example, HF/C₂H₅OH = 2:1 in the case of regular n-type silicon, electrochemical etching of silicon does not occur if the hole concentration is not sufficiently high. Because of the low absorptivity of the 1064 nm laser, the hole concentration at the irradiated surface is predicted to be low because only a few electrons in the valence band can jump to the conduction band to generate holes.

Additionally, the reason for electrochemical etching on the backside surface is as follows. When n-type silicon is irradiated
with a Nd:YAG laser with a wavelength of 1064 nm, its free carriers absorb most of the photon energy and become hot carriers. Hence, the Fermi level is changed to a quasi-Fermi level when receiving the laser irradiation, as shown in Figure 3b. Because of the formation of the quasi-Fermi level, the irradiated n-type region is converted into a quasi-positive-type region, that is, a “p-type” region (Figure 3c). Here, a quasi-pn junction is formed between the frontside Si/HF interface (“p-type”) and the backside Si/HF interface (n-type). The hot electrons formed through the free-carrier absorption effect cause a current to flow from the n-type to “p-type” regions (quasi-forward bias). In other words, the forward bias leads to an increase in the number of holes in a region near the backside Si/electrolyte interface. With an increasing irradiation

Figure 5. SEM images of the surfaces of silicon specimens photoetched at an electrolyte concentration of HF/C₂H₅OH = 2:1. Etching occurred on the back side.

Figure 6. SEM images of the surfaces of silicon specimens photoetched at an electrolyte concentration of HF/C₂H₅OH = 1:1. Etching occurred on both sides after 2 h (a,b) and 12 h (c,d).
time, the continuous increase in the number of holes breaks Si/Si bonds on the surface. The strong electropositivity induced by the increased number of holes also promotes the bonding of fluorine ions to the formed dangling bonds of silicon by repelling hydrogen ions, thereby decomposing the passivated silicon surface. Therefore, the formation of Si/F bonds first and then H2SiF6 clusters begins the electrochemical etching and PL PS layer formation. 21 The photoetching reaction by the 1064 nm laser produces PL PS layers on both sides if HF/C2H5OH = 1:1 or 1:2; otherwise, a PL PS layer appears only on the back side, as shown in Figure 4.

The SEM observations of the surfaces of silicon specimens photoetched under various electrolyte conditions are summarized in Figures 5−7. In the SEM images for HF/C2H5OH = 2:1, when the etching time was 30−60 min, the etching region had a small sheet-like structure, as shown in Figure 5a. With an increasing photoetching time, the number of sheet-like structures increased, and some gradually peeled off. When the photoetching time reached 3 h, new trenches were observed in the sheet-like structure (Figure 5b). When the photoetching time was 5 h, the original sheet-like structure disappeared, resulting in a new trench and sheet-like structure (Figure 5c). When the photoetching time reached 12 h, new grooves and sheet-like structures occurred in the original sheet-like structure (Figure 5d). The photoetching reaction resulted in the cyclic formation and etching of a trench and sheet-like structure. The other two cases had similar results, and their SEM images (of both the front and back sides) are shown in Figures 6 and 7.

■ CONCLUSIONS

According to the PL measurements, when the volume ratio of the solution is HF/C2H5OH = 2:1, the average size of the nanograins (usually >3 nm) is variable with lasering time. When the volume ratio is 1:1 or 1:2, on both the laser-irradiated and non-laser-irradiated sides, the average size of the nanocrystalline grains is also usually >3 nm. In short, the redox level affects the location of the formed nanocrystals and their size. The concentration effect of the electrolyte on photoetching by the 1064 nm laser produces PL PS layers on both sides if HF/C2H5OH = 1:1 or 1:2; otherwise, the PL PS layer appears only on the back side. The repeatability of the experiment is excellent, despite not having current density control by an applied bias. The hypothesis of the quasi-pn-structure mechanism provides a valid explanation for the occurrence of silicon etching on the back side while it is not being irradiated. The driving force of holes flowing to the backside interface involved in photoetching is provided by free-carrier absorption or efficient band gap absorption (wavelength <600 μm). There is room for further investigation of the injected current density causing electrochemical etching.

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Notes
The authors declare no competing financial interest.

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