Sharpening Si Nanocrystals on the Bulk Surface by Nanoscale Electrochemistry through Controlling the Hole Current with the Irradiation of Near-Infrared Laser

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Numerous Si nanocrystals on the bulk surface can be efficiently sharpened by a HF-based electrochemical etching with the irradiation of near-infrared (NIR) laser simultaneously. Under the NIR laser-irradiation, the electrons excited from the B-Si complex inhibited the growth of the anodized layer and promoted the formation of nanocrystals by controlling the number of holes that participate in anodization. The effect of NIR laser-irradiation enhanced the photoluminescence by 7–10 times as compared to that obtained when anodization was performed in the dark for growing a normal porous silicon. The transmission electron microscopy images showed clearly that nanocrystals (<3 nm) were embedded at the interface of the bulk surface and the anodized layer.

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Recently, Si nanocrystals have gained immense attention owing to their application in fabricating photonic devices.1–3 Much research has been conducted on the synthesis of Si nanocrystals in certain matrices through crystallization of Si clusters inserted by ion implantation,1 colloidal,4,5 electrochemistry,6 and sol-gel processing7 methods; however, studies on the use of nanoscale electrochemistry focused on the thickness of anodized layer for synthesizing Si nanocrystals are scarce. Here, we demonstrate a simple method, anodization under the thickness of anodized layer for synthesizing Si nanocrystals are scarce. Here, we demonstrate a simple method, anodization under the irradiation of NIR laser, sharpening Si nanocrystals with the crystal orientation identified with bulk Si embedded at the interface of the anodized layer and the bulk surface. It is well-known that anodization8 can produce pores or cylindrical cavities in the anodized layer on the Si substrates, usually referenced as porous silicon, which are made use of in many opto-electronic, biomedical, and MEMS applications.9–13 Our study reveals the anodized layer displays some outstanding features such as extremely high intensity of photoluminescence (PL) while the layer thickness is confined within the range of nanometers. Pavesi et al.14 put forth a relationship between the PL intensity and the number of the excited nanocrystals, \( N^* \): \[ PL \propto N^*/\tau_R \], where \( \tau_R \) is the radiative lifetime. In the absence of some lattices in bulk silicon caused by HF etching during anodization, Si nanocrystals are formed within the Si columns present in the anodized layer through the formation of crystal blocks15 while the pore walls are a few nanometre thick.16,17 In electrochemistry, holes dominate the dissolution of Si via anodization to form porous structures.18 Hence, controlling the hole current allows us to modify the structural details such as pore size or layer depth directly by adjusting the current density, substrate resistivity (dopant/electrolyte concentration), and electrolyte concentration. It is generally observed that the laser-irradiation promotes etching on the anodization of n-type Si.19,21 However, laser-irradiation exhibits an opposite effect for p-type Si because of the generation of a hole-depletion region on the surface owing to the downward bending energy band at the interface of the hydrofluoride (HF) electrolyte. Several studies6,10,22,23 have investigated the inhibition phenomenon by using 100–700 nm laser light. However, the use of near-infrared (NIR) lasers (750–2000 nm) is rare owing to the extremely low absorption coefficient of Si. Here we found that the use of a NIR laser (830 nm) can excite electrons from silicon-boron (Si-B) complexes to selectively resist the dissolution enforced by anodization, which then sharpens the Si nanocrystals displaying the characteristics of quantum dots.18 Although an 830 nm NIR laser (having a reflectivity of 32%, an absorption depth of 15 \( \mu \)m, and an absorption coefficient of \( 7 \times 10^4 \text{ cm}^{-1} \)) displays weak photo-absorption under normal anodization, in the study of heavy boron doped silicon, we found that the thickness of the anodized layer on heavily boron doping Si was still reduced to a few nanometres.

The experimental setup illustrated in Fig. 1a shows the irradiated spot at the center of the specimen. In the designed system, the irradiated and non-irradiated (dark) regions were obtained simultaneously under the same electrochemical conditions for direct comparison. Since the anodized layer in this study was few tens of nanometres thick, the following chemical equations can be used to explain the model for Si dissolution, which occurs mostly at the interface between the bulk surface and the electrolyte: 18,23

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

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

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

In a HF-based electrolyte solution, a downward bending energy band occurs in the vicinity of the interface of p-type Si, which is an impediment for the generation of holes.18 In other words, the number of holes is reduced via the electron-hole recombination with the electrons excited by the laser absorption, as shown in Fig. 1b. Hence, the irradiation of laser suppresses the growth of the anodized layer. In general, there are three mechanisms24 by which electrons are generated by laser absorption: intrinsic (band-to-band), extrinsic (impurity level-to-band), and free-carrier absorption. In the present study, the effect of free-carrier absorption was neglected because the laser wavelength was not sufficient long (<1.0 nm).24

Materials and Methods

We used B-doped, p-type single-crystal (100) Si wafers that were pre-cut into 5 cm × 5 cm sections with resistivities of 1–10 \( \Omega \) cm for p+ Si specimens \([B]= (1.34–14.6) \times 10^{15}\text{cm}^{-3}\) and 0.001–0.005 \( \Omega \) cm for p++ Si specimens \([B]= (5–10) \times 10^{17}\text{cm}^{-3}\). Prior to anodizing, all the Si specimens were cleaned at 80 °C in the following solutions: \( \text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 1:1:5 \) and \( \text{HCl:H}_2\text{O}_2:\text{H}_2\text{O} = 1:1:6 \). After cleaning, we removed the native oxide layer on the Si sample by briefly dipping in HF solution prior to anodization. The electrochemical anodization was performed at a constant current density of 10 mA/cm² with a platinum cathode in the electrolyte (mixture of 49.5% HF and 99.5% ethanol in a 1:1 volume ratio). During the anodization, an optical system from the NIR laser (830 nm; maximum power = 5.0 mW) created a spot of light having a diameter of 1.0 mm at the surface of the specimens.

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Results and Discussion

To investigate the effects of laser-irradiation on anodization, the power of the laser was increased from 1.0 to 5.0 mW in the steps of 1.0 mW while maintaining a constant current density of 10 mA/cm² for 10 min. After the anodization, the dark region exhibited the typical color of porous Si, while the irradiated region retained its original...
Table I. The formation rate (nm/minute) and degree of inhibition (%) of the porous Si at two B doping levels under various output powers of the near-IR laser during electrochemical etching for 10 min. The degree of inhibition on the \( p^+ \) and \( p^- \) specimens approaches closer at higher laser intensities.

| laser power (mW) | boron concentration | formation rate of anodized layer (nm/minute) | degree of inhibition (%) |
|------------------|---------------------|---------------------------------------------|--------------------------|
| \( p^+ \) (0.5–1) \( \times 10^{20} / \text{cm}^3 \) | 1.0 | 35 (90%) | \(< 0.2 \times \) |
|                  | 2.0 | 14 (96%) | \(< 0.2 \times \) |
|                  | 3.0 | 10 (97%) | \(< 0.2 \times \) |
|                  | 4.0 | 7 (98%)  | \(< 0.2 \times \) |
|                  | 5.0 | 0.2 < (100%) | \(< 0.2 \times \) |
| \( p^- \) (0.13–1.46) \( \times 10^{16} / \text{cm}^3 \) | 1.0 | 72 (72%) | \(< 0.2 \times \) |
|                  | 2.0 | 48 (82%) | \(< 0.2 \times \) |
|                  | 3.0 | 42 (84%) | \(< 0.2 \times \) |
|                  | 4.0 | 25 (90%) | \(< 0.2 \times \) |

bright color. The anodized layer was examined using a UV lamp (Fig. 2a, top) and a fluorescence microscopy (15 W, 325 nm; Fig. 2a, bottom). The irradiated region emitted a bright yellow light, while the rest of the anodized layer appeared dark. From the field-emission transmission electron microscopy images shown in Fig. 2b, it can be clearly observed that a transition zone appeared across the irradiated and dark regions, and the depth of the anodized layer varied with the two-dimensional intensity profile of a Gaussian beam. The cross-sectional pictures of the laser-irradiated spot obtained by transmission electron microscopy (TEM) showed that the anodized layer (amorphous region) was a few nanometres thick at the center (Fig. 2c). Furthermore, near the rim of the laser irradiated region, Fig. 2d shows a number of Si nanocrystals (< 3.0 nm) embedded at the interface of the bulk surface and anodized layer in an amorphous matrix inside the irradiated region. The creation of an amorphous matrix may be because of the formation of micro-porous Si. We believe that the production of individual crystalline fragments forming nanocrystals is because of the excitation of Si-B complexes by laser-irradiation.

Figure 4. The PL measurement of the anodized Si layer irradiated by a NIR laser at varied intensities at a current density of 10 mA/cm² for 10 min. The PL intensity of the anodized \( p^- \) Si layer increased by up to eight times with an increase in the intensity of the NIR laser as compared to that obtained in the dark (a), the increase in the PL intensity of the anodized \( p^+ \) Si layer was 20% more than that of the \( p^- \) Si layer and 1,000% more than that obtained in the dark region under the same anodizing conditions (b), laser-irradiation at various intensities did not alter the PL peak locations when a constant current was applied. However, a change in the magnitude of the applied current changed the PL peak locations in the irradiated region (c).
resulting in the emission of electrons, which resist the Si dissolution enforced by the hole current.

The depth of the anodized layer was reduced with an increase in the intensity of the laser, as shown in Fig. 3a. The significantly reduction of the anodized layer in the laser-irradiated region should not be due to the over-etching by an increased temperature or electropolishing. Because the large thermal reservoir formed by the HF-based electrolyte could keep the constant temperature. No boiling or bubbles was observed in the laser-irradiated region during the anodization. The applied current density was not sufficient high for electropolishing and the laser irradiation did not increase the number of holes but electrons. Moreover, the top surfaces of the anodized layers in the irradiated and dark regions were continuous, straight, and flat to show the inhibition effect on the growth of anodized layer. By the observation of atomic force microscopy (AFM), the surface roughness of anodized layer increases with the enhancement of the power of the incident laser as shown in Figure 3b. The surface roughness of the laser-irradiated region in the p+ sample is much higher than that in the p++ sample after anodization. In the dark regions, the depths of the anodized layer, i.e., the porous layers, formed under the same anodizing conditions were 3,500 and 2,600 nm for the p++ and p+ Si specimens, respectively. The morphologies of the anodized layer formed in the dark (Fig. 3c) and laser-irradiated regions (Figs. 3d and 3e) were compared. Figure 3e clearly shows that the NIR laser-irradiation increased the number of nano-sized Si blocks present on the anodized layer. Table 1 compares the degree of inhibition (%) for the anodized layer in the p− and p++ Si specimens. It was revealed that the inhibition was higher in the p++ specimens at lower laser intensities.

However, when the laser intensity increased beyond a critical value, the degree of inhibition was found to be almost the same in both the specimens (when the anodization was complete). This result indicates that the discharge of additional electrons from B acceptor levels (∼0.56–0.71 eV in Si23) was initiated by extrinsic absorption. The discharged electrons were then spontaneously accelerated toward the interface by the downward bending band, which then resulted in electron-hole recombinations. The laser-irradiation could not ionize the Si-B complex because the temperature was not sufficiently high. Thus, we can conclude that at lower laser intensities, the dominant factor for controlling the inhibition is extrinsic absorption.

For the p− Si specimen, laser-irradiation not only inhibited the growth of the anodized layer but also increased the photoluminescence (PL) by eight times as compared to that obtained during anodization in the dark, as shown in Fig. 4a.

The increase in PL intensity for the p++ Si specimen was 20% more than that for the p− Si specimen under the same NIR laser-irradiation anodizing conditions (Fig. 4b). This indicates that the extrinsic absorption in the p++ Si specimen increases its PL intensity without altering the PL peak location (i.e., wavelength). However, the magnitude of the applied current density changed the PL peak location in the irradiated region, as shown in Fig. 4c. It is because the current density changes the size of Si nanocrystals by modifying their pore sizes. In addition, micro-Raman spectroscopy at an excitation wavelength of 532 nm was used to characterize the Si nanostructures in terms of the wavelength and intensity of the excitation beam.26 For monocrystalline Si, the Raman spectrum is symmetric, and its first-order peak shifts by 520.5 cm−1.27 In the p− Si specimen, most of the incoming laser light was absorbed intrinsically not extrinsically. The slight shift in the Raman spectrum (<1 cm−1) with laser-irradiation at varying intensities implies that the laser intensity influenced the thickness of the anodized layer more than the size of the Si nanocrystals, as shown in Fig. 5a. However, the change in peak locations in the Raman spectrum of the p++ Si specimen, as shown in Fig. 5b suggests that the extrinsic absorption affects the size of the Si nanocrystals directly.

In the region where the intensity of the laser beam irradiating the p++ Si specimen was high, the Raman peak was observed at 520.5 cm−1. This peak can be attributed to the fact that the thickness of the anodized layer is too low to avoid disturbances from the underlying Si substrate. In consideration of the Raman-scattering profiles of the monocrystalline Si, we found that the longitudinal spectrum around 520.5 cm−1 exhibited a dip or anti-resonance on the high Raman-shift side and broadened asymmetrically toward the low Raman-shift side. The asymmetry displays a continuous enhancement and gradual shifting of the characteristics of the Fano line shape28 on increasing the NIR laser intensity at a given current density. The measurement results may be interpreted by the interaction of a continuum of electronic states and the optical phonon response2 amongst the Si nanocrystals in the anodized layer. According to the formula PL ∝ Nvτk,14 we suggest a potential mechanism for improving the PL intensity: nanoscale thickness driven by nanoscale electrochemistry in the control of hole current increases the number of nanocrystals that interact with the surrounding amorphous Si matrix and the Si substrate that produces superior photosensitive and photovoltaic properties.29 Figure 2d confirms that the anodized layer is an assembly of Si nanocrystal spheres and an amorphous phase.30,31 Compared with a 633 nm laser,2 the inhibition effect of the 830 nm laser on the anodization is weaker due to the lower absorption in silicon. However, the PL peak locations were the same (635 nm) even though the wavelength of the incident laser was different. It might be inferred from these results that the wavelength of the incident laser does not obviously change the size of nanocrystals, but the current density of anodization does. The PL intensity is increased by enhancing the inhibition degree on anodization.
through higher laser absorption (shorter wavelength or higher intensity). The most notable feature in the laser-irradiated region is that the thinner anodization layer includes more nanocrystals (i.e., higher PL intensity).

Conclusions

The study points out the effect of extrinsic and intrinsic absorption on Si during the electrochemical processing driven by a NIR laser. We demonstrated that a NIR laser can drive the nanoscale electrochemistry of Si through extrinsic and/or intrinsic absorption to control the number of holes by recombination with the excited electrons. The thickness of the anodized layer was confined to a few nanometres, which enhanced the PL intensity greatly. The as-anodized layer in the irradiated spot was much thinner and rougher than that in the dark region, thus resulting in easy sharpening of Si nanocrystals with identical crystal orientation embedded in the anodized layer. It is a simple route to multiply the PL intensity of Si nanocrystals with identical crystal orientation embedded in the anodized layer. It is a simple route to multiply the PL intensity of Si nanocrystals with identical crystal orientation embedded in the anodized layer. The numerous Si nanocrystals confined within the nanoscale anodized layer trigger a uniform and high PL intensity, which can further be considered for the synthesis of a reliable active layer for fabricating a Si-based laser.32

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