The enhancement of photoluminescence of n-type porous silicon by Hall-effect assistance during electrochemical anodization

Jia-Chuan Lin a,*, Wei-Chih Tsai b, Po-Wen Lee c

a Department of Electronics Engineering, St. John's University, 499, Section 4, Tam King Road, Tamsui, Taipei 25135, Taiwan, ROC
b Institute of Microelectronics, Department of Electrical Engineering, National Cheng Kung University, Taiwan 70101, Taiwan, ROC
c Institute of Material Science and manufacturing, Chinese Culture University, Taipei 11114, Taiwan, ROC

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Abstract

In this study, n-type porous silicon (n-PS) films with high-aspect-ratio Si-tips are formed with the assistance of Hall-effect during the electrochemical anodization. Lorentz force sweeps down the majority carriers (electrons) in n-type Si to enhance the anodization etching. Surface layers are inverted from n-type to p-type, so sufficient holes can continuously appear on the surface to participate in chemical reaction during the etching process. Illumination is not necessary in this process, so the problem of illumination-depth limitation is solved. The etching current, morphology, and photoluminescence of the n-PS prepared in this way are investigated. Strong visible photoluminescence emissions at room temperature are demonstrated on n-PS.

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1. Introduction

Porous silicon (PS) structures consisting of many pores and pillars are widely used to yield efficient photoluminescence (PL) or electroluminescence (EL) at room temperature [1,2]. Many PS-based optoelectronic devices have been researched [3–6]. The PS formation techniques have been developed, including electrochemical anodization [7–9], stain etching [10–12], spark-erosion [13] and vapor etching technique [14,15]. Among them, electrochemical anodization is the most commonly used.

The electrochemical anodization etching is performed in a hydrogen fluoride (HF) solution. The etching rates are controlled by adjusting the electrolyte compositions and etching current densities. It is well known that the etching current is governed by the hole accumulation (or generation) at the Si surface to assist anodic oxidation during the electrochemical etching.

For p-type Si, the holes are the majority charge carriers, so the p-type PS (p-PS) layers are fairly easily produced. Conversely, n-type PS (n-PS) is very difficult to form, as a result of the lack of holes. Previously, most of the research done on the PL of PS has been made on hole-rich p-type Si. Yet, the utilization of n-PS is also important for the applications on n-substrate based light emitting diode (LED) technology and microelectronic technology [16,17]. It is well known that the etching rates are controlled by adjusting the electrolyte compositions and etching current densities. Furthermore, etching current is governed by the hole concentration (accumulation) in the adjacent regions of HF electrolyte and Si atoms to assist anodic oxidation during the electrochemical etching.

Up till now, to get an n-PS, illumination has still been the popular way (even indispensable way) to generate the holes required in the electrochemical etching process on the hole-poor n-type samples [18,19]. Yet the actual photo-energy absorbing by Si atoms is very sensitive to...
the illumination-source intensity and electrolyte environment, and the conditions are not constant in the process. Since the illumination intensity is related to the distance, besides the absorption coefficient and the wavelength, only top-layer atoms are photo-excited and only the surface layers under illumination generate the electron-hole pairs. The etching rate will gradually decrease with depth from top- to bottom- layers because the illumination is very difficult to reach the deeper layers. Therefore, cone-shape pores in PS structures are often formed in this way [9]. In other words, the only-illumination-assisted etching approach is depth-limited. The illumination related factors and limitation may affect the PS morphology and formation. A cone-shape PS structure is often formed.

In this paper, an alternative hole-assistance way (named as Hall-effect-assisted way) is proposed to enhance the PL on n-PS without any illumination. In the Hall-effect-assistance way, the hole supplying is generated from the carrier sweeping by Lorentz force. The inversion layer (from n-type to p-type) is created on the upper layers. Besides, the illumination-free etching container can be well designed as a hermetic container with a strong cover for the safety of handling corrosive HF electrolyte.

It is interesting that a sharpened pyramid Si-tips are obtained. In our study, the Si-tips are well-aligned and straight. It is known that the Si-tips are of particular interests on their high-aspect ratio and unique electronic properties. Such properties are helpful to Si-based field emission devices [20,21]. Many methods have been developed for synthesis of Si-tips, such as laser ablation [22], physical evaporation [23], reactive ion etching [24], oxide-assisted growth [25], and chemical vapor deposition growth [26]. In this article, the Hall-assisted way proposed can also be served as a simple way of Si-tips formation. Most importantly, a strong PL phenomenon appearing on the n-type Si-tips is very similar to the PL on p-PS in our study.

2. Experimental

The schematic diagram of the experimental setup for preparing n-PS is given in Fig. 1a. First, the main body of the HF electrolyte container is made of Teflon materials. A mixture of HF: C₂H₅OH = 1:1 is utilized as the etching solvent here. The apparatus is designed with a vertical arrangement. The sample is face-up so as to easily remove the hydrogen bubbles from the PS surface. No illumination equipment is needed in our process design. The PS samples are prepared on n-type Si (100). A Si wafer with copper (Cu) contact is served as anode, while cathode is made by platinum (Pt). A sintered aluminum (Al) film is used to form an intimate backside ohmic contact to Si sample prior to the etching process. The electrochemical anodization processes are exposed to the Hall-effect-assisted environment. A lateral electrical field (a voltage \( V_x \)) with the indium-contact is biased on the samples in \( x \)-direction and makes a current \( I_x \). In \( y \)-direction, a magnetic field \( (B_y) \) is placed perpendicular to the current \( I_x \). Charge carriers flowing in the \( x \)-direction will experience a Lorentz force \( (F_z = qE_z = qV_x \times B_y) \), as indicated in the Fig. 1. The majority carriers (electrons) are swept down by \( F_z \). A Hall voltage \( (V_{1H}) \) across the semiconductor is built in \( z \)-direction. By applying a sufficiently large bias-voltage and a magnetic field density, the upper layers of the semiconductor are depleted and then inverted from an n-type to a p-type semiconductor. Enough holes can reveal on the upper layers to participate in chemical reaction during the etching process. The schematic mechanism is plotted in Fig. 1(b).

The illustrative equation of the overall process during PS formation can be expressed as follows:

\[
\text{Si} + 2\text{HF} + 2h^+ \rightarrow \text{SiF}_2 + 2\text{H}^+
\]
\[
\text{SiF}_2 + 4\text{HF} \rightarrow \text{H}_2 + \text{H}_2\text{SiF}_6
\]

The etching rate is determined by the hole accumulation in the adjacent regions of the HF electrolyte and Si atoms. It can be found that the hole accumulation increases with the magnetic field. A stronger magnetic field will cause a larger Lorentz force \( (F_z = qV_x \times B_y) \) and Hall voltage. So a larger hole concentration will be produced on upper layer that causes a stronger etching effect. The magnetic field controls the hole accumulation, PS formation, and etching effect. By adjusting the magnitude of the correspondent magnetic field and voltage, sharpened Si-tips can be fabricated.

3. Results and discussion

Since \( F_z = qV_x \times B_y \), different PS structures reflect differences in the magnitude of the correspondent magnetic field and voltage. Electro polishing occurs for high magnetic field and voltage. At lower magnetic field and voltage, the dissolution process is changing and PS layer is formed. By adjusting the magnitude of the correspondent magnetic field and...
voltage, sharpened Si-tips can be fabricated. Under a vertical anodization voltage of 30 V, Hall-effect assistance with a magnetic field \( (B_z) \) of 10 mT and a voltage \( (V_x) \) of 30 V, which are the optimum conditions successfully support the etching process without any illumination sources. The top view and cross-section scanning electron microscope (SEM) images of the PS sample are shown in Figs. 2a and b, respectively. A larger voltage drop across the \( x \)-direction will cause a larger gradient-situation of etching extent of PS. To clearly show the gradient-situation for further investigation, a larger \( V_x \) is adopted in this study. If a uniformed PS film is needed, a small bias voltage \( (V_x) \), a small device area, or rotating Hall-effect apparatus are advised to solve this non-uniformity problem. Four regions (A, B, C and D) are defined on the sample for article describing, as shown in Fig. 2. The PS films have high-aspect-ratio Si-tips because the hole-supplying mechanism is bottom-up. The mechanism is different from the conventional illumination-assisted method. In conventional way, the hole generation only relies on the illuminated surface atoms.

All the Si-tips are vertical align to the substrate surface. The heights of Si-tips are about 78 \( \mu \)m (region A), 50 \( \mu \)m (region B), 31 \( \mu \)m (region C) and 16 \( \mu \)m (region D), respectively. Their diameters are 22 \( \mu \)m (region A), 18 \( \mu \)m (region B), 16 \( \mu \)m (region C) and 11 \( \mu \)m (region D), respectively. Fig. 2c shows the schematic of the tip height and distribution for the four regions. The experiment results are helpful to understand the variation of morphology under different etching conduction and extent.

Fig. 3 shows the variation in time of anodization current under a constant voltage of 30 V. With the hole-effect-assistance on n-Si (case-1), the curve tendency of anodization current is very similar to that on p-Si (case-2) that is fairly different to conventional n-Si without any hole-assistance (case-3). The increasing tendencies with time in case-1 and case-2 are resulted from the successful processing of chemical reaction which produces the hole drift current as well as the thinning down of bulk-Si layers which decrease the total resistances. The total resistance of the galvano-circuit can be express as follows:

\[
R_{\text{total}} = R_{\text{electrolyte}} + R_{\text{measurement-system}} + R_{\text{etched-layer}} + R_{\text{bulk-Si-layer}}
\]

In case-1 and case-2, the etched layers that are formed with slim Si-tips let the electrolyte among the tips serve as the major conducting path. Therefore the dominant variation of total resistance \( (R_{\text{total}}) \) is the term of bulk-Si layer \( (R_{\text{bulk-Si-layer}}) \) and hence the current will increase with the decreasing of \( R_{\text{bulk-Si-layer}} \). However, in case-3, the chemical reaction cannot keep going for the lack of holes. Slight etching forms some narrow pore and Si-pillars. The
Fig. 3. The variation in time of anodization current: the hole-effect-assistance on n-Si (case-1), conventional p-Si (case-2) and conventional n-Si without any hole-assistance (case-3).

Fig. 4. (a) The PL spectra from A to D regions of n-PS samples and (b) the naked-eye photos of the n-PS samples under normal light (left side figure) and UV light (right side figure) at room temperature.
resistances of Si-pillars are larger than that of bulk-Si-layer ($R_{\text{etched-layer}} > R_{\text{bulk-Si-layer}}$), so the dominant variation of $R_{\text{total}}$ is the changing from $R_{\text{bulk-Si-layer}}$ to $R_{\text{etched-layer}}$. Such situation is different from case-1 and case-2. As to the initial-state points (time = 0) of current, a drop from 0.80 A (case-3) to 0.33 A (case-1) results from the electron depletion by Hall-effect on the surface layer in n-Si and hence the increasing of $R_{\text{bulk-Si-layer}}$.

In conventional illuminated n-PS, after surface pores (of few µm) are formed, photo-energy is not completely received by the deeper layers. Therefore, the deeper layers are difficult to form the required PS in the darkness [27]. Only a thin part of PS layer contributes in the PL. In our method, the visible luminescence of the n-PS is similar to the hole-rich p-PS.

An excitation wavelength of 325 nm from a He–Cd laser is used for the PL measurements. Fig. 4a are the PL spectra of A–D regions under the Hall-effect assistance ($B_y = 10$ mT and $V_x = 30$ V). Fig. 4b shows the naked-eye photos of the PS samples under normal light (left-side figure) and ultraviolet (UV) light (right-side figure) at room temperature. Obviously, the PS sample produces a strong emission of orange-red luminescence under UV illumination. The PL intensity is inversely proportional to the size of Si-tip that appears on A–D regions gradually. The high PL intensity in region D can be attributed to its small size of tip-width. The results consist with the quantum confinement theory [28]. In the quantum confinement model, the visible PL phenomenon is explained by the changes of the Si band structure when dimensions are reduced to the nano-scale size [2,29].

4. Conclusions

In conclusion, a new electrochemical anodization way for the enhancement of PL on n-PS with Hall-effect assistance is proposed. The etching processes are anisotropic and hence the sharpened Si-tips are self-aligned and straight. It is useful for the fabrication of Si-tips by an easy electrochemical anodization way under normal temperature without any deposition method. In addition, a gradient intensity of PL can be controlled by lateral electric field on an identical sample. A strong visible light is obtained on n-PS at room temperature. It is concluded that the PL emission on n-Si can be drastically enhanced by Hall-effect-assisted method.

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References