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Author(s)	Sato, Taketomo; Mizohata, Akinori
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Photoelectrochemical Etching and Removal of the Irregular Top Layer Formed on InP Porous Nanostructures

Taketomo Sato^z and Akinori Mizohata

Research Center for Integrated Quantum Electronics (RCIQE), Hokkaido University, Sapporo, 060-8628, Japan

A photoelectrochemical (PEC) process was developed to remove the irregular top layer from InP porous nanostructures. After anodic formation of a nanopore array, the PEC process repeated in the same electrolyte under illumination. The etching rate of the pore surfaces was strongly associated with their structural properties, being greater in the irregular top layer. The irregular top layer was completely removed by monitoring and controlling the anodic photocurrents in the ramped bias mode.

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A lot of research has been devoted to producing high-density arrays of nanostructures due to both their applications to future quantum electronic and optoelectronic devices and to downsizing chemical and biochemical sensors.¹ The porous structure formed by the electrochemical anodic process is one of the more promising building-block candidates of the aforementioned devices. The porous alumina made from aluminum films has particular promise^{2,3} because of its unique nanohole array structures, which are formed in a self-organized manner, and has been used as a template for various devices. The direct formation of porous structures has also been reported on semiconductor materials such as Si,⁴⁻⁶ GaAs,^{7,8} GaP,^{9,10} InP,¹¹⁻¹³ GaN,¹⁴ and CdSe.⁸ The structural properties and their tunability have been intensely investigated on III-V materials in an effort to improve electrical and optical properties.

We recently succeeded in anodically forming arrays of straight nanopores on n-InP(001) substrates.¹⁵⁻¹⁷ The nanopores were laterally separated by InP nanowalls several tens of nanometers thick and formed in a straight vertical direction greater than several tens of micrometers. We previously reported that pore diameter and wall thickness can be controlled by adjusting the electrochemical anodic and cathodic conditions.¹⁷ However, a disordered irregular layer usually forms during the initial stage of pore formation and partly remains on top of the ordered porous layer. Because this irregular layer has a thickness in the range from a few hundred nanometers to several micrometers, it degrades electrical and optical properties. Thus, complete removal of the irregular top layer has been one of the key issues in wide application of porous nanostructures for semiconductor.

We report here on a photoelectrochemical (PEC) process developed to completely remove the irregular top layer from the InP porous surfaces. The PEC process can be repeated continuously after porous structures are anodically formed in the same electrolyte. Our present approach is much simpler and more controllable than other methods such as dry etching and conventional chemical etching.

Our PEC process is schematically shown in Fig. 1a. The template porous structures were first formed by an anodic reaction in the dark,¹⁶ and then the porous surface was photoelectrochemically etched in the same electrolyte under illumination. A series of electrochemical processes was conducted using a standard cell with three electrodes: a semiconductor electrode as a working electrode (WE), a Pt counter electrode, and a saturated calomel electrode (SCE) as a reference. In this study, a (001) n-type InP electrode ($n = 1 \times 10^{18} \text{ cm}^{-3}$) was used as a WE, whose potential, V_s , with respect to SCE, was precisely controlled by a potentiostat with a function generator. An electrolyte consisting of 1 M HCl (200 mL) with HNO₃ (3 mL) was used throughout the experiment.

A constant bias was first applied to the semiconductor electrode to obtain high-density porous structures. Figure 1b shows typical

scanning electron microscope (SEM) images of the template porous sample formed at $V_s = 5 \text{ V}$ for 60 s. As previously reported,¹⁶ the straight nanopores in the array were over 10 μm in depth, but the irregular layer partially remained on the top of the ordered porous structure. A cross-sectional SEM image showed that the total thickness of the anodized porous region was 27.6 μm including the irregular top region with a thickness of 4.1 μm . The average pore diameter of the present template was about 30 nm, which is much less than the pore diameter observed in the straight pore region under the irregular top layer.¹⁶ After the pores were formed, we attempted to remove the irregular top layer using PEC etching under the illumination of a tungsten lamp with an intensity of 10 mW/cm². An anodic bias was applied in the ramped mode to control the etching depth by controlling the number of cycles in the ramped bias and to investigate the effect of the PEC process on the porous surface by voltammetry.

The solid curve in Fig. 2 shows the measured anodic current obtained on the InP porous template during six cycles of continuously applied ramped bias under illumination. V_s was swept at a rate of 50 mV/s from 0 to 1 V in the positive direction and then in the negative one, as shown in the inset waveform. As shown in Fig. 2, the highest current density of 5.3 mA/cm² was observed at $V_s = 1 \text{ V}$ in the first cycle. When the ramped bias was repeatedly applied, the current peaks observed in each cycle gradually decreased and then approached the saturation value of 4.0 mA/cm². The result obtained here indicates that the InP porous surface was undergoing some anodic reaction under illumination. However, the behavior of the current transition obtained here is different from that usually obtained on a planar semiconductor electrode. When planar InP substrate was subjected to ramped bias,¹⁸ the photocurrents increased as the number of ramped bias cycles increased because the passive layers, such as native oxides, were anodically dissolved.

Figures 3a and b are plan-view and cross-sectional SEM images of the sample after application of three and six cycles of ramped bias, respectively. We found that the PEC process greatly modified the surface morphology. As shown in Fig. 3a, the lateral size of pores were larger than those of the porous template shown in Fig. 1b. We observed in the SEM cross section that the thickness of the irregular top layer on the porous template decreased from 4.1 to 1.4 μm .

Application of six cycles of ramped bias completely removed the irregular top layer, and the regular array of straight pores appeared on the surface, as shown in Fig. 3b. It is important to remember that the pore shape was a square defined by four equivalent {100} planes, which is similar to the shape of the porous structures after the cathodic decomposition process.¹⁷ This similarity is due to the strong dependence of the etching rate on crystal orientation, where the {100} planes preferentially appeared on the wall surface due to their slow etching rate. The lateral thickness of the InP nanowalls was less than 20 nm near the surface, which is thinner than the initial value of the template porous sample. These results indicate that the porous surface was etched by a PEC reaction.

^z E-mail: taketomo@rciqe.hokudai.ac.jp

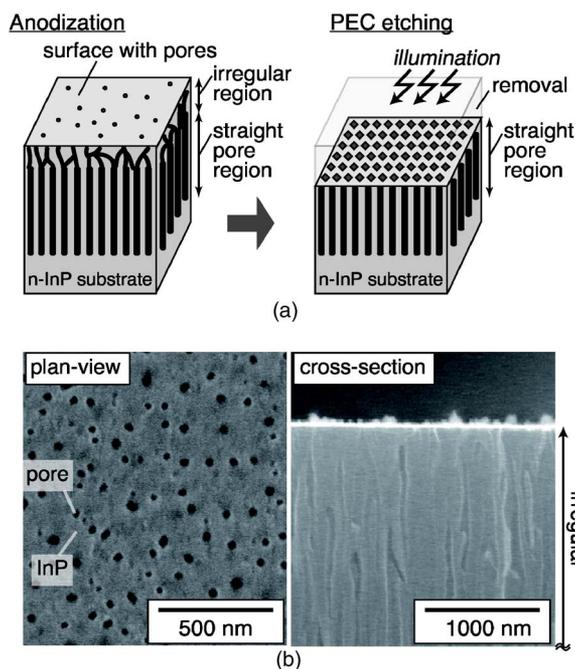


Figure 1. (Color online) (a) Schematic illustrations of experimental procedure and (b) plan-view and cross-sectional SEM images of porous template sample.

The etching rate of the InP porous nanostructures was investigated using SEM observation. Figure 4 shows the plot of the etching depth, d , measured from the top surface as a function of the cycle number of the ramped bias applied during the PEC process. It was found that there was an inflection point in the etching curve around the fifth cycle. The surface of the InP porous structure started to be etched at a rate of $1.2 \mu\text{m}/\text{cycle}$. After the inflection point, as shown in Fig. 4, the etching rate decreased appreciably to less than $0.2 \mu\text{m}/\text{cycle}$. This behavior is consistent with the current transition seen in Fig. 2. It seems clear that the etching rate decreased along with the anodic currents, contributing to the electrochemical dissolution of the InP porous surface.

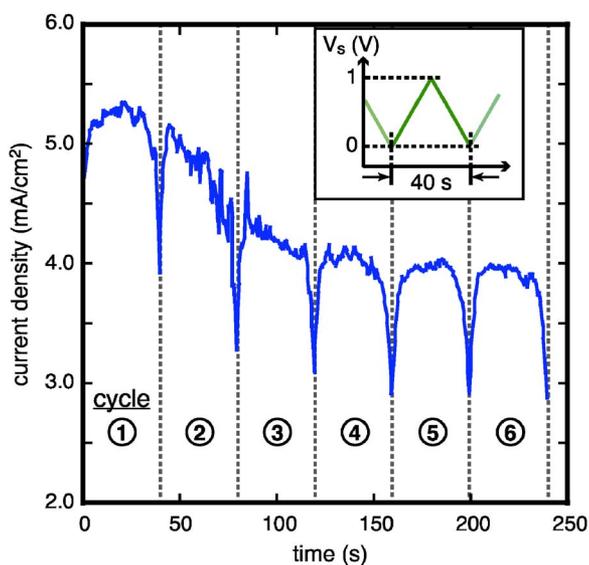


Figure 2. (Color online) Anodic currents measured on porous sample under illumination. Inset shows applied waveform in ramped bias mode.

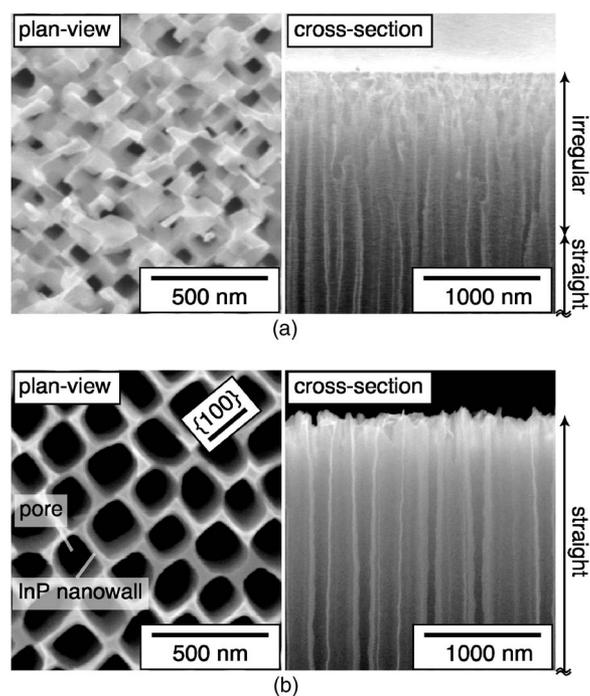


Figure 3. Plan-view and cross-sectional SEM images of porous samples after ramped bias applied (a) with 3 cycles and (b) with 6 cycles.

One explanation for this is that the amount of anodic photocurrents was strongly associated with the structural properties of the InP porous nanostructures. At the beginning of the PEC process, the surface etching started with a large photocurrent due to the hole generation caused by the illumination in the irregular pore region. After the complete removal of the irregular layer with a thickness of $4.1 \mu\text{m}$, the etching rate decreased, as shown in Fig. 4, because the effective area subjected to illumination became small on the surface, with InP nanowalls being thinner in the straight pore region. This model qualitatively explains the observed behavior on the PEC etching of the InP porous nanostructures. These results indicate that the

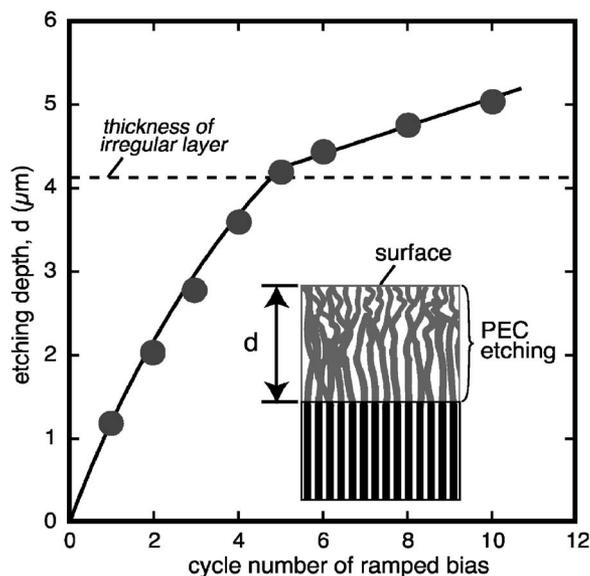


Figure 4. Relationship between average etching depth, d , and cycle number of ramped bias applied to sample. Solid and dotted lines indicate eye-guide of etching curve and initial thickness of irregular top layer, respectively.

irregular top layer can be completely removed from the surface of InP porous nanostructures by the PEC process controlling and monitoring the anodic photocurrents.

In summary, a PEC process was developed to remove the irregular top layer from porous InP nanostructures. The PEC etching was conducted in ramped bias mode under illumination, and the complete removal of the irregular layer was made possible by monitoring and controlling the anodic photocurrents. The results obtained here are promising for practical application of these unique InP nanostructures, which cannot be formed using conventional methods.

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References

1. Y. Wang, Z. Tang, and N. A. Kotov, *Mater. Today*, **8**, 20 (2005).
2. H. Masuda, M. Nagae, T. Morikawa, and K. Nishio, *Jpn. J. Appl. Phys., Part 2*, **45**, L406 (2006).
3. G. S. Huang, X. L. Wu, G. G. Siu, and P. K. Chu, *Solid State Commun.*, **137**, 621 (2006).
4. Y. Arita, *J. Cryst. Growth*, **45**, 383 (1978).
5. R. L. Smith, S.-F. Chuang, and S. D. Collins, *J. Electron. Mater.*, **17**, 533 (1988).
6. L. T. Canham, *Appl. Phys. Lett.*, **57**, 1046 (1990).
7. P. Schmuki, J. Fraser, C. M. Vitus, M. J. Graham, and H. S. Isaacs, *J. Electrochem. Soc.*, **143**, 3316 (1996).
8. I. M. Tiginyanu, V. V. Ursaki, E. Monaico, E. Foca, and H. Föll, *Electrochem. Solid-State Lett.*, **10**, D127 (2007).
9. A. Anedda, A. Serpi, V. A. Karavanskii, I. M. Tiginyanu, and V. M. Ichizli, *Appl. Phys. Lett.*, **67**, 3316 (1995).
10. K. Kuriyama, K. Ushiyama, K. Ohbora, Y. Miyamoto, and S. Takeda, *Phys. Rev. B*, **58**, 1103 (1998).
11. T. Takizawa, S. Arai, and M. Nakahara, *Jpn. J. Appl. Phys., Part 2*, **33**, L643 (1994).
12. T. Baba and M. Koma, *Jpn. J. Appl. Phys., Part 1*, **34**, 1405 (1995).
13. A. Hamamatsu, C. Kaneshiro, H. Fujikura, and H. Hasegawa, *J. Electroanal. Chem.*, **473**, 223 (1999).
14. M. Mynbaeva, A. Titkov, A. Kryganovskii, V. Ratnikov, K. Mynbaev, H. Huhtinen, R. Laiho, and V. Dmitriev, *Appl. Phys. Lett.*, **76**, 1113 (2000).
15. H. Fujikura, A. Liu, A. Hamamatsu, T. Sato, and H. Hasegawa, *Jpn. J. Appl. Phys., Part 1*, **39**, 4616 (2000).
16. T. Sato, T. Fujino, and H. Hasegawa, *Appl. Surf. Sci.*, **252**, 5457 (2006).
17. T. Sato, T. Fujino, and T. Hashizume, *Electrochem. Solid-State Lett.*, **10**, H153 (2007).
18. C. Kaneshiro, T. Sato, and H. Hasegawa, *Jpn. J. Appl. Phys., Part 1*, **38**, 1147 (1999).