

材料表面半導体薄膜の構造及び電子物性に関する研究

Superlattice made from Indium Phosphide

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1. Introduction

Since the discovery of efficient room-temperature visible photoluminescence of porous silicon formed by partial electrochemical dissolution of the surface^[1], porous silicon has attracted much attention due to wide variety of possibilities for optoelectronics and electronics device fabrication^[2,3]. Compound semiconductors such as GaAs^[4-9] and InP^[10-13] have also been investigated in the form of porous layers recently and many different properties relative to the bulk materials have been revealed.

Porous GaAs can be electrochemically formed in HCl and Cl ion containing solutions^[6-9]. From these latter porous structures, visible photoluminescence in the green wavelength region of the spectrum can be observed^[4,5].

For n-type (111) InP, porous structures were obtained by photoassisted etching in HCl electrolytes^[10, 11]. These porous structures showed a weak blueshift in their photoluminescence spectrum that was attributed to quantum confinement^[11]. On the other hand, for porous n-type (100) InP samples polarized in HCl electrolytes under illumination^[12], in contrast to the expected blueshift due to a quantum confinement, a redshift of the photoluminescence response was observed that was attributed to a well defined new surface state level on the anodized pore wall.

Schmuki et al. also reported that porous structures can be obtained on n-type (100) InP samples polarized in HCl, HBr and HF electrolytes^[13]. The morphology of the pores strongly depends on illumination. At high illumination intensity, electropolishing takes place instead of pore formation. The finest pore structure was obtained in the dark. Structures formed in HF show visible photoluminescence in the yellow to red range of the spectrum, whereas for HCl and HBr treated samples, no significant visible photoluminescence was obtained.

Recently, several new and novel application of porous semiconductor also has been developed. Porous silicon superlattice with a wide variation of porosities can be produced by changing the etching current density^[14-16]. The increase of the porosity results in a reduction of the refractive index of porous silicon layers, which should change their dielectric properties. The sponge-like network of remaining silicon and pores behave as a quasi-continuous optical medium. This concept is the basis of the variety of dielectric porous silicon structures like antireflection coatings for waveguides^[17], microcavities^[18-20] and distributed Bragg reflectors^[14, 21] which have been realized so far. In all devices, the refractive index is varied in depth

by changing the current density and the time duration in the course of the material fabrication. This procedure results in a stack of alternative layers with different porosities, refractive indices and thickness. It has been demonstrated that these devices can be used as sensors for various type of chemical compounds and DNA^[18, 22-23], since a filling of the pores with dielectric substances modifies the average refractive index of each layer and thus change the optical response of the stack.

This project aims at producing porous superlattice on prototypical III-V compound semiconductor, n-type (100) InP in the acid solution and investigating the potential for the application as sensors for various chemical compounds and DNA. In this report, especially, emphasis is to investigate the influence of the electrochemical and chemical conditions on the structure and morphology of porous stacking layer.

2. Experimental

The materials studied were n-type (100) InP wafers doped with $3-10 \times 10^{18} \text{ cm}^{-3}$ S. Prior to each experiment, the samples were degreased by ultrasonically successively in acetone, isopropanol and methanol, followed by rinsing with distilled water and then finally drying with N₂ gas. Contact to the InP wafer was established by scratching InGa eutectic on the backside on the sample. After cleaning, the sample was pressed against o-ring in an electrochemical cell leaving 0.12 cm² exposed to the electrolyte or alternatively by immersing the bottom half of a sample (held by a copper clip on a dot of InGa) into the electrolyte. Experiments were carried out in 1M HCl(200 mL) with or without 1, 5M HNO₃(3 mL) or K₂PtCl₆(1 g). All solutions were prepared from analytical grade chemicals and deionized water.

For anodized polarization, a EG&G Galvanostat Model 273A was used. The electrochemical cell consisted of a conventional three-electrode configuration with platinum gauze as a counter electrode and a Haber-Luggin capillary with a Ag/AgCl/3.3M KCl electrode as a reference electrode. The sample was immersed in the electrolyte, then polarized with the applied current modulated as pulse mode. The higher and lower currents of square wave pulse, I_H and I_L, respectively, and the time of each pulse, t_H and t_L, respectively, were varied to produce multi porous layers with a wide variety of thickness and structure. At the end of the electrochemical treatment, the sample was immediately rinsed with ethanol and distilled water, and then dried with N₂ gas. All experiments were carried out at room temperature

in aerated solutions.

For the structural and morphology characterization of the anodized samples, cross-sectional scanning electron microscope (SEM) observations were carried out using a JEOL 6400 SEM.

3 . Results and Discussion

Anodic reactions on n-type InP under positive potentials require holes. For n-type semiconductor, depletion of the majority carriers, i.e. electrons, takes place and Schottky barrier (potential barrier) is set up at the substrate / electrolyte interface. A sufficient number of holes (minority carriers) can only be supplied by applying high voltage to the substrate to cause avalanche breakdown. The nature and rates of the anodic reactions depend on the relative position of the redox potentials with respect to the semiconductor band, which is affected by the pH of the electrolyte, the applied voltage and semiconductor parameters. In this work, the electrochemical etching is realized by galvanostatic polarization, which applied currents are ranged from 1 mA to 100 mA. In this current range, avalanche breakdown is expected to take place.

The porous superlattices consist of a stack of two layers

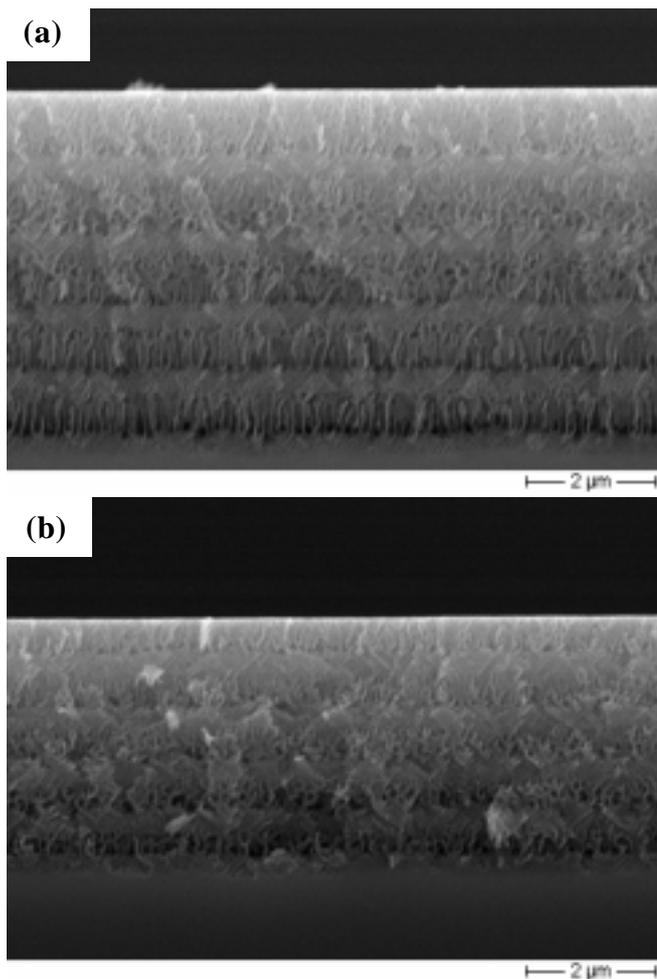


Figure 1 Cross-sectional SEM images of the porous superlattice samples anodized under various conditions. (a) $I_H, t_H = 100 \text{ mA}, 1 \text{ s}, I_L, t_L = 10 \text{ mA}, 5 \text{ s}$ and (b) $I_H, t_H = 100 \text{ mA}, 0.05 \text{ s}, I_L, t_L = 10 \text{ mA}, 5 \text{ s}$.

with alternating high and low porosity by changing the anodizing currents periodically. Figures 1, 2 show a series of cross-sectional SEM micrographs of the porous surface of the samples anodized in 1M HCl + 1M HNO₃. As shown in Figs. 1, 2, anodization produce pores, penetrating from the surface to the bulk. Furthermore, the difference of the structure and morphology between alternative layers can be observed

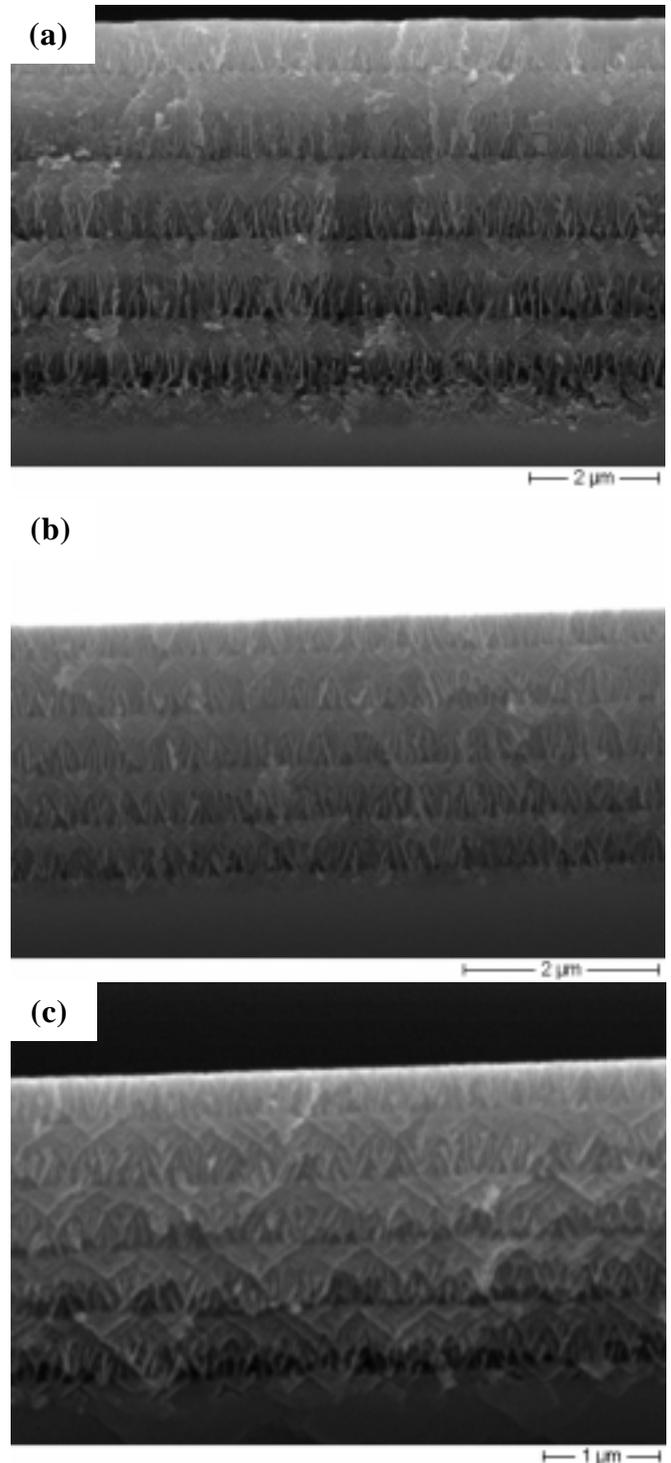


Figure 2 Cross-sectional SEM images of the porous superlattice samples anodized under various conditions. (a) $I_H, t_H = 50 \text{ mA}, 3 \text{ s}, I_L, t_L = 10 \text{ mA}, 10 \text{ s}$, (b) $I_H, t_H = 50 \text{ mA}, 1 \text{ s}, I_L, t_L = 10 \text{ mA}, 3 \text{ s}$ and (c) $I_H, t_H = 50 \text{ mA}, 1 \text{ s}, I_L, t_L = 1 \text{ mA}, 30 \text{ s}$.

clearly. Therefore, the superlattice can be produced by modulation of the applied current, and the structures of the pores should depend on the applied currents during process.

The superlattice structures shown in Fig. 1(a), (b) were produced by applied current sequence of $I_H = 100$ mA for $t_H = 1, 0.05$ s, respectively and $I_L = 10$ mA for $t_L = 5$ s which was repeated 5 times. Thickness of each layer could be almost constant, independent of the number of process cycle. As shown in Fig. 1, at low current as 10 mA, tilted pores with respect to the (100) plane were formed, resulting in the formation of a facet-like cross-sectional structure; pores were aligned along $\langle 111 \rangle$ and $\langle \bar{1}\bar{1}1 \rangle$ directions. Therefore, $\langle 111 \rangle$ is considered to be the preferential direction for the formation of the pores when the substrate was anodized at low current as 10 mA.

On the other hand, at high current such as 100 mA, pores close to the surface, consisting of tree-like structures of random branches, were formed, whereas near the bulk / porous layer interface, these branches decreased. Furthermore, for the sample anodized at 100 mA for $t_H = 1$ s shown in Fig. 1(a), these branches disappeared and fairly regular arrays of straight pores were formed. These pores had wavy walls, but basically they were running along the $\langle 001 \rangle$ -direction. It is evident that a preferential attack perpendicular to the (100) direction takes place, i.e. along $\langle 001 \rangle$. This is in agreement with works on photoelectrochemical etching of (001) n-type, which also shows preferential etching along the $\langle 001 \rangle$ axis^[12]. While the pore walls of the layer close to the sample surface are thick, they become thinner with multiplying the layer. This effect might take place due to change of the electrolyte concentration with the number of the process cycles caused by a limited diffusion in the narrow bottlenecks close to the surface.

Figures 2(a), (b) and (c) show the morphology of the superlattice structures which were produced by applied current sequence of $I_H = 50$ mA and $I_L = 1, 10$ mA. The morphologies of the multi-layer are almost similar to those shown in Fig. 1. At low current as 1, 10 mA, facet-like structures were observed. The size of each facet structure did not change with time, but the amount of the facet increased with anodization time shown in Fig. 2. At high current such as 50 mA, on the other hand, pores close to the surface, consisting of tree-like cross-sectional structures of random branches, were formed, whereas the amounts of branching decreased near the bulk / porous layer interface. Furthermore, for long period of anodization at 50 mA shown in Fig. 2(a), these branches disappeared and wavy walls pore were formed.

As shown in Figs. 1, 2, the porous morphologies produced by various currents should be classified in two types. The morphology of type I is a facet-like structure, which can be produced by low current anodization such as 1 or 10 mA. The size of the facet crystals could not change but the amount of them increases with time. On the other hand, the morphology of type II is a tree-like or wavy structure, depending on the process cycle. According to the previous paper reported by Fujikura et al.^[24], pore morphologies can be modified

depending on the chemical condition, i.e. the electrolytes. Therefore, the substrates were anodized in some electrolytes to investigate the influence of the electrolytes on the pore morphologies. Figure 3 shows the cross-sectional SEM micrographs of the samples produced by applied current sequence of $I_H = 50$ mA and $I_L = 10$ mA in (a) 1M HCl, (b) 1M HCl + 5 M HNO₃ and (c) 1M HCl + 1g K₂PtCl₆ solutions.

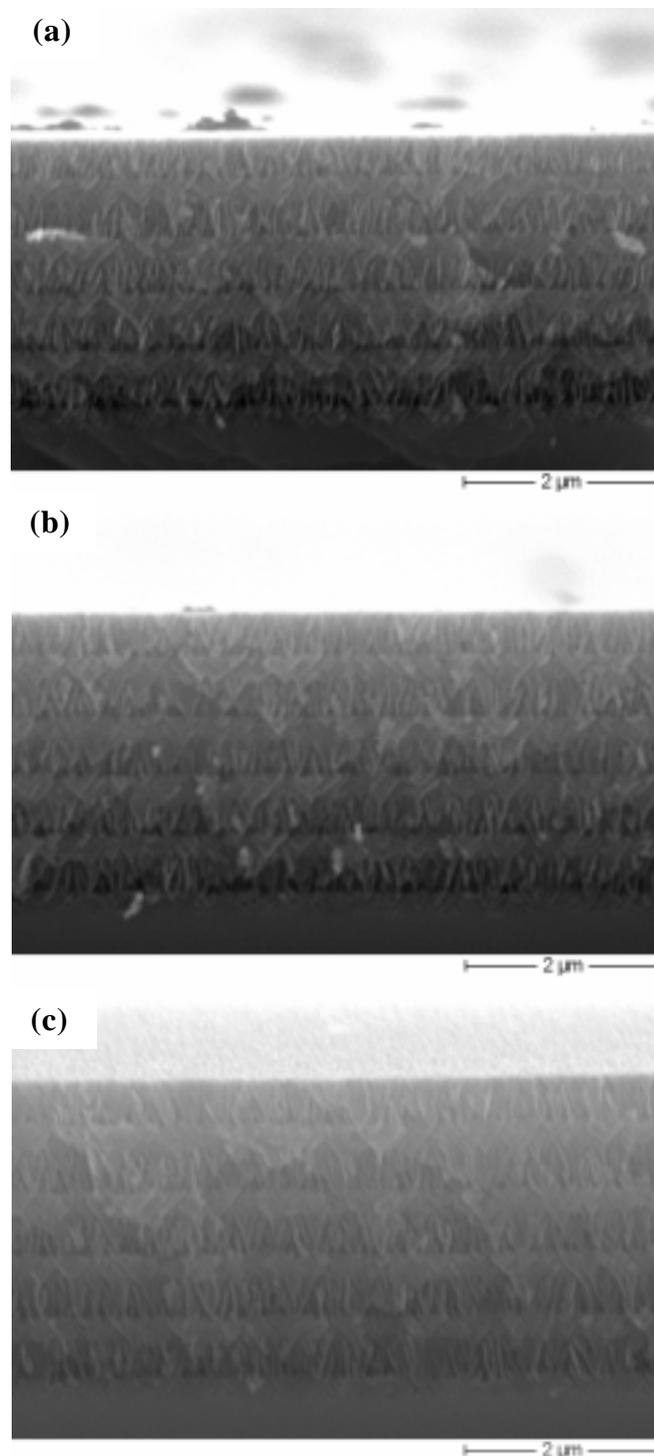


Figure 3 Cross-sectional SEM images of the porous superlattice samples produced by applied current sequence of $I_H = 50$ mA and $I_L = 10$ mA in (a) 1M HCl, (b) 1M HCl + 5 M HNO₃ and (c) 1M HCl + 1g K₂PtCl₆ solutions.

These structures were consisted of stacking of facet-like structure and tree-like structure periodically, which were almost same character as that shown in Fig. 2 (b). The reason why the structures showed no significant dependence on the electrolyte composition as reported by Fujikura et al.^[24] is currently not clear.

In III-V semiconductors, the formation of <001>-oriented straight pores without branches was reported by Hamamatsu et al. for n-type (001) InP^[12] and by Takazawa et al. for n-type (111) InP^[25]. In their paper, a brief experiment on n-type (100) InP substrate showed that the <111>-direction was preferential direction for pore formation. Such a tendency of the formation of <111>-oriented pores was also reported for n-type (100) GaAs. However, the formation of the superlattice consisted of alternative layers with different porosities have not been reported so far on III-V semiconductor. Therefore, the approach described here that is the formation of porous InP superlattices may open new perspectives for various applications. In the forthcoming work, we will investigate properties of these InP superlattices to clarify their potential as sensor application. Especially, optical measurements for sensor applications are highly promising with respect to a high selectivity and to a potentially greater ability to allow identification of particular adsorbates.

4. Conclusions

By changing the applied currents periodically in the acid solution, highly defined and regular superlattices were formed on n-type (100) InP surfaces for the first time.

The pore morphology, wall thickness and pore length could be changed depending on the applied current and process time. For low currents as 1 or 10 mA, the tilted pores were formed with respect to the (100) plane, resulting in the formation of a facet-like cross-sectional structure; pores were aligned along <111> and $\bar{1}\bar{1}\bar{1}$ directions. For high current such as 50 or 100 mA, on the other hand, tree-like or wavy pores were formed, depending on the duration of the process time.

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