Morphological characterization of porous InP superlattices

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Abstract

Porous superlattices n-type (100) InP are produced electrochemically on by changing the applied current or potential periodically in 1 M HCl + 1 M HNO3 solutions. The superlattice consists of stack of alternating two layers with various morphologies and porosities. The plan-view morphologies of the top surface of superlattice were almost same, and the pore size was varied in the nano-order range. On the other hand, the cross-sectional morphologies depend strongly on the electrochemical condition. For low applied currents or potentials such as 10 mA or 1.5 VAg/AgCl, respectively, porous layers with a facet-like structure were formed. The size of each facet did not change with the etching time, but the number of the facets increased with time. For high currents or potentials such as 50, 100 mA or 3 VAg/AgCl, respectively, a tree-like structure with random and/or tangled branches was observed. At a still higher potential of 5 VAg/AgCl, the porous layer exhibited fairly regular array of straight pores. Therefore, it is found that the morphology of the porous layer can be highly controlled by the applied current or potential.

Keywords: Compound semiconductor; n-type (100) InP; Pore formation; Superlattice; Nanostructures; 1 M HCl + 1 M HNO3 solution; Electrochemical anodization

1. Introduction

For over a decade, the localized dissolution of semiconductor materials and the formation of porous layers have generated a great deal of interest since Canham [1] reported efficient visible photoluminescence of porous silicon. For III–V compound semiconductors such as GaAs [2–4], InP [5–11] and InSb [12], formation of porous layers and their many different properties as compared to the bulk materials have also been investigated.

Recently, several new and novel applications of porous semiconductor materials also has been developed, taking advantage of the high surface area. It has been reported that a periodical variation of the formation parameters should lead to a periodical variation in the porosity of the porous layer with depth. Porous superlattices with a wide variety of porosities can be produced by periodically changing the etching current density or the doping concentration of substrates [13–17]. The increase of the porosity results in a reduction of the refractive index of the porous layers, which should change their dielectric properties. Therefore, the optical properties can periodically vary with depth in the porous superlattice layer. Such structures have been applied for waveguides, microcavity and distributed Bragg reflectors [14,15]. It has been also demonstrated that these devices can be used as sensors for various type of chemical species and DNA [15,18–20] since a filling of the pores with dielectric substances modifies the average refractive index of each layer and thus can change the optical response of the superlattice.

The present work aims at producing porous superlattices on a typical III–V compound semiconductor, InP in 1 M HCl + 1 M HNO3 solution. Previous investigations on GaAs and InP [2–4,8,11] showed that for sufficiently highly doped n-type materials porosification can be achieved without photo irradiation. Therefore, in the present work, emphasis is to characterize the morphology of porous superlattices formed under dark conditions.
2. Experimental

The materials studied were \textit{n}-type (100) InP wafers doped with $3 \times 10^{18}$ cm$^{-3}$ S. Prior to each experiment, the samples were degreased by ultrasonicating successively in acetone, isopropanol and methanol, followed by rinsing with distilled water and then finally drying with nitrogen gas flow. Contact to the InP wafer was established by smearing InGa eutectic on the backside of the sample. After cleaning, the sample was fixed on an electrochemical cell with o-ring, leaving 0.12 cm$^2$ exposed to the electrolyte. Experiments were carried out in 1 M HCl + 1 M HNO$_3$ at room temperature. The electrolyte was prepared from analytical grade chemicals and deionized water.

For anodic polarization, an EG & G Potentiostat/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/3.3 M KCl electrode as a reference electrode. The sample was immersed in the electrolyte, then polarized with the applied current or potential modulated as pulse mode. The higher and lower current (or potential) of square wave pulse, $I_H$ (or $E_H$) and $I_L$, respectively, and the time of each pulse, $t_H$ and $t_L$, respectively, were varied to produce stacks of porous layers with a wide variety of thickness and structure. At the end of the electrochemical treatment, the sample surface was immediately rinsed with ethanol and distilled water, and then dried with nitrogen gas flow. All experiments were carried out at room temperature in aerated solutions.

Plan view and cross-sectional scanning electron microscope (SEM) observations and analysis of the composition of each layer were carried out using a JEOL 6500 Field Emission Gun SEM equipped with Energy Dispersive Spectrometer (EDS).

3. Results and discussion

In order to explain the porosification process of \textit{n}-type semiconductors in the dark, the behavior of \textit{n}-type materials under anodic bias is considered. Depletion of the majority carriers, i.e. electrons, takes place and a blocking Schottky barrier (potential barrier) is set up at the substrate/electrolyte interface. A sufficient number of holes (minority carriers) can be supplied to cause avalanche breakdown when high voltage is applied to the substrate. The nature and rate of the anodic reactions depend on the redox potential with respect to the electronic energy band of semiconductor material, which is affected by the pH of the electrolyte, the applied voltage and semiconductor parameters. In this work, applied potentials or currents used ranged from 1.5 to 7 V$_{Ag/AgCl}$, or from 1 to 100 mA, respectively. In this potential and current range, avalanche breakdown is expected to take place.

![Fig. 1](image_url)

Fig. 1. SEM micrographs for the porous superlattice produced by applied current sequence of $I_H, t_H = 50$ mA, 3 s and $I_L, t_L = 10$ mA, 10 s in 1 M HCl + 1 M HNO$_3$: (a) plan-view; (b) cross-section.
These pores were basically running along the $\langle 001 \rangle$-direction, indicating a preferential attack perpendicular to the (100) plane. This result is the same as the photoelectrochemical etching of (001) $n$-type InP, which also shows preferential etching along the (001)-axis [7]. Fig. 1(b) shows a typical plan-view image of the top surface of the superlattice. The plan-view morphology observed is nearly independent of the electrochemical conditions in that the pores were almost circular and randomly located. However, the size of pores varied in the nano-meter range depending on the electrochemical conditions.

Fig. 2(a)–(c) show superlattices produced under the following electrochemical conditions: (a) $E_H, t_H = 1.5 \text{ V}_{\text{Ag/AgCl}}, 0.5 \text{ s}$ and $I_L, t_L = 10 \text{ mA}, 3 \text{ s}$, (b) $E_H, t_H = 3 \text{ V}_{\text{Ag/AgCl}}, 0.5 \text{ s}$ and $I_L, t_L = 10 \text{ mA}, 3 \text{ s}$ and (c) $E_H, t_H = 5 \text{ V}_{\text{Ag/AgCl}}, 0.5 \text{ s}$ and $I_L, t_L = 10 \text{ mA}, 3 \text{ s}$. At low currents such as 10 mA, facet-like structures were formed as already shown in Fig. 1. The size of each facet structure did not change with time, but the number of the facets increased with anodization time. For low applied potentials such as 1.5 V$_{\text{Ag/AgCl}}$, the cross-sectional morphology was facet-like. This facet-like morphology was observed for the layer formed at 10 mA. For a high applied potential such as 3 V$_{\text{Ag/AgCl}}$ a layer consisting of tree-like porous structures with random and tangled branches was formed close to the surface. Near to the bulk/porous layer interface, a coarser porosity is observed. Basically, the pores are also running along the $\langle 001 \rangle$-direction as mentioned above. The boundaries between the pores (pore walls) become thinner the deeper the porous structure grows. This behavior may be due to a 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.

For galvanostatic polarization at 100 mA, the morphology is almost the same as that for the sample anodized at 3 V$_{\text{Ag/AgCl}}$, i.e. the layer showed tree-like structures with random and tangled branches. Finally, as presented in Fig. 2(c), at 5 V$_{\text{Ag/AgCl}}$ fairly regular arrays of straight pores with wavy walls were formed and pores were running along the (001)-direction.

For the sample anodized at 7 V$_{\text{Ag/AgCl}}$ the porous layer was lifted off. Fig. 3 shows the bottom view of a lift-off layer (the top view morphology is almost as same as Fig. 1(a)).

![Cross-sectional SEM images of the porous superlattice samples anodized under various conditions.](image1)

![Bottom view of the lift-off layer produced by periodically changing the electrochemical condition:](image2)

![Cross-sectional SEM images of the porous superlattice samples anodized under various conditions. (a) $E_H, t_H = 1.5 \text{ V}, 0.5 \text{ s}$, $I_L, t_L = 10 \text{ mA}, 3 \text{ s}$, (b) $E_H, t_H = 3 \text{ V}, 0.5 \text{ s}$, $I_L, t_L = 10 \text{ mA}, 3 \text{ s}$ and (c) $E_H, t_H = 5 \text{ V}, 0.25 \text{ s}$, $I_L, t_L = 10 \text{ mA}, 5 \text{ s}$.](image3)
In order to obtain information on the composition of the porous superlattice, especially to examine if selective dissolution of one of components (In or P) takes place, EDS profiles were acquired on the superlattice. As presented in Table 1, the EDS analysis for the porous layer formed at 1.5 \( V_{\text{Ag}/\text{AgCl}} \) or 10 mA clearly showed an enrichment of phosphorus compared with the porous layer formed at a higher applied current or potential. Although the difference in the phosphorus concentration between two porous layers is within 1 at \%, it is concluded that some selective dissolution of indium may take place. However, the correlation between the morphology and the composition of each layer is currently not clear.

For III–V semiconductors, many different properties of single porous layers have been investigated. However, formation of superlattices consisting of alternative layers with different porosities have so far not been reported for III–V semiconductors. Therefore, the formation of porous InP superlattices may open new perspectives for various applications. In the present work, by changing the applied current/potential periodically in 1 M HCl or 10 mA, highly defined and ordered superlattices were formed on \( n \)-type (100) InP surface. Properties of these InP superlattices will be investigated to clarify their potential in sensor applications in future work. 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. Conclusion

By changing the applied current or potential periodically in 1 M HCl + 1 M HNO\(_3\) solutions, highly defined and ordered superlattices with various morphologies and porosities were formed on \( n \)-type (100) InP.

The cross-sectional morphologies, including pore size and wall thickness could be changed, depending on the applied current, potential and process time. For 1, 10 mA or 1.5 \( V_{\text{Ag}/\text{AgCl}} \), the pores formed were tilted with respect to the (100) plane, resulting in the formation of a facet-like cross-sectional structure. The size of each facet did not change with time, but the number of the facets increased with anodization time. For 50 mA, tree-like pores with non-tangled random branches were formed. On the other hand, for 100 mA or 3 \( V_{\text{Ag}/\text{AgCl}}\), the porous layers exhibit tree-like structures with tangled and random branches or wavy walls, depending on the duration of the process time. Furthermore, polarization at 5 \( V_{\text{Ag}/\text{AgCl}}\) led to formation of layers with fairly regular arrays of straight pores. The plan-view morphologies of the top surface of superlattice were almost the same, and the size of pores was changed in the nano-meter range depending on the electrochemical conditions.

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