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## Optical Properties of Size-Controlled Porous Nanostructures Formed on n-InP (001) Substrates by Electrochemical Process

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### 1. Introduction

Recently, intensive research efforts have been made on the formation of semiconductor nanostructures for future quantum electronic and photonic applications. Among various formation technologies, the electrochemical process is a unique one, utilizing the electrochemical reactions at a semiconductor/electrolyte interface. It has attractive features such as low process temperature, low process damage, process simplicity, electrical controllability of process and low cost. The most famous application of the electrochemical process is the formation of porous structures [1,2] utilizing the anodic reaction. We have recently succeeded in formation of the highly regular arrays of straight nanopores directly on n-InP (001) substrates, by optimizing the electrochemical conditions [3,4].

The purpose of this paper is to explore the optical properties of the size-controlled porous nanostructures formed on InP (001) substrates by the electrochemical process. In order to further reduce the size of nanostructures, the novel continuous process changing the polarity was applied for the first time.

### 2. Experimental

The setup of the electrochemical process used in this study is shown in Fig. 1. The process was performed using a standard cell with three electrodes, i.e., a (001) n-type InP electrode ( $n=1 \times 10^{18} \text{ cm}^{-3}$ ), a Pt counter electrode and reference saturated calomel electrode (S.C.E). For current supply, a GeAu/Ni ohmic contact was made on the backside of the InP substrate by using the conventional evaporation and annealing process.

Anodization was firstly carried out in the HCl-based electrolyte containing  $\text{HNO}_3$  for the formation of high-density porous structures. The pore structure generally consisted of the top irregular region including the surface oxide layer and the pore region underneath, as

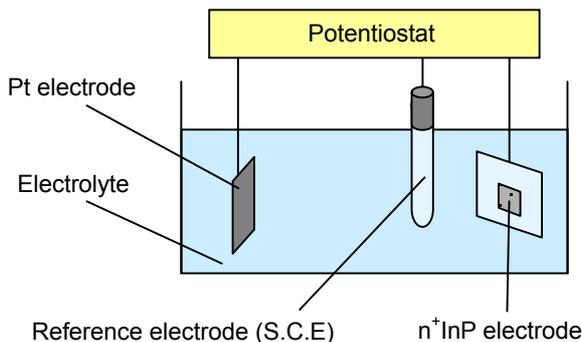


Fig. 1 Setup of electrochemical process used in this study.

schematically shown in Fig. 2. The most uniform and straight nanopore arrays were obtained by anodization at  $V_a=5\text{V}$  in the dark [4].

After the formation of porous structures, it was attempted to reduce the wall thickness by continuous process changing the polarity of the porous InP electrode from a positive to a negative. The overpotential was continuously swept to  $V_c=-1\text{V}$  for 40s in the same electrolyte.

The structural and optical properties of the InP porous structures were investigated using the scanning electron microscope (SEM) and the photoluminescence (PL) methods, respectively.

### 3. Results and Discussion

Figures 3(a) and (b) show the SEM images of the porous structure fabricated by the first anodization process

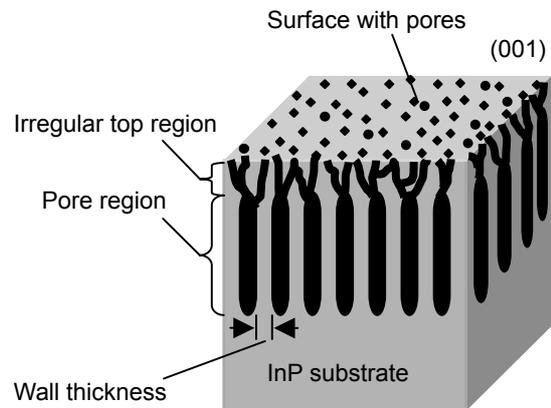


Fig. 2 Schematic illustration of porous structure.

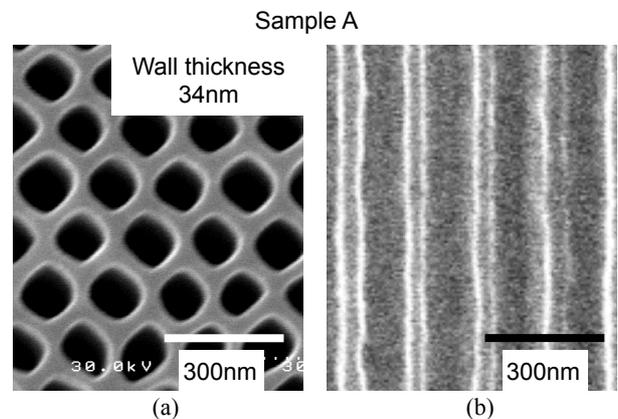


Fig. 3 (a) Plan-view and (b) cross-sectional SEM images of porous structure fabricated by anodization at  $V_a=5\text{V}$  (Sample A).

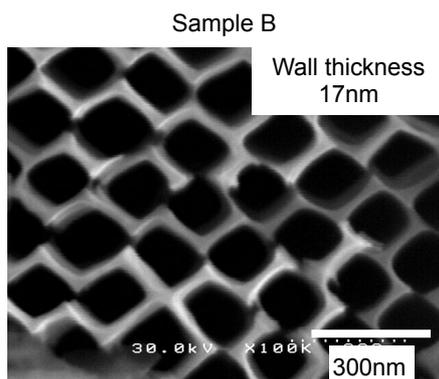


Fig. 4 Plan view of the sample after the cathodic sweep to  $V_c = -1V$  for 40s in the same electrolyte (Sample B).

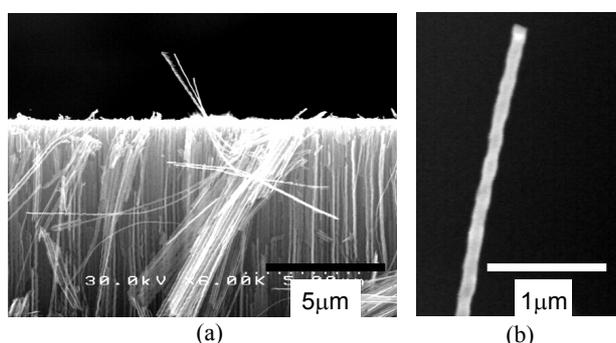


Fig. 5 (a) Cross-sectional SEM image of the sample cleaved after the cathodic sweep and (b) enlarged view of the nanowire-like structure.

(Sample A). After peeling off the irregular top layer, a periodic array of quasi-square shaped pores defined by  $\{100\}$  planes appeared. As seen in Fig. 3(b), the straight nanopores with uniform wall thickness were obtained. The average thickness of pore walls was found to be 34nm from SEM observation.

Figure 4 shows the plan view of Sample B after the continuous process changing the polarity of the InP electrode. It was found that the wall thickness was getting thinner by applying the cathodic bias of -1V. This is because the pore surface was etched into the HCl-based electrolyte during the bias sweep due to the electrochemical reaction took place on the pore surface. The average thickness of pore walls was reduced down to 17nm.

Figure 5(a) shows the cross-sectional SEM image of the sample cleaved after the cathodic sweep. The porous structure was partly broken and separated into many pieces. As shown in Fig. 5(b), it was found that the nanowire-like structures were produced from narrowed InP walls. It seems that further optimization of the process conditions leads to the precise control of the nanowire size as well as the wall thickness of InP nanopores.

Figures 6(a) and (b) show the PL spectra obtained from Samples A and B at 250K and their peak positions plotted as a function of the temperature, respectively. PL measurements were also performed on the planer InP substrate as a reference. The positions of PL peaks obtained from the Samples A and B clearly showed a significant blue

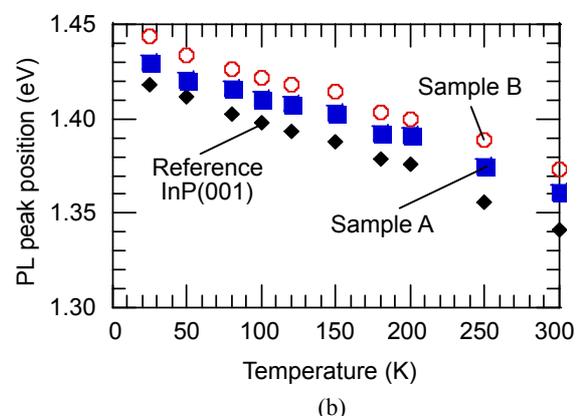
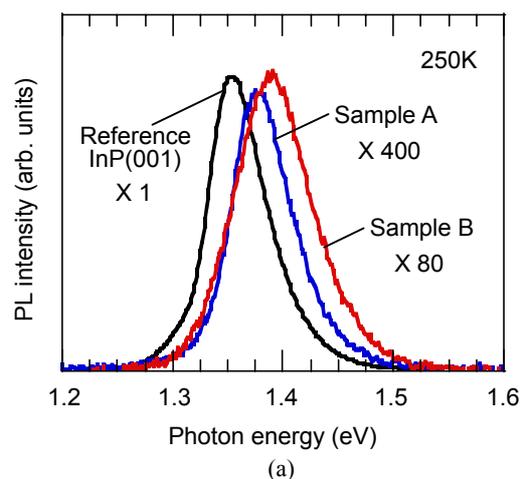


Fig. 6 (a) PL spectra measured at 250K and (b) temperature dependence of position of PL peaks obtained from Sample A, Sample B and planer reference sample.

shift about 13 meV and 26 meV, respectively, with reference to that of the band emission obtained from the reference sample. The amount of energy shift was strongly dependent on the wall thickness. As the temperature decreased, the peak position of both samples shifted to higher energy positions keeping the same slope with that of the reference sample, as shown in Fig. 6(b). This is consistent with the well-known temperature dependence of the band gap energy. We believe that the observed blue shift is most probably due to the quantum confinement in the InP pore wall.

These results indicate that the present continuous process utilizing the electrochemical anodic and cathodic reactions is very promising for the formation of the high-density array of InP nanostructures with a strong quantum confinement.

## References

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