Electrochemical Formation of Chaotic and Regular Nanostructures on (001) and (111)B InP Substrates and Their Photoluminescence Characterizations*

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Attempts were made to form various nanostructures on InP substrates using anodization process. Surprisingly wide varieties of nanostructures were obtained. They included zigzag pore arrays and chaotic porous structures on (111)B substrate, and quasi-periodic straight nanopore arrays on (001) substrate. Straight pore samples showed blue-shifted peaks due to quantum confinement whereas no clear energy shifts were observed in (111)B samples. Zigzag and straight pore samples also showed red-shifted PL emissions probably due to emission from surface state continuum. [DOI: 10.1380/ejssnt.2006.184]

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I. INTRODUCTION

Recently, intensive research efforts have been made on self-assembled formation of nano-structure arrays as key technologies for future quantum electronic and photonic applications. Among various formation technologies of semiconductor nanostructures, the electrochemical process is a unique one that have 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 for semiconductor nanostructure formation is formation of porous Si by the anodic reaction in the electrolyte [1]. From Si porous structures, photoluminescence (PL) with a peak at an energy position higher than the Si band gap energy of 1.1 eV was observed, showing evidence of quantum confinement [2]. Several groups have later reported on porous structures made of III-V semiconductor materials such as GaAs [3, 4], GaP [5] and InP [6–9]. We have recently succeeded in anodic formation of arrays of straight nanopores on n-InP (001) substrates, where the straightness of pores in depth direction was dramatically improved using HCl based electrolytes [7–9]. It has been found that the structural features such as pore diameter and pore depth could be successfully controlled by the anodization voltage, processing time, ion species and concentration of electrolytes [9].

The purpose of this paper is to further explore structural varieties in InP nanostructures obtainable and to investigate optical properties of resultant InP porous nanostructures. Anodization of (001) and (111)B oriented n-type InP using a HCl-based electrolyte produced not only regular nanopore arrays but also chaotic nanostructures. Temperature dependence of the PL spectra provided information on their electronic structures.

The setup of the electrochemical process used in this study is shown in Fig. 1(a). The electrochemical anodization was performed using a standard cell with three electrodes, i.e., an n-type InP electrode (n = 1 x 10^18 cm^-3), a Pt counter electrode and a reference saturated calomel electrode (S.C.E). In this study, two kinds of substrates, (001) and (111)B InP substrates, were employed. For current supply, a GeAu/Ni ohmic contact was made on the backside of the InP substrate by using the conventional metal evaporation and annealing process.

Anodization was carried out in the following HCl-based electrolyte containing HNO3.

\[ 1.0 \text{ M } \text{HCl} \text{ 200 ml } + \text{HNO}_3 \text{ 3 ml} \quad (1) \]

In all the experiments, the overpotential of the n-InP electrode for the anodization, \( \nu_a \), was supplied in d.c. mode in the dark.

The pore structure generally consisted of the top irregular region including the surface oxide layer and the pore region underneath, as schematically shown in Fig. 1(b). The thickness of the top irregular region is typically 500 nm to 1 μm, whereas the thickness of the underlying pore region depended on the anodization conditions and can become longer than 80 μm. In this study, the structural properties of various porous samples were investigated using scanning electron microscope (SEM) using Hitachi S-4100 system.

In order to investigate the optical properties of the nanostructures produced by anodization, photoluminescence (PL) measurements have been performed over a temperature range from 20 K to 300 K, using the 514.5 nm line of an Ar^+ laser as the excitation source. The PL signals were detected by an optical multi-channel analyzing system (Acton Research Corporation) with a 0.75 m grating spectrometer and a CCD camera cooled by liquid N2.

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II. EXPERIMENTAL

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III. RESULTS AND DISCUSSION

A. Structural properties of anodized InP

1. Surface and cross-sectional structures

Surprisingly wide varieties of surface and cross-sectional structures were obtained by changing substrate orientations and electrochemical conditions. Figures 2(a), (b) and (c) show the plan views and cross-sectional images of typical three examples of the structures obtained by anodization. They are Sample A, Sample B and Sample C which were formed, respectively on a (111)B substrate at an anodization voltage of $V_a = 1$ V, on (111)B substrate at $V_a = 3$ V and on (001) substrate at $V_a = 5$ V.

As shown in Fig. 2(a) for the Sample A, an array of pores having a triangular shape was formed on (111)B substrates at a relatively low overpotential of 1 V. The triangles were aligned in the same direction with three sides being parallel to three equivalent $<\overline{1}10>$-orientations. In its cross-section, the Sample A showed straight pores on average in the depth direction, but their walls were zigzag shaped.

In the case of the Sample B anodized at a higher overpotential of 3 V, an almost chaotic porous structure was formed, as shown in Fig. 2(b). Here, pore sizes became so large, flakes of pore walls make up a random frame work.

On the other hand, self-organized regular straight pore patterns appeared on the (001) surface in the Sample C, after peeling off the irregular top layer. As shown in Fig. 2(c), a quasi-periodic array of quasi-square shaped pores defined by {100} planes is seen in its plan-view on the (001) substrate. It is also seen that these square shaped pores are aligned in a hexagonal lattice, showing a highly dense packing structure. In its cross-section, remarkably straight pores are formed quasi periodically in the depth direction. In this case, the average pore size of 140 nm and the average wall thickness of 34 nm were obtained.

This result indicates that the cross-sectional structure of the pore region is determined in a self-limiting nature by the saturation of a pore diameter laterally limited by depletion of hole supply together with chemical dissolution of wall into electrolyte.

As for the pore structure in the depth direction, its straightness was remarkably better for the Sample C, as compared with those of the Sample A and the Sample B. In fact, we have found from the results of a wide range of experiment, the (001) direction is the much more suitable orientation for forming uniform and straight nanopores.

2. Formation mechanism and possible applications

It is very surprising that the same simple anodization can lead to such wide varieties of structures just by changing the substrate orientation and anodization condition. Even in the same substrate orientation, it was found that the quite different nanostructures were produced by changing the overpotential.

On the other hand, basic reaction forming nanostructure must be the same. Previously, we decided this reaction to be the following [9] by a detailed anodization experiments in the anodic dissolution mode.

$$\text{InP} + 8\text{OH}^- + 8\text{h}^+ = \frac{1}{3}\text{In}_2\text{O}_3 + \frac{1}{3}\text{In(PO}_3)_4 + 4\text{H}_2\text{O}. \quad (2)$$

Complications may come from various factors such as the mechanism and spatial pattern of hole supply, dissolution of electrochemical reaction products, diffusion of ion-species through the structures already formed, and direct attack of InP by ordinary chemical reaction by acidic electrolyte etc. For simplicity, general features obtained here may be roughly explained in terms of two different competing tendencies. One is to form pores in the preferred directions of weak bonds that are easily attacked by the electrolyte. The other is the tendency of forming straight pores along the direction of the electric field which is producing holes required for the reaction by an impact ionization. Both tendencies are strongly correlated with the surface orientation of substrates and anodization voltages. However, it is difficult at the present time to discuss in detail.
stage to state something more concrete and predictive beyond such a qualitative discussion. It is really surprising that such a simple electrochemical process can lead to varieties of structures, whereas the ordinary wet chemical etching never leads to such varieties. Particularly, strong dependence on the substrate orientation can not be well explained. The whole system may be regarded as a highly non-linear reaction-diffusion system where non-linearity results from the hole supply via an impact ionization.

On the other hand, from the application viewpoint, such kinds of unique nanostructures can not be obtained by the conventional ‘top-down’ semiconductor VLSI technology including lithography and etching. Even for regular nanopore arrays, the conventional approach can never produce such arrays of deep pores with nanometer feature sizes into high quality semiconductors. Potential applications of such regular pore arrays include (1) high speed and highly sensitive photodetectors, (2) large capacitors for memory nodes and for energy storage for RFID (radio frequency identification) chips, (3) templates for growth of III-V quantum wires and dots, (4) formation of photonic crystals and other optical applications and (5) various sensor applications. However, whether such applications can be actually realized depends on fine structural tunability and additional processing capabilities of the nanostructures. As for more chaotic structures obtained on the (111)B substrate, they are obviously beyond the fabrication capability of the conventional top-down technology.
They might turn out to be useful in special type of sensors such as ‘electronic nose’ due to very large surface-to-volume ratio.

### B. Optical properties of anodized InP

#### 1. Results of temperature dependent PL measurements

Figure 3 shows the PL spectra taken at three different temperatures for Samples A and B formed on (111)B substrate. PL spectra of the planar substrate (111)B were also measured as a reference sample for the purpose of comparison. Their peaks are indicated as ‘reference’ in Fig. 3. Here, the PL peak height is normalized by the PL peak height of the reference sample at 25 K shown at the bottom.

As seen in Fig. 3, positions of the main peak of the Sample A, label as peak 1 in Fig. 3, and the PL peak of Sample B were found to be almost same with that of the band edge emission peak obtained on the reference (111)B sample. Here, all peaks had larger full width at half maximum (FWHM) values as compared with those of the peak from the band emission from the (001) reference InP sample, probably due to the poorer crystal quality of the bulk (111)B substrate.

As the measurement temperature was decreased, the positions of the main peaks of Samples A and B followed the reference peak. At the same time, an additional peak, labeled as the peak 2 in Fig. 3, newly appeared in the Sample A at a lower energy position than the reference peak position, whereas no additional peak appeared in the Sample B.

Similarly, the PL spectra taken at three different tem-
FIG. 5: Temperature dependence of (a) position and (b) normalized intensities of PL peaks obtained from Sample A and Sample B.

FIG. 6: Temperature dependence of (a) position and (b) normalized intensities of PL peaks obtained from Sample C.

The PL positions and PL intensities of the Samples, A, B, C obtained from the detailed temperature dependent PL measurements are summarized in Figs. 5(a) and (b) for the Samples A and B formed on the (111)B substrate, and for the Sample C formed on (001) substrate in Figs. 6(a) and (b), respectively. The PL intensities of all the samples are normalized by the PL intensity of the band edge emission peak taken on the reference (001) sample at 25 K as shown in Fig. 6(b).

Let us briefly discuss the PL emission mechanism with reference to Figs. 5 and 6. As the temperature decreased, the PL peaks of the band emission from both (111)B and (001) reference substrates shifted to higher energy positions keeping the same slope, and this is consistent with
As for the Samples A and B, the main peak 1 of Sample A and the PL peak of Sample B follow the same temperature dependence of the reference peaks with keeping nearly the constant intensity ratios with the reference sample as seen in Fig. 4.

Thus, Samples A and B show ordinary band edge emission in spite of their complicated structures. This is most probably because the remaining wall thicknesses of the structures in Samples A and B are still thick in most part, and they do not show significant quantum confinement effects.

On the other hand, the small PL peak 2 of the Sample A could be recognized only at low temperatures below 80 K partly due to the detection limit, and the intensity increased as the temperature was decreased. Its energy position was found to keep a constant energy separation of 230 meV below the main peak within the measurable range.

As for the Sample C, two different peaks, i.e., a blue-shifted peak 3 and a red-shifted peak 4, were clearly observed. As seen in Fig. 6(a), the energy peak position of peak 3 kept a constant blue shift of 13 meV above the reference, and that of the peak 4, a constant shift of 90 meV below the reference. As seen in Fig. 6(b), the peak 4 can be observed at low temperatures below 160 K. As the temperature further decreased, the intensity of the peak 4 rapidly increased and surpassed the height of the peak 3 around 90 K.

One possible mechanism for the blue shift as observed in the peak 3 could be due to stress-induced increase of energy band gap in the InP pore structure. However, the pore formation is generally stress-relieving process with increased spatial freedom, and such a mechanism is highly unlikely. Increase of blue shift with decrease of the pore wall thickness as explained below also makes this mechanism unlikely.

We believe that the observed blue shift is most probably due to the quantum confinement in the InP pore wall, because the amount of energy shift was found to be strongly dependent on the pore wall thickness. Namely, in the present sample C, the observed blue shift of the peak 3 was 13 meV, and the measured average thickness of the pore wall was 34 nm according to SEM observation. On the other hand, in our previous study [8], a larger blue shift of 24 meV was obtained in a thinner wall thickness of 14 nm in a similar regular pore structure. This systematic shift indicates that the blue-shifted emission is due to quantum confinement. Quantitatively, the observed shift of 13 meV of peak 3 corresponds to the summation of quantization energy for electron (11 meV) and hole (2 meV) expected for a vacuum/InP quantum well with a well width of 21 nm. This is a reasonable value as an effective wall thickness, since the actual wall thickness of 34 nm is expected to be reduced by 10 nm or so due to the dead layer formation by the surface depletion.

The observed PL behavior involving two kinds of emission peaks seen in Samples A and C can be explained by assuming the presence of a broad surface state continuum with a peak in the band gap as well as the presence of electron and hole quantum states inside the pore walls in Sample C. Our models for the PL emission for the Samples A and C are shown in Fig. 7. At low temperatures, photo-generated electrons are captured by the broad state continuum at first and then radiatively recombine with holes, giving red-shifted emissions for both samples. The peak position of the broad state continuum is assumed to lie at 230 meV below the conduction band minimum, $E_C$, for the Sample A and that for the Sample C is assumed at 90 meV. As the temperature increased, the electrons begin to escape from the state continuum due to the thermal energy, reducing the intensities of the red-shifted peaks 2 and 4. As higher temperatures, this path is completely quenched by thermal excitation, and electrons directly recombine between quantum confined states.

In order further to clarify the PL behavior of the red-
shifted peaks 2 and 4 in Samples A and C, the measured excitation power dependences of these peaks are plotted in Fig. 8 together with that of the near band-edge PL peak 3 with a small blue shift. Measurements were done at 25 K, and the PL intensities are normalized by the intensity of the band-edge emission peak of the reference sample at 25 K and at the photon flux density of $1.3 \times 10^{18}$ cm$^{-2}$s$^{-1}$.

As seen in Fig. 8, the intensity of peak 3 increased linearly with the excitation photon flux density as is usually expected. However, intensities of red-shifted peaks 2 and 4 showed clear saturation at high photon flux intensities. We believe that such saturation behavior can be explained as follows in terms of the model shown in Fig. 7, namely, a radiative transition through surface states.

Replacing the surface continuum with a discrete surface state with a sheet density of $N_{ss}$ for simplicity, and ignoring thermal emission of electrons from surface states to the conduction band because of a low temperature, the number of surface states, $N_{ss}$, capturing electrons at the surface can be described by the following simple rate equation.

$$\frac{\partial N_{ss}}{\partial t} = N_{ss}C_n(1 - f)n - N_{ss}ephpfp,$$  \hspace{1cm} (3)

where $C_n$ and $ephp$ are the capture and radiative emission rates of the surface state, and $n$ and $p$ are the electron and the hole concentrations at the surface, respectively. $f$ is the occupation function of the surface states. Under the steady-state condition, this gives the following equations for the occupation function and PL intensity, $I$, resulting from the radiative transition from the surface state to the valence band.

$$f = \frac{C_nn}{C_n + ephp},$$  \hspace{1cm} (4)

$$I \propto fephp = \frac{C_nnephp}{C_n + ephp}.$$  \hspace{1cm} (5)

Since InP used in this study is highly doped n-type materials, we can safely assume that $n$ is given by the donor concentrations within the excitation power levels we used. On the other hand, $p$ is mainly due to photo-excitation, and thus should be proportional to the excitation photon flux density. Now, according to Eq. (5), the intensity, $I$, at low excitations with $ephp << C_n$, should increase in proportion to $p$ and thus to the excitation photon flux density, whereas, $I$ should saturate and become constant under high excitations with $ephp >> C_n$. The latter is due to the fact that the radiative transition becomes rate-limited, not by the radiative transition rate itself, but by capture of electrons from the conduction band. Thus, the behavior observed here can be explained in terms of radiative transition through surface states. Of course, the same argument naturally applies to a bulk radiative recombination center. However, surface state is much more likely, since there was no such PL peaks in our bulk reference sample, and since the observed PL peak position was dependent on the surface preparation method.

However, it should be also mentioned here that, although we assumed that the radiative process for the red-shifted peak is a transition from the surface state to the valence band edge in our model shown in Fig. 7, this is one possible case and another model assuming a radiative transition from the conduction band edge to the surface state is equally applicable, including the above discussion related to the rate equation. Thus, further study is necessary to really identify the origin and nature of the surface states.

IV. CONCLUSION

In this paper, attempts were made to form various nanostructures on (111)B and (001) InP substrates by an electrochemical anodization process using a HCl-based electrolyte. Surprisingly wide varieties of surface and cross-sectional structures were obtained by changing substrate orientations and electrochemical conditions in spite of the fact that the basic chemical reaction remains the same. They included zigzag pore arrays and chaotic porous structures on (111)B substrates, and quasi-periodic straight nanopore arrays on (001) substrate. Straight pore samples on (001) substrate showed blue-shifted peaks due to quantum confinement whereas no clear energy shifts were observed in (111)B samples. Zigzag and straight pore samples also showed red-shifted PL emissions due to radiative transitions involving surface state continuum.

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