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<td>Author(s)</td>
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Investigation on Optical Absorption Properties of Electrochemically Formed Porous InP using Photoelectric Conversion Devices

Yusuke Kumazaki, Tomohito Kudo, Zenji Yatabe, and Taketomo Sato
Research Center for Integrated Quantum Electronics, and Graduate School of Information Science and Technology, Hokkaido University, N-13, W-8, Kita-ku, Sapporo 060-8628, Japan

ABSTRACT
We investigated the optical absorption properties of InP porous structures formed by the electrochemical process using photoelectric conversion (PC) devices formed on p-n junction substrates. The photocurrent measurements revealed that the current from PC devices changed in response to the incident light power and the thickness of the top layer on the p-n interface. Since the photocarriers contributing to the observed photocurrents are excited by the photons reaching the p-n interface through the top layer, the photocurrents give us information on the optical absorption properties of the top layer. The photocurrents observed on a porous device with a porous structure in the top layer were lower than that of a non-porous device, indicating that the absorption properties of InP were enhanced after the formation of porous structures. This phenomenon can be explained in terms of absorption coefficient, $\alpha$, increased by the light scattering and the sub-bandgap absorption in the porous layer.

Keywords: porous structure, indium phosphide (InP), optical absorption property, photocurrent, photoelectric conversion device

*Corresponding author. E-mail address: kumazaki@rciqe.hokudai.ac.jp

1. Introduction
The high-density formation of semiconductor nanostructures targeting applications such as quantum and optoelectronic devices has been intensely researched. Among the various structures, porous structures, which are a high-density array of nanometer-sized pores formed by using an electrochemical process, are one of the most promising nanostructures due to their unique features such as their large surface and low optical reflectance [1]. Anodic porous etching on Si and Ge was first reported by A. Uhlir at Bell Labs in 1956 [2]. After that, various compound semiconductors, such as GaAs [3-5], InP [6-9], GaP [10, 11], GaN [12-14] and SiC [15-17] were studied. For porous InP in particular, it is known that straight pores can be uniformly formed in the vertical direction under optimal conditions [18, 19]. In addition, we have recently reported that an extremely low reflectance of below 0.4% was observed for porous InP in the UV, visible, and near-infrared ranges [20]. These findings suggest that porous structures are promising materials for use in photoelectric conversion devices such as solar cells [21, 22] and photo detectors [23]. Therefore, the optical absorption properties of porous structures need to be determined so they can be used in such devices. It was previously reported that the absorption efficiency is enhanced after the formation of porous structures in indirect bandgap materials such as GaP [24-26] and SiC [27]. However, there are few reports on direct bandgap materials. One report showed that the absorption efficiency of InP decreased after the formation of porous structures due to the high-density surface states and lower electric field of pore wall [28].

The purpose of this paper is to clarify the optical absorption properties of these InP porous structures by conducting photocurrent measurements of photoelectric conversion (PC) devices. Our proposed PC device has either a porous or a non-porous layer as the top layer formed directly on p-n junction substrates. We first studied the fundamental operation of our PC devices. Then, the photocurrents between the porous and non-porous devices were compared to determine the optical absorption properties of the InP porous layer.

2. Experimental Procedure
The device structure and the experimental setup for the photoelectrical measurements are schematically shown in Fig. 1. This device consists of a top layer such as a porous or non-porous layer, three ohmic electrodes, and a p-n junction with an n-type InP layer ($n = 8 \times 10^{17}$ cm$^{-3}$) grown on a highly-doped p-type substrate. The porous structure of the porous device was electrochemically formed in the top layer shown in Fig. 1 using a standard cell with an electrolyte consisting of 1M irradiation ($\lambda = 514.5$ nm)

![Fig. 1. Schematic illustration of device structure and experimental setup.]
HCl (200 ml) and HNO₃ (3 ml) [19]. The AuZn/Ni-ohmic contact was first made on the backside of the p-type InP substrate to supply the electrochemical current. The anodic bias and anodization time were set at 7 V and 4 s, respectively, to form porous structures only in the n-type layer. Moreover, the distance between the bottom of the porous layer and the p-n interface was set at longer than the minority carrier diffusion length in the n-InP (L_p ≈ 240 nm [29]) to eliminate any influence from the pore tips. SEM images of the top and cross-section of the porous structures are shown in Fig. 2 (a), and the photo image of the top of the PC device is shown in Fig. 2 (b). The thickness of the top layer, d_top, of porous and non-porous devices were 4.3 µm and 2 ~ 5 µm, respectively. After the formation of the porous structures, the sample was partly etched into a convex shape at a width of 1 mm using photolithography and a wet etching process, in which the GeAu/Ni ohmic contacts were formed.

The optical absorption properties in this study were investigated by measuring the photocurrents, I₁ and I₂, shown in Fig. 1. The measurements were carried out by changing the irradiation-light power using an Ar⁺ ion laser at a wavelength of 514.5 nm. Only the carriers excited near the p-n interface are separated by the electric field in the depletion layer and collected by the electrodes. Since such carriers are excited by the photons reaching the p-n interface through the top layer, the photocurrents provide us with information on the optical absorption properties of the top layer. If high photocurrents are observed, it indicates that the absorbance of the top layer is low. However, the observation of low photocurrents indicates there is high absorbance of the top layer. Thus, the optical absorption properties of the porous device can be evaluated by comparing them with those of the non-porous device formed as a reference.

3. Results and Discussion

3.1 Basic operation properties of PC devices

The photocurrent measurements were carried out using the non-porous device, which had no porous structures in the top layer, to clarify the basic operation properties of our PC device. Figure 3 shows the current response properties of the non-porous device measured using a light intensity, P_IN, of 2500 µW, which was turned on at t = 500 s and off at t = 1500 s. As shown in Fig. 3, the currents, I₁ and I₂, respectively measured by the back and top electrodes, responded to the light irradiation. Here, I₁ was positive due to the collection of holes by the back electrode. On the other hand, I₂ was negative due to the collection of electrons by the top electrode. There was no current decay under the light irradiation, indicating that stable photocurrents with quick responses were observed. When the ΔI₁ and ΔI₂ are defined as the photocurrents measured by the back and top electrodes, respectively, we found that the ΔI₁ was approximately two times as large as that for the ΔI₂.

The current ratio, ΔI₂/ΔI₁, was measured on the non-porous device as a function of the position of the light irradiation, x, defined in Fig. 2 (b) in order to further clarify the operation principle of the present PC device. As shown in Fig. 4, the ratio of ΔI₂/ΔI₁ linearly increased as a function of x, and became nearly 50 % at x = 0. This behavior can be explained by taking the collection rate of the photocarriers in the top and back electrodes into consideration. The excited electrons due to the photon absorption were collected by the top two electrodes, A and B, whereas the holes were collected by the one back electrode. In terms of the current continuity, the summation of the currents observed in the top two electrodes should be equal to the current observed in the back electrode. Since the irradiation point was close to electrode B, namely at a small x, the excited electrons were preferentially collected in electrode B rather than in electrode A. In such a situation, the proportion of the ΔI₂ to the total current decreased, resulting in a small ΔI₂/ΔI₁, as shown in Fig. 4. As the irradiation point moved...
Towards electrode A, the $\Delta I_2/I_1$ value expectedly increased with the increase in $\Delta I_2$ because the excited electrons were preferentially collected in electrode A. The linear relationship shown in Fig. 4 indicates that the excited electrons near the p-n interface were divided in rough proportion to the distance from the light irradiation points to each top electrode. We found from this result that the light irradiation point can be adjusted by monitoring the center of the PC device.

Then, the effect of the top layer on the photocurrent response was investigated using the non-porous PC device. Figure 5 shows the photocurrents, $I_{1\text{top}}$, measured by changing the thickness of the top layer, $d_{\text{top}}$, defined in Fig. 1. We found that the $I_{1\text{top}}$ value increased with a decrease in $d_{\text{top}}$. The correlation coefficient, $R$, obtained by the exponential fitting on the experimental data was 0.989. The number of photocarriers contributing photocurrents can be considered in proportion to the photon flux reaching the p-n interface. The photon flux, $\Phi$, is given by the following equation:

$$\Phi = \Phi_0 \exp(-\alpha d).$$  \hspace{1cm} (1)

In Eq. (1), $\alpha$ is the absorption coefficient, $d$ is the optical-path length, and $\Phi_0$ is the incident photon flux given by

$$\Phi_0 = \frac{P_\text{IN}}{E} = \frac{\lambda}{hc}P_\text{IN},$$  \hspace{1cm} (2)

where $h$, $\lambda$, and $c$ are the Planck's constant, the wavelength, and the velocity of the incident light, respectively. The light intensity, $P_\text{IN}$, and the product of the absorption coefficient, $\alpha$, and the optical-path length, $d$, are important for the discussion of optical absorption properties. Since the photocurrents, $I_{1\text{top}}$, are assumed in proportion to the photon flux, $\Phi$, the following equation is derived by using Eqs. (1) and (2):

$$\Delta I_1 = \frac{\lambda P_\text{IN}}{h c} \exp(-\alpha d_{\text{top}}).$$  \hspace{1cm} (3)

The results shown in Fig. 5 are very consistent with that from using Eq. (3), where the photocurrents, $\Delta I_1$, are described as an exponential function of the geometrical thickness of the top layer, $d_{\text{top}}$. We found from these results that the photocurrents changed under the influence of the number of photocarriers generated near the p-n interface, which gave us the information on the optical absorption properties of the top layer.

3.2 Comparison between porous and non-porous devices

The photocurrent response of present PC devices was compared by changing the top layer such as the non-porous and porous layers. Figure 6 shows the current response of a porous PC device to the incident light at various power levels, $P_\text{IN}$. We found that the photocurrents, $I_{1\text{top}}$, increased with the $P_\text{IN}$ in quick response to the light switching. This is consistent with the theoretical description of the photocurrents obtained using Eq. (3). For more discussion, the $I_{1\text{top}}$ of non-porous and porous devices are compared in Fig. 7, plotted as a function of the $P_\text{IN}$. Both the non-porous and porous devices showed a similar behavior, the $I_{1\text{top}}$ linearly increased with $P_\text{IN}$. The correlation coefficients obtained by linear fitting on the experimental data were greater than or equal to 0.998. However, the current value differed substantially, where the photocurrent of the porous device was approximately 40% that of the non-porous device. As mentioned above for Eq. (3), a low photocurrent indicates a high absorbance in the top layer since the photocarriers generated near the p-n interface decreased exponentially with an increase in the absorption coefficient, $\alpha$. These results suggest that the absorption coefficient of the porous layer is higher than that of the non-porous layer.

A previous study reported that a smaller
The absorption coefficient was obtained in the porous InP, as compared with a bulk InP [28]. According to the literature, the absorption coefficient was estimated from the photocurrents observed at the electrolyte/InP interface inside the porous layer. The low photocurrents observed in the porous layer were explained in terms of the surface states and lower electric field at the pore walls. Since the surface states at the pore walls act as recombination centers, the photocurrents observed at the electrolyte/InP interface decreased, resulting in the underestimation of the absorption coefficient. In addition to this, the low built-in potential at the electrolyte/InP interface reduces the charge separation and promotes the recombination of excited carriers in the surface states. On the other hand, our PC devices are designed to separate the porous layer from both the p-n interface and the carrier-collecting electrode. Since the photocurrents flow in a channel far from the porous layer in such a configuration, it can be measured to avoid the negative effects of the surface states at the pore walls.

One of the possible reasons for the enhancement of the absorption property is light scattering within the porous layer [25]. We believe that the number of absorbed photons increases in the porous layer due to the significant increase in optical-path length by the light scattering. Since the $d_{top}$ is defined as a geometrical thickness of the top layer, in this study, the effect of the increased optical-path length will be included in the $\alpha$, as shown in Eq. (3). Another possible reason is the sub-bandgap absorption in the porous layer [24, 26]. Sub-bandgap is formed within the original bandgap of InP by the localized levels such as the lattice defects, impurities in the bulk, and surface states. The optical absorption process caused by the localized levels is schematically shown in Fig. 8. Carriers can exist in the forbidden band due to the localized levels, which allows carriers to excite (b) from the valence band (VB) to the localized levels, (c) from the localized levels to the conduction band (CB), and (d) from the localized levels to other localized levels in addition to (a), which is the general excitation from VB to CB. Since the surface area of the porous layer is about fifty times as large as that of the non-porous layer, the localized levels, especially those caused by the surface states, might increase and lead to enhancement of the absorbance.

4. Conclusion

The optical absorption properties of InP porous structures formed by using the electrochemical process were investigated using PC devices formed on p-n junction substrates. The photocurrent measured on non-porous PC devices exponentially increased with the decrease in the thickness of the top layer on the p-n interface, which was consistent with the proportional relation between the photon flux and the number of photocarriers generated near the p-n interface. From the results of the photocurrent measurement by changing the incident light power, lower photocurrents were observed on the porous device, as compared with that of the non-porous device, indicating that the absorption properties of InP were enhanced after the formation of porous structures. The enhancement of absorption properties can be explained in terms of absorption coefficient, $\alpha$, increased by the light scattering and the sub-bandgap absorption in the porous layer. We believe that porous structures are promising materials for use in
photoelectric conversion devices such as solar cells and photodetectors because of their unique features such as their large surface area, low reflectance properties, and high absorption properties.

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