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Large Photocurrent-response Observed at Pt/InP Schottky Interface Formed on Anodic Porous Structure

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Abstract

A photoelectric-conversion device—based on an InP porous structure utilizing the large surface area inside pores and the low reflectance on the porous surface—is proposed. The InP walls inside the pores are covered with thin platinum films that form a Schottky barrier yielding an electric field that separates photo carriers generated under illumination. The coverage of the platinum film and its optical reflectance depended largely on the surface morphology of the porous structure. Removal of the irregular top layer formed at the initial stage of the pore formation effectively improved the coverage of the platinum film, which showed a very low optical reflectance (i.e., below 3.2%). According to current-voltage measurements under illumination, the platinum/porous InP showed larger photocurrents and higher responsivity than those of a reference planar sample.

Keywords: photoelectric conversion, porous structure, indium phosphide (InP), platinum, electrochemical method, current-voltage (*I-V*), SEM, optical reflectance

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Introduction

High-density formation of semiconductor nanostructures—targeting applications such as quantum and optoelectronic devices—has been intensely researched. Mainstream approaches for forming semiconductor nanostructures have used conventional methods such as dry-etching and crystal-growth processes. However, there are severe limitations on downsizing and increasing the density of nanostructures because most approaches require lithography for defining the size and position of the nanostructures. One alternative approach is an electrochemical process, which can form various semiconductor nanostructures in a self-assembled fashion. The porous structure formed by anodic etching is the most well-known application of an electrochemical process, where a high-density array of nanometer- or micrometer-sized pores is formed over a large area on the semiconductor surface.

Anodic porous etching on Si and Ge was first reported by A. Uhlir at Bell Labs in 1956 [1]. After that, various compound semiconductors, such as GaAs [2,3], InP [4-7], GaP [8,9] and GaN [10], were studied. However, most previous studies targeted their structural and optical properties; few reported on the application of porous structures to active devices. The authors recently reported that the optical reflectance of an InP surface decreases considerably after anodic porous etching [11]. In particular, low reflectance below 0.4% was obtained in ultra-violet (UV), visible, and near-infrared ranges by improving the surface morphology of the porous structure. This finding suggests that surface-controlled porous structures are promising materials for application to photoelectric-conversion devices such as solar cells and photo detectors.

In the present study, utilizing the large surface area and low-reflectance properties of an InP porous structure, a photoelectric-conversion device is proposed. The fabrication process for this device was optimized in view of structural and optical reflectance properties. Moreover, to clarify the performance of the device in terms of photoelectric conversion efficiency, the current-voltage (*I-V*) characteristics of the device under illumination were investigated.

2. Experimental details

The proposed device—based on a porous InP structure—is schematically shown in **Fig. 1**. A potential barrier for separating the photo-carriers generated under illumination is formed on the InP walls inside pores. In this study, a platinum film was used for this purpose because the high Schottky barrier is provided to n-type semiconductor due to a large work function of platinum (5.65 eV) [12]. The photo-carriers generated under

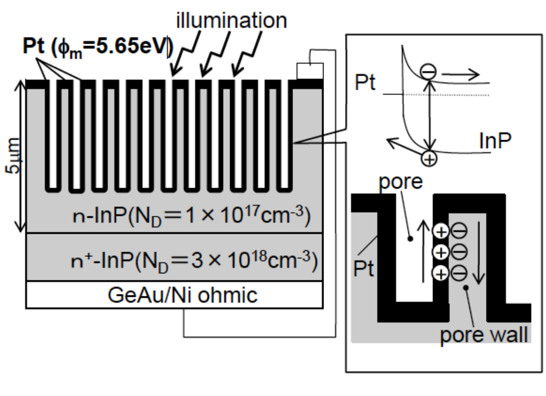

Fig. 1: Schematic illustration of the photoelectric-conversion device based on a InP porous structure.

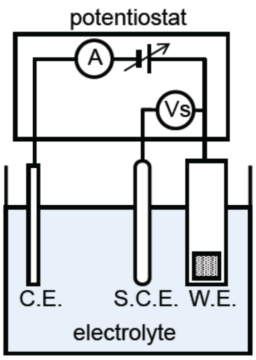

Fig. 2: Setup of the electrochemical process used for forming the porous structure, removing the irregular top layer, and forming the platinum film.

illumination are separated by the electric field in the depletion region and collected on the top and back electrodes, as shown in **Fig. 1**. The proposed device is expected to increase the efficiency of photoelectric-conversion devices such as a photo-detector and a solar cell due to its unique features, namely, large surface area inside pores and low reflectance.

As semiconductor materials for the device fabrication, n-type InP (001) epitaxial wafers were used. Epitaxial layers with a thickness of 5 μm were grown on n^+InP substrates by standard metal-organic vapor-phase epitaxy with silicon doping of 1×10^{17} cm^{-3}. To supply currents for forming the porous structures, a Ge/Au/Ni ohmic contact layer was evaporated on the backside of the samples and annealed in nitrogen for 5 min at 380˚C.

The experimental setup of the electrochemical process is schematically shown in **Fig. 2**. The porous structure was formed in the n-type epitaxial layer by using a standard cell with three electrodes, namely, an InP electrode as a working electrode (W.E.), a platinum counter electrode (C.E.), and a saturated calomel electrode (S.C.E) as a reference. The electrolyte consists of 1 M HCl (200 ml) with HNO_3 (3 ml). Anodic bias was applied to the semiconductor electrode to obtain high-density porous structures. The anodic bias and anodization time were set at 20 V and 5 s.

As previously reported, a disordered irregular layer formed during the initial stage of pore formation when the pores formed and partly remained on top of the ordered porous layer [6]. To remove the irregular top layer, the porous surface was then photo-electrochemically etched at an anodic bias of 1.5 V in the same electrolyte under illumination [13]. After the irregular top layer was removed by the photoelectrochemical (PEC) etching, a cathodic bias was applied to a porous structure in a H_2PtCl_6 electrolyte in order to form a thin platinum film on the wall inside the pores. To improve the uniformity of the platinum film, a pulsed bias mode was used [14,15]. In this study, the formation of porous structures, the PEC etching, and the cathodic formation of platinum was carried out using the same setup shown in **Fig. 2** by changing the electrolytes and bias conditions. After the electrochemical process,

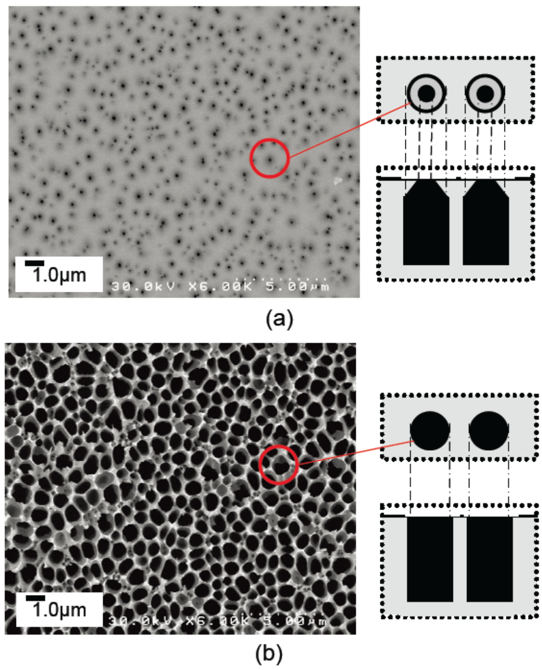

Fig. 3: Top view SEM images of the InP porous structures and its schematic illustration. (a) Sample just after the pore formation and (b) sample after the removal of the irregular top layer formed on the surface.

the sample was washed in deionized water and dried well for optical and electrical characterizations performed in the air.

Structural properties and optical-reflectance properties were investigated by using a Hitachi S-4100 scanning electron microscope (SEM) with an operating voltage of 30kV and a Shimazu UV-1700 UV-visible spectrometer, respectively. *I-V* measurements were carried out in the air using a Keithley 2602A source meter with a contact probing system. A tungsten lamp was used as a light source for the photoelectrical measurements. For purpose of comparison, a platinum/planar InP without a porous structure was prepared by the cathodic formation of platinum on the planar InP substrate.

3. Results and Discussion

3.1 Formation of platinum/porous InP structures

The effect of the irregular top layers on the formation of platinum films was investigated first. SEM images of the reference surface just after the formation of the porous structure and the etched surface after the PEC process are shown in **Figs. 3(a) and (b)**, respectively. As shown in **Fig. 3(a)**, small pores with a diameter of about 80 nm were formed on the surface at the initial stage of the pore formation. Furthermore, inner pores (with a large diameter) can be seen through the irregular top layer as a lightly shaded circle around each pore. After the PEC process, as shown in **Fig. 3(b),** the pore diameter increased to 450 nm (on average). This result indicates that the irregular top layer was completely removed by the PEC process and the inner pores

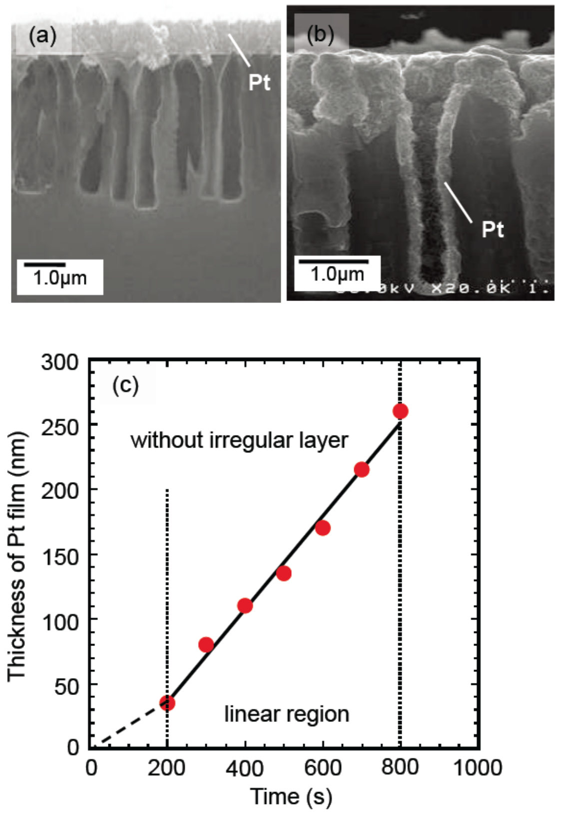

Fig. 4: Cross-sectional SEM images of the sample after platinum formation: (a) on the porous structure with the irregular top layer and (b) on the porous structure after the removal of the irregular top layer. (c) Correlation between average thickness of platinum film formed on the walls inside the pores and processing time for forming the cathodic platinum.

appeared on the etched surface.

Cross-sectional SEM images of the samples after the platinum formation on the porous structure with and without the irregular top layer are shown in **Figs. 4(a) and (b)**, respectively. The coverage of the platinum films on the walls inside pores depends strongly on the surface morphology of the porous structures. As shown in **Fig. 4(a)**, the platinum film formed only on the irregular top layer and not on the wall surface inside the pores. This result indicates that each pore is completely closed by a platinum film in the initial stage of platinum formation. On the contrary, the coverage of the platinum film on the walls inside the pores is improved in the sample without the irregular top layer, as shown in **Fig. 4(b)**. A platinum film with an average thickness of about 280 nm was formed on the wall surface inside the pores, indicating that cathodic currents were supplied from the InP wall inside the pores. Similar structure has been reported in the case using a conductive porous template such as a Si porous structure [16]. Average thickness of the platinum film is plotted against processing time of the cathodic formation in **Fig. 4(c)**. This result indicates that the thickness of the platinum film formed on the wall inside the pores can be controlled by the processing time.

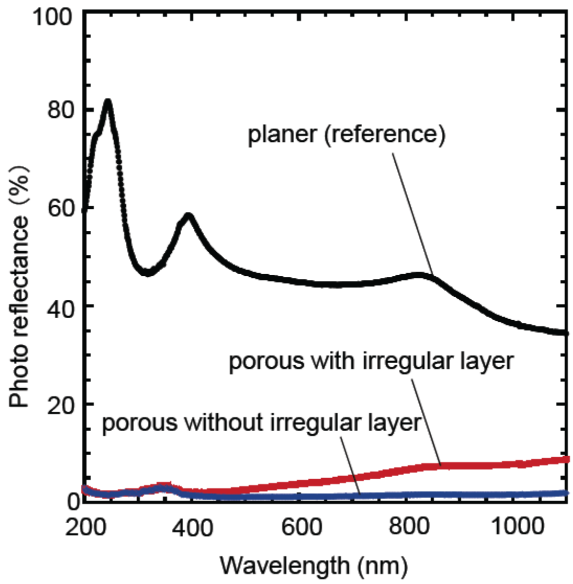

Fig. 5: Surface-reflectance spectra measured for three samples as a function of wavelength of incident light.

The effect of the structural properties on the surface reflectance of the porous structure was investigated by comparing three samples, as shown in **Fig. 5**. First, the reflectance of the planar sample was higher than 30% over the measurement range. Typical peaks, attributed to the interband transitions, were observed around 250, 400, and 850 nm [17]. The reflectance of the porous sample was 20 to 30% lower than that of the reference sample. Especially, the reflectance of the porous sample without the irregular top layer was considerably decreased, namely, to lower than 3.2% over the measurement range. These results are very similar to those for a porous structure without platinum films reported in a previous work [11]. It was found that the low- reflectance properties of the InP porous structures remained after the formation of the platinum film.

3.2 Current-voltage (I-V) characteristics under illumination

The basic photoelectrical properties of the porous sample were investigated by comparing those of a planar sample formed as a reference. The current-voltage (*I-V*) characteristics of the platinum/planar InP and the platinum/porous InP sample without the irregular top layer are shown in **Figs. 6(a) and (b)**, respectively. The average thickness of the platinum film formed on the wall inside the pores was 72 nm. The current density was calculated from the geometrical surface area of the top platinum films where the forward bias was applied. As shown in **Figs. 6(a) and (b)**, the *I-V* characteristics obtained on both samples show a clear rectifying behavior, indicating the formation of a Schottky barrier at the Pt/InP interface. However, the photocurrents measured under illumination depend largely on the sample structure. The reverse current for the platinum/planar InP sample is about 10 mA/cm^2 under illumination, which is 3 mA larger than that obtained in

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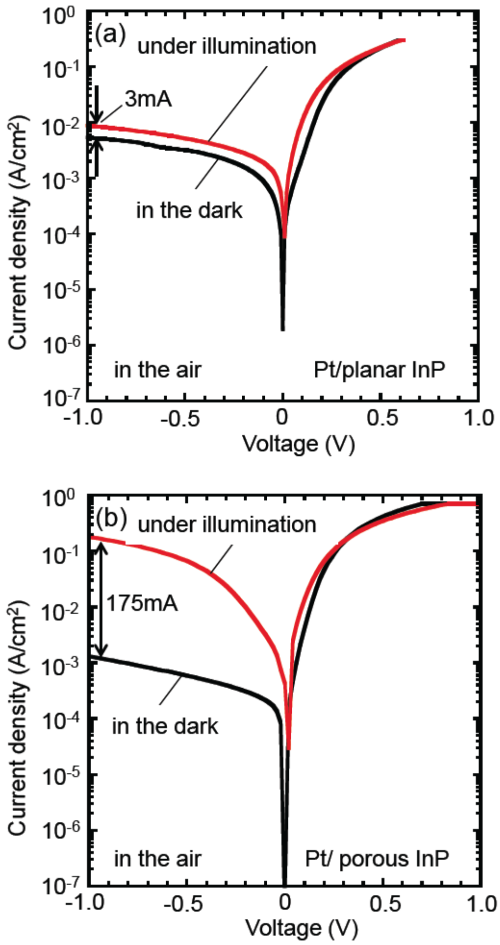

Fig. 6: Current-voltage (*I-V*) characteristics measured under illumination using a white light for two samples. (a) Platinum/planar InP sample and (b) platinum/porous InP sample without irregular top layer.

the dark, as shown in **Fig. 6(a)**. On the contrary, the reverse current of the platinum/porous InP sample is about 200 mA under illumination, which is 175 mA larger than that obtained in the dark, as shown in **Fig. 6(b)**.

To further clarify the photo current response properties of the porous sample, the optical responsivity was investigated under monochromatic illumination by using a band-path filter for the 514.5-nm wavelength. Responsivity, R, is defined as

$$R = \frac{J_L}{P_{in}} \quad , \qquad (1)$$

where J_L is the density of photocurrents, and P_{in} is incident light power.

The responsivity of the porous sample is compared with that of the reference planar sample in **Fig. 7**. The photocurrents, J_L, were obtained by applying a reverse bias from 0 to -1.0 V, and P_{in} was set at 3.7 mW/cm^2 (by using a power meter). The responsivity of the reference planar sample was below 0.15 A/W in the bias range used for the present measurements. On the contrary, the responsivity of the porous sample depends largely on the

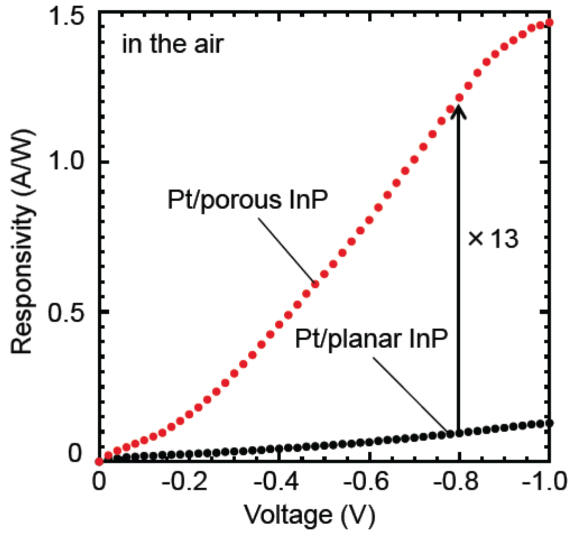

Fig. 7: Optical responsivity measured under monochromatic illumination using the band-path filter for 514.5-nm wavelength.

applied reverse bias, for example, it is 13 times larger than that of the reference planar sample at a bias of -0.8 V. These results indicate that the photoelectric-conversion efficiency of the porous sample is higher than that of the planar sample with the same geometrical area.

Large photocurrents on a porous InP electrode in an electrolyte during electrochemical measurements have been reported [11,18]. Photocurrents (including faradaic and non-faradaic currents) increased in proportion to pore depth or effective area inside a pore. Similarly in the air, it seems that the major factor that enhances the photocurrents observed in this study is the increase in the total area at the platinum/InP interface. In consideration of the cylindrical pores, the effective surface area including the wall surface was estimated to be about seven times larger than that of the planar sample used in this study. It is concluded from this estimation that the increased photocurrents shown in **Fig. 7** cannot be explained only by the effect of the increased surface area. Another possible reason for the increase in photocurrents is the optical-reflectance properties of the porous structure, as shown in **Fig. 5**. The low reflectance of the porous structure is expected to enhance the efficiency of the light collection in the pores.

In contrast with the large photocurrents, the present device showed the small photovoltages, as shown in **Fig. 6(b)**. This is probably due to the poor potential barrier formed at Pt/InP interface. For the photovoltaic application, further improvement on the device structure is necessary, such as employing the pn-junction interface instead of the Schottky interface on the pore wall. We believe that the porous structure—with unique features such as low optical reflectance and large wall surface—is a good candidate for a building block of photoelectric conversion devices.

4. Conclusion

A photoelectric-conversion device based on an InP porous structure was proposed. The removal of the irregular top layer formed on the porous strcture effectively improved the coverage of a platinum film on the wall surface inside the pores, where optical reflectance was very low (below 3.2%). According to *I-V* measurements under illumination, the platinum/porous InP showed larger photocurrents and higher responsivity than those of a reference planar sample. This result can be explained by the two unique features of the InP porous structures: the large surface area inside the pores and the low reflectance.

Acknowledgements

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