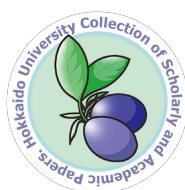




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## Electrochemical Etching of Indium Phosphide Surfaces Studied by Voltammetry and Scanned Probe Microscopes

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### Abstract

Using voltammetry, X-ray photoemission spectroscopy (XPS), in situ electrochemical scanning tunneling microscopy (STM), ex situ atomic force microscopy (AFM) and scanning electron microscope (SEM) measurements, electrochemical etching modes for n-InP surfaces were investigated and optimized for uniform and controlled etching in an HCl electrolyte. The voltammograms indicated the presence of active and passive regions. The surfaces obtained in the active region were clean and featureless with an rms roughness of 1.8 nm. On the other hand, the oxide covered surfaces obtained in the passive region were nonuniform and porous. Etching characteristics of the d.c. photo-anodic mode and the pulsed avalanche mode were then investigated and compared. Both modes were found to be highly controllable and produced uniform and clean surfaces, consuming eight holes per molecule of InP. In particular, the pulsed avalanche etching mode realized an extremely high etch rate of  $3 \times 10^{-5}$  nm/pulse.

KEYWORD: InP, etching, electrochemical process, voltammetry, scanned probe microscope

### 1. Introduction

Scaling down of device feature size to the nanometer order is a recent general trend, not only for Si devices, but also for III-V devices. Thus, the etching process, the spatial uniformity and the precise controllability of the etching depth along with minimal process-induced damages have become increasingly important. Owing to its low damage nature, wet etching in various acid solutions<sup>1)</sup> is widely used in various steps of InP and related material fabrication. However, precise control of the etching depth is extremely difficult in wet etching, because the etch rate is very sensitive to the temperature and the local fluctuation of the etchant composition.

On the other hand, electrochemical etching appears to be promising for achieving high controllability, since the anodic reaction can be precisely controlled by the amount of charge according to Faraday's law of electrolysis. However, it is not clear at present whether it is possible to perform uniform and controlled etching of n-InP by the electrochemical reactions on InP surfaces in the electrolyte. In the literature, only limited works<sup>2-5)</sup> have been reported on the anodic etching of InP, and their etch rate and uniformity have not been clarified. More recent anodization experiments<sup>6-9)</sup> on InP using HCl electrolyte have led to the formation of InP porous structures. Although such an anodization mode is interesting for the formation of quantum structures and photonic crystals, it is not suitable for uniform etching. On the other hand, it has also been recently shown by our group that electrochemical etching applied just before electrodeposition is effective for the realization of well-behaved Schottky diodes with oxide-free, stress-free and pinning free interfaces for InP<sup>10)</sup>. Similar results have been reported for n-GaAs Schottky contacts<sup>11)</sup>. However, the mechanism, the etch uniformity and the etch rate of such a predeposition etching process have not been clarified yet.

The purpose of this study is to clarify and optimize electrochemical etching modes for uniform and controlled etching of InP surfaces in the HCl electrolyte. First, the basic reactions and properties of the surface were investigated by cyclic voltammogram and XPS, STM and AFM measurements. Then, the etching characteristics in the d.c. photo-anodic mode and the

pulsed avalanche mode were investigated and compared. Both modes were found to be highly controllable and produce uniform and clean surfaces. The etch reaction was found to consume eight holes per molecule of InP in contrast to the case of GaAs where six holes were consumed. In particular, the pulsed avalanche etching mode realized an extremely high etch depth controllability of  $3 \times 10^{-5}$  nm/pulse.

## 2. Experimental

Anodic reactions on the n-InP are schematically shown in Fig. 1. Anodic reactions under positive potentials are known to require holes. Since holes are minority carriers for the n-type semiconductor, a sufficient number of holes can only be supplied by applying high voltage to the substrate to cause avalanche breakdown or by illuminating the electrode with light to cause photo-generation, as shown in Figs. 1(a) and 1(b), respectively. The nature and rates of the anodic reactions depend on the relative position of the redox potential with respect to the semiconductor band, which is strongly affected by the pH of the electrolyte. Namely, the redox potential is shifted downward with respect to the semiconductor band at a rate of 60 mV/pH.

The electrochemical etching of InP is realized as a result of anodic reaction. Either electrical avalanche or light illumination with an intensity of  $20 \text{ mW/cm}^2$  was utilized in this study to induce anodic reactions on n-InP. Electrochemical anodic etching experiments were performed using a standard cell with three electrodes, i.e., an InP electrode, a Pt counter electrode and a reference saturated calomel electrode (S.C.E.), as shown in Fig. 2(a). The potential on the InP electrode was controlled with respect to the S.C.E. by a potentiostat. The potential was applied in d.c., ramped or pulsed mode in order to cause etching as well as to investigate the nature of the electrochemical reaction on the surfaces by voltammetry. The electrolyte was a dilute HCl solution with a pH of 1.0. N-type InP(100) bulk materials with a carrier concentration of  $5 \times 10^{15} \text{ cm}^{-3}$  were used as the InP electrode. For the current supply, GeAu/Ni films were deposited on the back surface of the substrate and sintered at  $370^\circ \text{C}$  in  $\text{N}_2$  flow.

In order to investigate etch depth and surface morphology, in situ STM, ex situ AFM, and SEM measurements were carried out using the Nanoscope IIIa system and the Hitachi 4100 system. The setup for in situ STM measurement is shown in Fig.2(b). XPS measurements of the surface were carried out using Perkin-Elmer spectrometer (1600C) under excitation by monochromated  $\text{AlK}\alpha$  line.

## 3. Results and Discussion

### 3.1 Voltammetric study of anodic reactions

Solid curves in Figs. 3 and 4 show typical measured cyclic voltammograms obtained on as-received n-InP wafers in the dark and under illumination by a tungsten lamp, respectively. The overpotential was swept at a rate of 50 mV/s starting from -0.50 V (vs S.C.E.) to the positive potential direction first, and then turning to the negative one.

In the dark, no anodic current flowed at small overpotentials because of the presence of an electrolytic Schottky barrier at the n-InP/electrolyte interface, as shown in Fig.1. Above +1.0 V (vs S.C.E.), the anodic current started to flow. When illuminated by a tungsten lamp at an intensity of  $20 \text{ mW/cm}^2$  from a distance of 5 cm, on the other hand, the photo-anodic current started to flow at -0.40 V (vs S.C.E.), as seen in Fig.4, indicating the onset of an anodic reaction even at a negative overpotential due to the photovoltaic effect.

After the onset of anodic current, the cyclic voltammograms in Figs.3 and 4 behave in a similar fashion. Namely, they show peak hysteresis, indicating the occurrence of the so-called active-passive transition<sup>4)</sup>. Hence, at small overpotentials, active anodic dissolution takes place. On the other hand, at larger overpotentials beyond the peaks, the semiconductor surface is covered with a passive oxide film, leading to passivation.

### 3.2 Surface morphology and XPS study

In order to confirm the basic reactions seen on the voltammograms, the surface properties of the electrochemically processed n-InP surfaces were studied by in situ electrochemical STM and ex situ AFM techniques. In situ electrochemical STM images were taken with the substrate bias fixed around the flat-band potentials. This was done because electrochemical reactions could be suppressed as no transfer of electrons and ions, except for electrons for imaging, takes place between the InP electrode and the electrolyte around the flat-band potential. The applied potentials of the InP electrode and the STM tip were set at -0.9 V and +0.4 V (vs Pt), respectively. For easier electrical contact, a highly doped n<sup>+</sup>-InP sample with an electron concentration of  $1 \times 10^{18} \text{ cm}^{-3}$  was used. The in situ STM image of the surface just after anodic etching in the active region is shown in Fig.5(a). This surface was found to be smooth and featureless with an rms roughness of 2.5 nm. Ex situ AFM observations also confirmed a featureless and smooth surface with a similar rms roughness value. This value was found to be significantly better than that obtained after conventional sulfuric acid-based wet etching. For example, etching with a standard solution of  $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 3 : 1 : 1$  gave a minimum rms AFM value of 4.8 nm, sometimes resulting in a much rougher and streakier surface with height variations of 10-20 nm.

In contrast to the surface obtained in the active region, the surface obtained in the passive region showed distinct features. As an example, an SEM micrograph of the n-InP surface taken after anodic reaction in the passive region is shown in Fig.5(b). The surface was prepared by applying a d.c. potential of 2.0 V to the substrate for 2-3 minutes under illumination. This surface exhibited a porous structure involving oxide components. Further study revealed that a porous (100) InP structure similar to that reported for the (111) InP surface<sup>6-9)</sup> is formed in this passive region of the overpotential as discussed elsewhere<sup>12)</sup>.

XPS studies were also carried out on the anodically processed surfaces of n-InP in order to further confirm the presence of active-passive transition. Top and bottom traces in Fig. 6 show typical XPS core-level spectra of the InP surfaces obtained at overpotentials before and beyond the current peak, respectively in the voltammogram.

As seen in Fig. 6, the XPS spectra differ markedly for the two cases. Those for the surface obtained in the active-region agree with the spectra for pure InP with a small amount of native oxide that was presumably formed during sample transfer in air from the cell to the XPS chamber.

On the other hand, the spectra obtained from the surface in the passive region indicated the presence of an extremely thick anodic film, as expected. The chemical composition of such an anodic oxide layer appears to be very complex. It has been reported that anodically grown films consist mainly of  $\text{In}_2\text{O}_3$ <sup>13)</sup>. However, more detailed analysis has also indicated that the anodic oxide layer consists of  $\text{In}_2\text{O}_3$  and  $\text{In}(\text{PO}_3)_3$ <sup>14)</sup>.

Thus, the results of surface morphology and composition study are consistent with the reaction behavior indicated by the voltammograms, and show that careful adjustment of the overpotential is absolutely necessary to obtain clean and smooth etched surfaces with precisely controlled etch depths.

### 3.3 Characteristics of the d.c. photo-anodic etching mode

As observed from the voltammogram, a promising way to achieve uniform etching is to induce active anodic dissolution by illuminating the surface with light. In this case, no external voltage source is necessary, because a d.c. photocurrent flows due to the photovoltaic effect. The etch depth can be controlled by integrating the photocurrent and monitoring the sheet charge density,  $Q$ , passing through the surface. Namely, the etch depth,  $t$ , can be related to  $Q$  through the following equation on the basis of Faraday's law of electrolysis.

$$t = \frac{M}{xFd} Q \quad (1)$$

where  $F$  is Faraday's constant (96,485.3 C/mol),  $M$  and  $d$  are the molecular weight and the density of InP, respectively, and  $x$  is the number of holes required to etch one molecule of InP.

First, the effect of such an anodic etching in the d.c. photo-anodic etching mode was investigated by voltammetry. Before the photo-anodic etching, a passive oxide was formed at a sample bias of +0.2 V under illumination by a tungsten lamp at an intensity of 20 mW/cm<sup>2</sup>. Then, during etching, the anodic potential was set at +0.0 V under the same illumination intensity. The cyclic voltammogram after this photo-anodic etching is shown by a broken curve in Fig. 4. The onset potential of the anodic photocurrent was shifted slightly to the more negative side and the maximum current was increased after the photo-anodic etching. This indicates that the surface became cleaner after etching.

According to SEM observation, the surface after etching was flat and featureless. The AFM rms roughness after anodic etching in the d.c. photo-anodic etching mode was typically 2.5 nm.

Next, a detailed study was carried out on the controllability of the etch depth. For selective etching, circular photoresist window patterns were used as masks, and the depth was measured by taking step profiles by AFM. The measured etch depth is plotted in Fig. 7 as a function of the integrated sheet charge density  $Q$ .  $Q$  was determined by integrating the anodic photocurrent density which was measured as a function of time in the zero bias mode. It is seen in Fig. 7 that the etching depth increases proportionally to the integrated sheet charge density. Thus, this result indicates that the etching depth in the acid solution can be controlled by monitoring and controlling the integrated sheet charge density of photocurrent supplied to the n-InP substrate. Using a typical tungsten lamp, an etch rate of typically 30-40 nm/min can be realized.

From the results shown in Fig. 7, one can determine the value of  $x$  in eq.(1), and obtain information about the basic chemical reaction. Using  $M = 145.77$  and  $d = 4.79$  for InP,  $x$  was found to be 8.0. Thus, eight holes are required to etch one molecule of InP. This is different from the case of GaAs where six holes are used to etch one GaAs molecule<sup>15)</sup>. In the latter case, the reaction involved is



However, no reliable value of  $x$  or a well-established reaction is reported for InP etching. Mention of  $x=6$  was made in the anodic dissolution experiment work by Faur et al.<sup>4)</sup>, but no supporting data were given. This value of  $x=6$  is difficult to explain because the existence of  $\text{P}_2\text{O}_3$  has never been reported. On the other hand, the value of  $x=8$  observed here can be explained either by



or by



All of  $\text{InPO}_4$ ,  $\text{In}_2\text{O}_3$  and  $\text{In}(\text{PO}_3)_3$  have been mentioned previously as oxides obtained by oxidation of InP<sup>16)</sup>. However, on the basis of detailed and reliable XPS analysis<sup>14)</sup> mentioned previously, we believe that the reaction in eq.(4) is more likely. Namely, the chemical reaction in both active and passive regions of the overpotential is one and the same and given by eq. (4).

### 3.4 Characteristics of the pulsed avalanche etching mode

For finer control of the etch depth in the nm range, the simple d.c. photo-anodic etching mode is not suitable because accurate control becomes very difficult. For such a purpose, the pulsed avalanche etching mode is obviously desirable, since charge supply can be controlled by the pulse number. In fact, we have already shown<sup>10)</sup> that such an etching mode is possible and useful as a predeposition process for metal electrodeposition in realizing an oxide-free interface. However, the etch rate and uniformity have not yet been systematically investigated.

In this study, the current density-overpotential relationship was examined first. The voltage and current waveforms used for this experiment and also for the etching experiments are schematically shown in Fig. 8(a). An example of the observed pulsed peak current-voltage characteristics, i.e.,  $J_p$ - $V_p$  relationship, is shown in Fig. 8(b) for the case of  $t_{\text{on}} = 10$  ms and  $t_{\text{period}} = 600$  ms, and is compared with the slowly ramped current-voltage characteristics. As seen in Fig.

8(b), the pulsed current is much higher than the slowly ramped current at the same overpotential, and does not show a peak. This can be explained by the fact that a finite time is required to cause active-passive transition, as shown in the case of anodic oxidation of GaAs<sup>17)</sup>. Thus, no current-blocking oxide layer is formed in a short pulse of ms duration. Therefore, in the pulsed mode, etching takes place during the pulsed-on time  $t_{on}$ , and the resultant high-density anodic products are removed from the surface vicinity during the pulse-off time,  $t_{off}$ , by diffusion.

Next, the effect of pulsed avalanche etching on the surface was examined from the voltammograms. The cyclic voltammograms after pulsed avalanche etching in the dark are shown by dashed curves A and B in Fig.3. Here, curve A was taken for the pulse waveform of  $t_{on} = 10$  ms,  $t_{period} = 1200$  ms,  $V_p = 5.0$  V and curve B, for the pulse waveform of  $t_{on} = 10$  ms,  $t_{period} = 2400$  ms,  $V_p = 5.0$  V. The overpotential was swept at a rate of 50 mV/s, starting from 0V (vs S.C.E.) to the positive potential direction first, and then turning to negative. As seen in Fig. 3, the anodic current for curve B was higher than that for curve A, indicating that a surface much cleaner than the air-exposed surface was obtained on curve B. The result confirms that sufficient removal of anodic products from the surface vicinity in the pulse-off time is important. Repeated measurements have shown that the duty ratio,  $t_{on}/t_{period}$ , should be larger than 1/120 for adequate removal of anodic products.

SEM observations of the etched surface indicated that the surface is flat and featureless, and the AFM rms roughness value of the surface was found to be as small as 1.8 nm.

Finally, etching depth was examined as a function of pulse number and pulse width, while keeping the pulse duty ratio constant at 1/240. The observed etching depth is plotted in Fig. 9(a) as a function of pulse number. The result indicates that the etch depth is proportional to the number of pulses applied, as expected. In Fig. 9(b), the observed etch rate is plotted vs pulse width. As expected, the etch rate increased monotonically with pulse width. Thus, etching depth in avalanche pulse etching can be easily controlled by pulse width and number. The observed etch rate is  $3 \times 10^{-5}$  nm/pulse for  $t_{on}/t_{period} = 1/240$  and  $V_p = 5.0$  V. Furthermore, the integrated sheet charge density was evaluated from the analysis of the pulse current waveforms, and  $t$ - $Q$  relationship in the pulsed avalanche etching mode is also plotted in Fig. 7. The data lie on the line of  $x=8$ , which shows that the same etching reaction as that in photo-anodic etching also occurs in this mode.

#### 4. Conclusion

Using voltammetry, XPS, in situ electrochemical STM, ex situ AFM and SEM measurements, electrochemical etching modes for n-InP surfaces were investigated and optimized for uniform and controlled etching in the HCl electrolyte. The voltammograms indicated the presence of active and passive regions. The surfaces obtained in the active region were clean and featureless with an rms roughness value of 1.8 nm. On the other hand, the oxide-covered surfaces obtained in the passive region were nonuniform and porous.

Etching characteristics in the d.c. photo-anodic mode and the pulsed avalanche mode were investigated and compared. Both modes were found to be highly controllable and produced uniform and clean surfaces. The etch reaction was found to consume eight holes per molecule of InP in contrast to the case of GaAs where six holes were consumed. The pulsed avalanche etching mode realized an extremely high etch rate of  $3 \times 10^{-5}$  nm/pulse.

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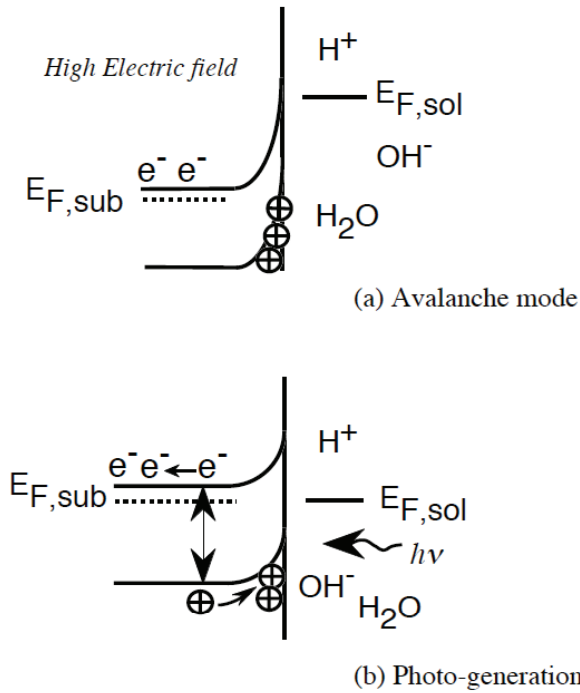


**Fig. 1** Schematic representation of bandbending of semiconductor surface in a solution. (a) Avalanche effect to generate electron-hole pair. (b) Illumination to generate electron-hole pair.

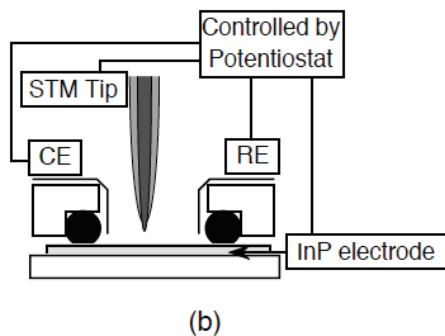
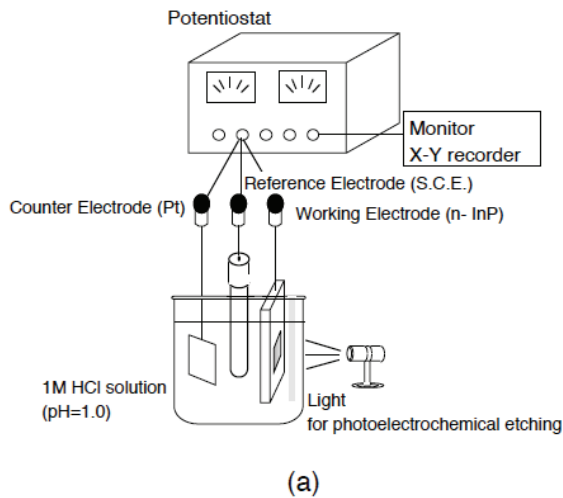


**Fig. 2** Setup for (a) electrochemical etching of n-InP, and (b) in situ STM observation in the electrolyte.

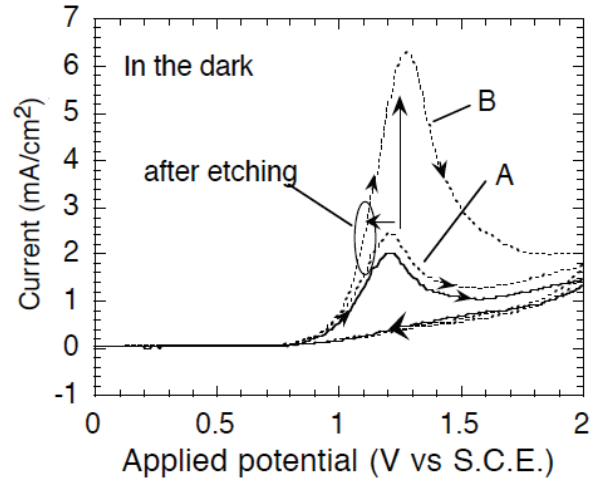


**Fig. 3** Cyclic voltammograms of n-InP with  $N_d=5 \times 10^{15} \text{ cm}^{-3}$  in a dilute HCl solution in the dark, before and after avalanche pulse etching.

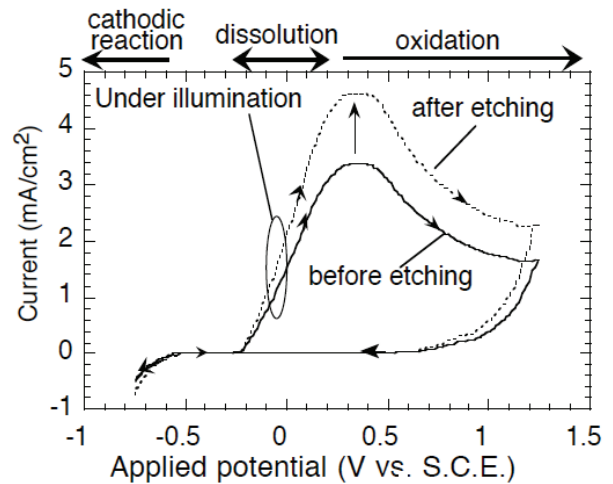
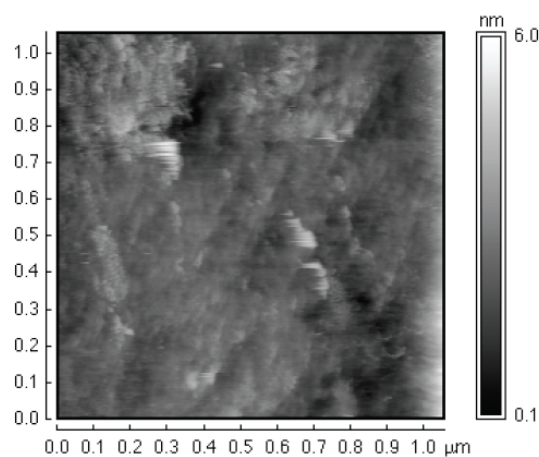
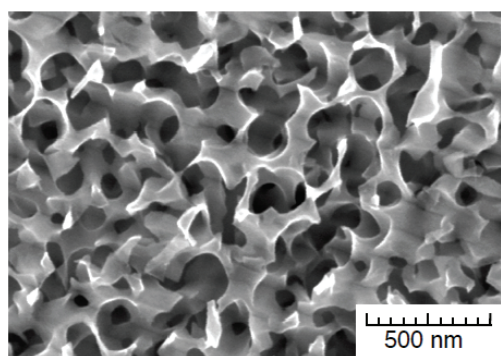


**Fig. 4** Cyclic voltammograms of n-InP with  $N_d=5 \times 10^{15} \text{ cm}^{-3}$  in a dilute HCl solution under illumination, before and after photo-anodic etching.



(a)



(b)

**Fig. 5** Surface morphology of n-InP surface after anodic reaction. (a) In situ STM image in the acid solution after anodic etching (InP;  $N_d = 1 \times 10^{18} \text{ cm}^{-3}$ ). (b) SEM micrograph after anodic oxidation.

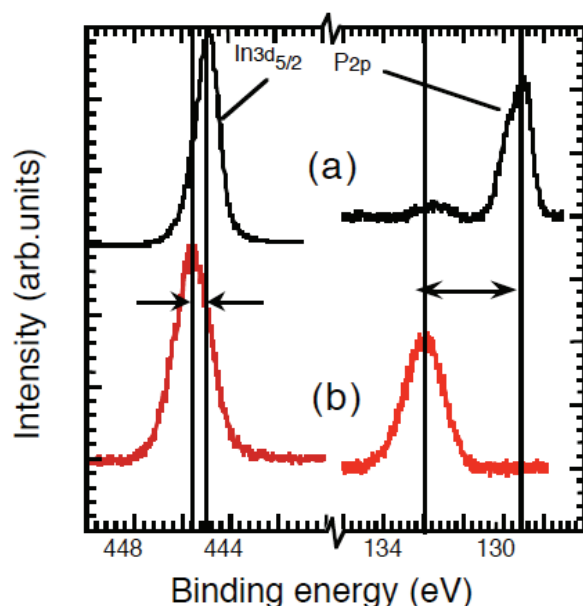


**Fig. 6** XPS spectra from InP surface and oxidized InP surface. (a) InP bulk. (b) Passivated surface.

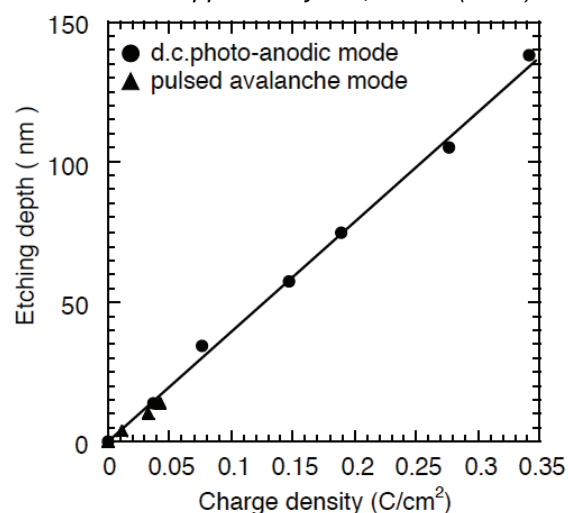
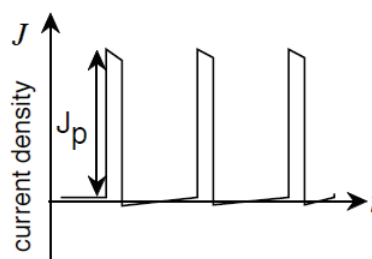
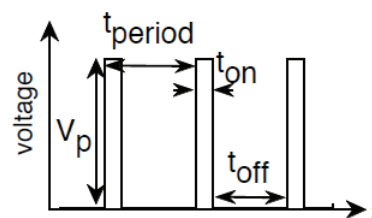
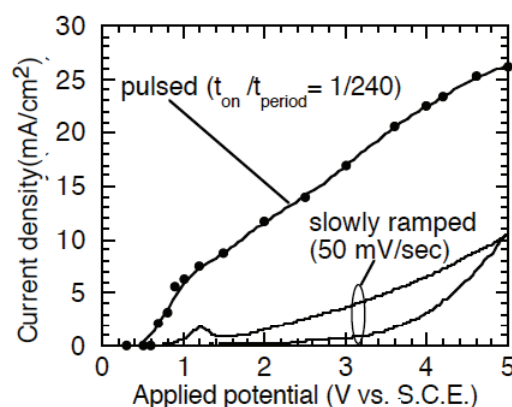


**Fig. 7** Relationship between etching depth and charge density in the d.c. photo-anodic mode and the pulsed avalanche mode.

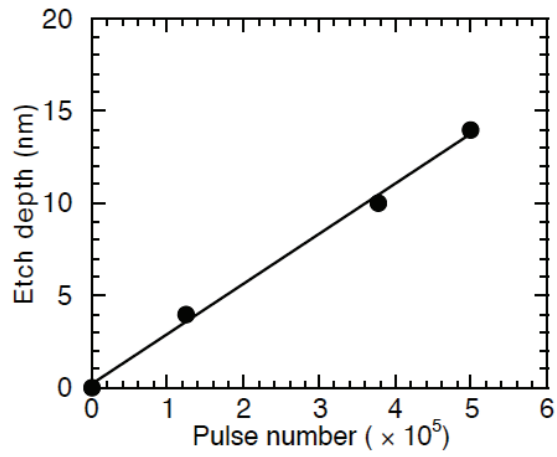


(a)

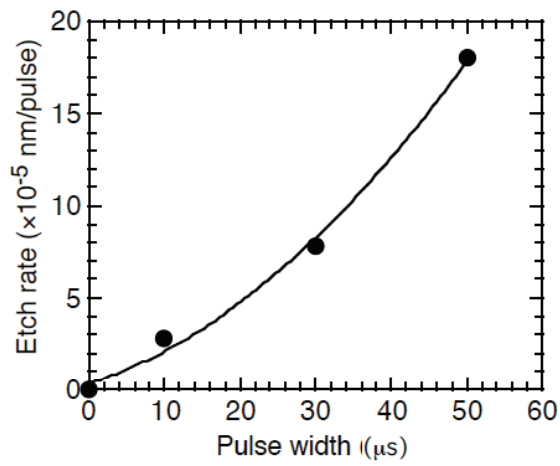


(b)

**Fig. 8** Typical current-voltage characteristics of n-InP in the acid solution. (a) Waveform of voltage and current for the pulsed mode. (b) Cyclic voltammograms of the ramped mode and the pulsed mode.



(a)



(b)

**Fig. 9** Etching depth and rate after avalanche pulses etching. (a) Dependence of etch depth on pulse number. (b) Dependence of etch rate on pulse width.