



Cathodic Decomposition and Anodic Dissolution and Changes in Surface Morphology of n-Type InP in HCl

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The cathodic decomposition of the n-InP(100) plane and followed by anodic dissolution of deposited indium were investigated in relation to surface roughening. The cathodic decomposition proceeded in parallel with hydrogen evolution when the n-InP(100) plane was cathodically polarized in 1.0 M HCl at potentials lower than -0.6 V (vs. standard hydrogen electrode). Metallic indium was deposited as a result of the cathodic decomposition, and anodically dissolved at potentials higher than -0.5 V during anodic potential sweep after the cathodic decomposition. The reaction fraction of cathodic decomposition could be determined from the ratio of the charge for anodic dissolution of deposited indium to the total charge for cathodic decomposition and hydrogen evolution, and took a maximum value of $x = 0.5$ for cathodic polarization at -0.75 V for 50 s. The changes in surface morphology of InP were observed with an atomic force microscope. The roughness of the InP surface increased with repeating the cathodic decomposition and anodic dissolution of deposited indium. When the cyclic potential steps between -0.75 V for 30 s and -0.3 V for 30 s were performed, the mean value of surface roughness, R_a , increased with increasing cycle number up to 150 cycles and then attained a steady state of $R_a = 25$ nm.

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InP is a promising material for high speed transistors and optoelectronic devices due to its high charge carrier mobility. The formation of porous InP or GaAs by anodic or photoanodic etching in HCl, HF, or H_2SO_4 was demonstrated¹⁻⁴ in analogy to the preparation of porous silicon with visible luminescence.⁵ Hamamatsu *et al.*² reported that a porous layer was formed due to photoanodic etching in HCl of n-type InP(100) surface, but it had a red shift of the photoluminescence (PL) response in contrary to the expected blue shift due to a quantum confinement. The red shift of the PL response was ascribed to the presence of surface states on the pore wall.

On the other hand, Schmuki *et al.*⁴ have recently found that a porous layer is formed due to anodic etching of n-type InP(100) surface in HF in dark and exhibits visible PL spectrum in the range of yellow to red. It has been suggested that the composition of the porous layer was closely associated with visible PL.⁴ Moreover, it has been reported⁶ that a stable surface film is formed on InP during anodic etching in H_2SO_4 and the semiconductive characteristics of InP itself are not restored unless the surface film is cathodically reduced. The surface film on porous layer of InP may suppress visible PL due to formation of surface states. Conversely, the visible luminescence may be originated from the surface film. The cathodic removal of surface film, therefore, is necessary to confirm the origin of visible PL from the InP surface subjected to anodic etching.

There have been several studies on cathodic polarization of InP.⁶⁻¹⁰ It is known that n-type InP decomposes under cathodic polarization in HCl or H_2SO_4 in the dark and the metallic indium deposited on InP surface as a result of the decomposition dissolves anodically during anodic potential sweep. The repetition of cathodic decomposition of InP and anodic dissolution of deposited indium may cause some surface roughening. No attempts, however, have been made so far on surface roughening due to the repetition of cathodic decomposition and anodic dissolution.

In this study, cathodic decomposition of an n-type InP(100) plane in HCl and anodic dissolution of deposited indium were investigated in detail from the viewpoint described above. Furthermore, the changes in surface morphology due to the repetition of cathodic decomposition and anodic dissolution were observed with an atomic force microscope (AFM) to explore the possibility for formation of porous layer.

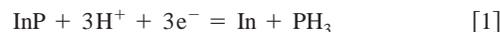
Experimental

Single crystal n-type InP(100) wafers (S-doped, $N_{D,Bulk} = 3.7 \times 10^{18} \text{ cm}^{-3}$, $R_s = 1.1 \times 10^{-3} \Omega \text{ cm}$) were used for experiments. The ohmic contacts were prepared with successive evaporation of Au-Ge (100 nm)/Ni (20 nm)/Au (70 nm), followed by annealing for 60 s at 653 K in a nitrogen atmosphere. The InP specimens cut into a size of 1.2×1.2 cm were set via O-ring with an inner diam of 1.0 cm into the electrochemical cell made from Diflon. A platinum net and a silver/silver chloride electrode were used as counter electrode and reference electrode, respectively. All potentials in this paper are referred to a standard hydrogen electrode (SHE). The electrolyte solution was 1.0 M HCl which was prepared from reagent grade chemicals and ultrapure water (Millipore Q). The solution was deaerated with ultrapure argon before and during experiments.

The repeated cathodic and anodic polarization experiments were performed with the following three different procedures: (i) cathodic polarization at $E_c = -0.7, -0.75, -0.8, -0.85, -0.9$, or -1.0 V for 1-50 s, followed by anodic potential sweep (10 mV s^{-1}) up to 0.1 V (SHE), (ii) cyclic voltammetry (CV) (10 or 100 mV s^{-1}) between -0.9 and 0.1 V, and (iii) cyclic potential steps between $E_{c,1} = -0.7, -0.75, -0.8, -0.85$, or -0.9 V for 30 s and $E_{a,1} = 0.3$ V for 30 s. The surface morphologies of the InP specimens subjected to the above procedures were observed in air with an AFM (Digital Instruments, Inc., Nanoscope IIIa).

Results and Discussion

Cathodic decomposition of InP and anodic dissolution of deposited indium.—Mott-Schottky analysis of potential dependent electrochemical impedance spectroscopy ($f = 100 \text{ mHz}$ to 1 MHz) has revealed¹⁰ that the flatband potential is -0.3 V for the n-type InP in 1.0 M HCl. If the n-type InP is cathodically polarized (in dark) in HCl, it decomposes according to



In parallel with hydrogen evolution



The reaction fraction of the cathodic decomposition, x , can be coulometrically evaluated if the metallic indium deposited on the InP surface during cathodic decomposition is subjected to the following anodic dissolution in the subsequent anodic potential sweep.¹⁰

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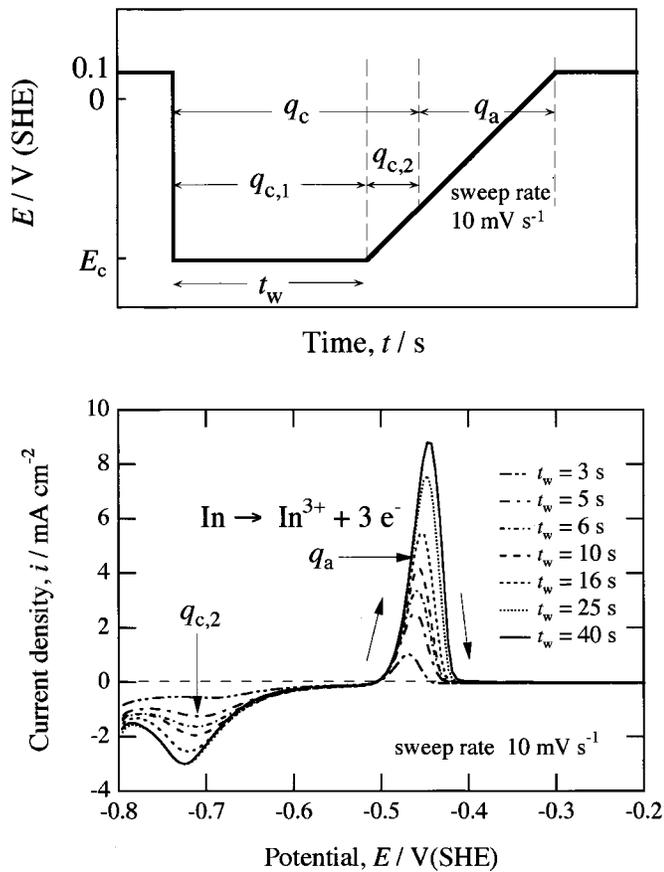


Figure 1. Potentiodynamic anodic polarization curves of the n-type InP in 1.0 M HCl after cathodic polarization at $E_c = -0.8$ V for t_w . The upper part of Fig. 1 represents schematically the experimental procedure.



The lower part of Fig. 1 shows the potentiodynamic anodic polarization curves (potential sweep rate: 10 mV s^{-1}) of n-InP after cathodic polarization at $E_c = -0.8$ V for t_w . The anodic current peak at -0.45 V increases with increasing t_w , which is ascribed to anodic dissolution of the metallic indium on the InP surface. As shown in the upper part of Fig. 1, the total cathodic charge, q_c , required for Reactions 1 and 2 is the sum of $q_{c,1}$ at E_c and $q_{c,2}$ in the sub-

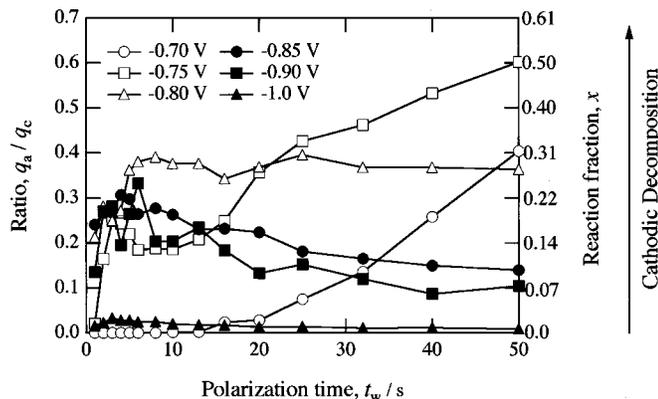
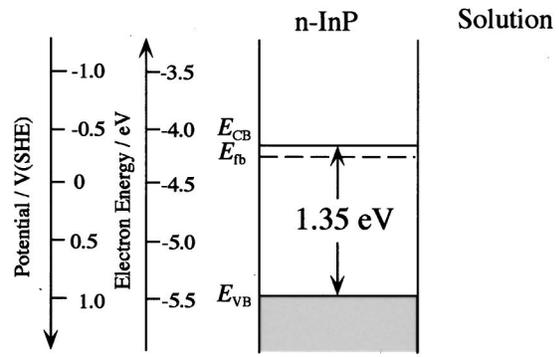
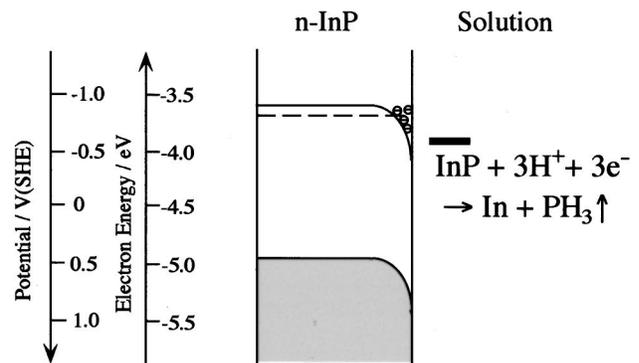


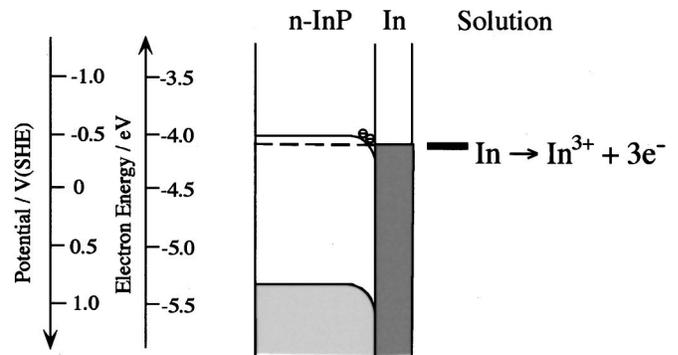
Figure 2. Ratio, q_a/q_c , and reaction fraction of cathodic decomposition, x , as a function of t_w at $E_c = -0.7, -0.75, -0.8, -0.85, -0.9,$ and -1.0 V in 1.0 M HCl.



(a) Flat Band Condition



(b) Cathodic Polarization at -0.8 V



(c) Anodic Dissolution of Indium at -0.45 V

Figure 3. Band model for explanation of cathodic decomposition of the n-type InP and anodic dissolution of the deposited indium.

sequent anodic potential sweep. On the other hand, the anodic charge, q_a , of the current peak at -0.45 V is that required for Reaction 3. The anodic oxidation of the n-type InP itself in HCl started at potentials higher than 0.4 V, supporting that the anodic current peak at -0.45 V is due to Reaction 3.

The following relation, therefore, holds between the ratio, q_a/q_c , and the reaction fraction of the cathodic decomposition, x

$$q_a/q_c = 3x/(x + 2) \quad [4]$$

Figure 2 shows the q_a/q_c and x vs. t_w curves at various E_c . It is seen from Fig. 2 that x depends on t_w and E_c and takes a maximum of $x = 0.5$ at $t_w = 50$ s and $E_c = -0.75$ V.

The following reaction was proposed for photocathodic decomposition of p-type InP^{11,12}

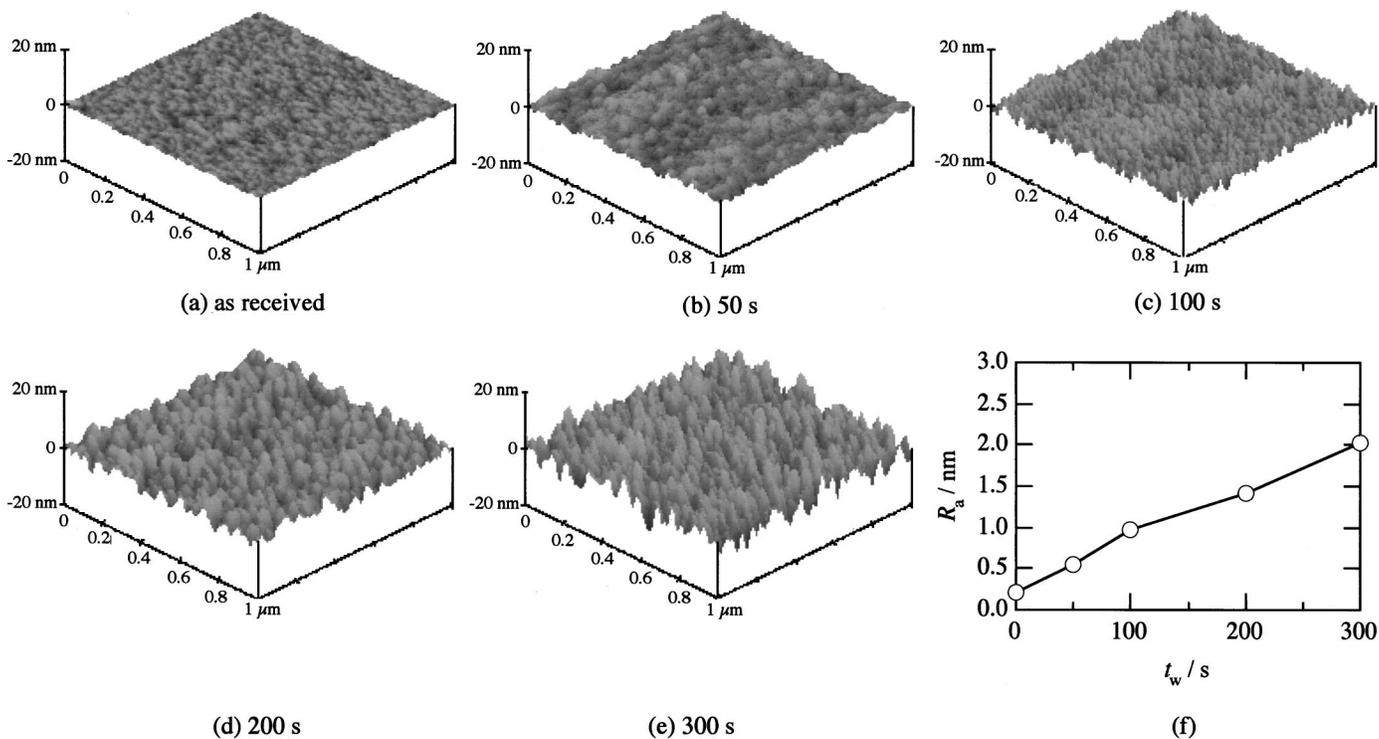
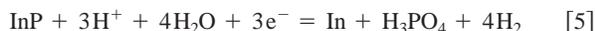


Figure 4. AFM images of the n-type InP surfaces (a) as received, (b) cathodically polarized at $E_s = -0.75$ V for $t_w = 50$ s, (c) 100 s, (d) 200 s, (e) 300 s, and (f) the mean value of surface roughness, R_a , as a function of t_w .



Bogdanoff *et al.*¹³ however, confirmed the presence of phosphine (PH_3) during photocathodic decomposition of p-type InP(111) surface in H_2SO_4 by using differential electrochemical mass spectroscopy. The reaction of Eq. 5, therefore, should be excluded for the cathodic decomposition of the n-type InP. Since the equilibrium potential of In/In^+ is close to that of In/In^{3+} according to Pourbaix diagram,¹⁴ the following reaction^{9,15} may be proposed for anodic dissolution of deposited indium



Assuming the reaction of Eq. 6, the experimental value of x would take three at $t_w = 50$ s and $E_c = -0.75$ V, indicating that the reaction of Eq. 6 should be excluded for anodic dissolution of deposited indium.

Figure 3 represents schematically the band model for explanation of cathodic decomposition of the n-type InP and anodic dissolution of the deposited indium. Since the flatband potential and bandgap of the n-type InP in 1.0 M HCl¹⁰ are -0.3 V and 1.35 eV, respectively, the band structure under the flatband condition is given by Fig. 3a. The band model in Fig. 3b corresponds to the case where the InP is cathodically polarized at -0.8 V. The energy level of the cathodic decomposition is located near at -0.6 V as estimated from Fig. 1. It is seen from Fig. 3b that the n-type InP is cathodically reduced, *i.e.*, decomposed by electrons accumulated in the conduction band of space charge layer. The Fermi level of electron in the n-type InP will be very close to the bottom level in the conduction band because of the high donor concentration of the material used. Moreover, the Fermi level of electron in metallic indium will be equivalent to -0.32 V which is close to the donor level or the bottom level in the conduction band of the n-type InP, since the work function of metallic indium is 4.12 eV¹⁶ and the energy level of standard hydrogen electrode is -4.44 eV.^{17,18} Therefore, the metallic indium deposited as a result of cathodic decomposition should lead to an ohmic con-

tact with the substrate InP. The deposition of metallic indium continues as far as the deposited layer is porous because H^+ and PH_3 can transport easily through the pores. The ohmic contact between deposited indium and substrate InP suggests that hydrogen evolution takes place not only on the substrate InP but also on the deposited indium layer. The band model in Fig. 3c corresponds to the case where the n-type InP is subjected to anodic potential sweep after cathodic decomposition. The anodic dissolution of the deposited indium layer proceeds easily at -0.45 V since electrons injected with the anodic dissolution can move from the indium layer into the substrate InP due to the ohmic contact between deposited indium and substrate InP.

Changes in surface morphology of InP.—The surface morphology of the InP subjected to cathodic polarization at E_s for t_w was observed with an AFM. Figure 4 shows the AFM images of the InP surfaces. The AFM images indicate that small particles of metallic indium were deposited on the InP surface due to cathodic decomposition. It seems that small particles accumulate on the InP surface

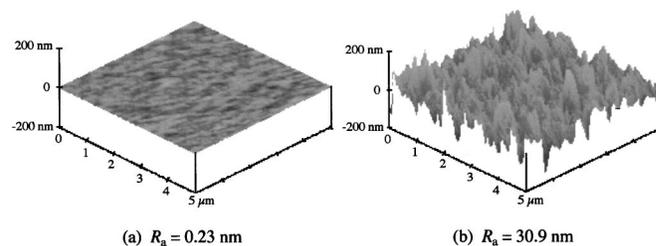


Figure 5. (a) AFM image of the n-type InP surface potentiodynamically polarized with a potential sweep rate of 10 mV s^{-1} up to 0.1 V after cathodic polarization at -0.8 V for 20 s, and (b) AFM image of the n-type InP surface after repeating ten times the procedure in a. R_a : Mean value of surface roughness.

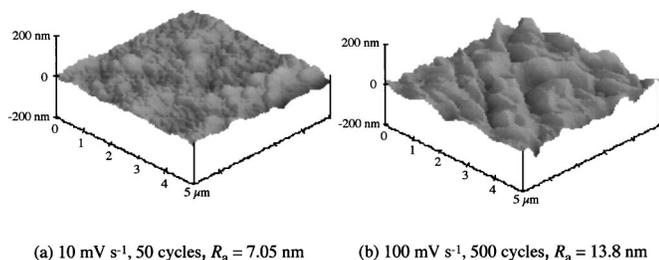


Figure 6. AFM images of the n-type InP surfaces after the CV at potential sweep rates of (a) 10 mV s^{-1} and (b) 100 mV s^{-1} between -0.9 and 0.1 V . The cycle numbers were adjusted to (a) 50 and (b) 500 to attain almost the same anodic charge of $q_a = 2 \text{ C cm}^{-2}$.

and grow like a needle with increasing t_w . Moreover, R_a increases with increasing t_w as seen from Fig. 4f. The continuous growth of the deposited indium layer means that the decomposition product, PH_3 , can transfer easily through the porous indium layer into bulk solution.

The AFM observation was also performed for the InP surfaces after anodic dissolution of metallic indium particles. Figure 5a shows the AFM image of the InP surface potentiodynamically polarized with a potential sweep rate of 10 mV s^{-1} up to 0.1 V (SHE) after cathodic polarization at -0.8 V for 20 s. On the other hand, Figure 5b shows the AFM image of the InP surface after repeating ten times the procedure of Fig. 5a. It is seen from comparison between the values of R_a in Fig. 5a and b that the surface roughness of the InP increases with increase in the cycle of cathodic decomposition and anodic dissolution.

Figure 6 shows the AFM images of the InP surfaces after CV at potential sweep rates of 10 mV s^{-1} . The average depth, d , of InP cathodically decomposed can be estimated from q_a by taking into account the density of InP ($\rho = 4.79 \text{ g cm}^{-3}$). The value of $q_a = 2 \text{ C cm}^{-2}$ corresponds to $d = 2.1 \mu\text{m}$. It is seen from Fig. 6 that the increase in potential sweep rate provides the increase in surface roughness even if the average decomposition depth is same. How-

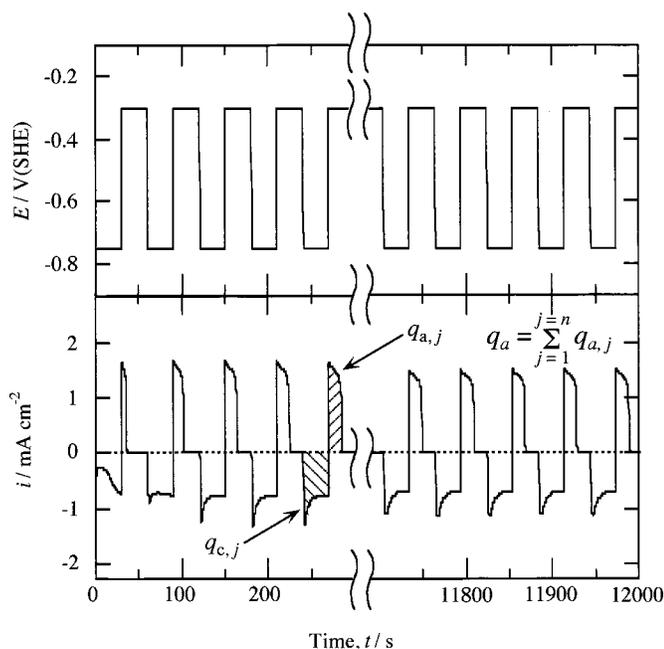


Figure 7. Typical current responses to the cyclic potential steps between $E_{c,1} = -0.75 \text{ V}$ for 30 s and $E_{a,1} = -0.3 \text{ V}$ for 30 s.

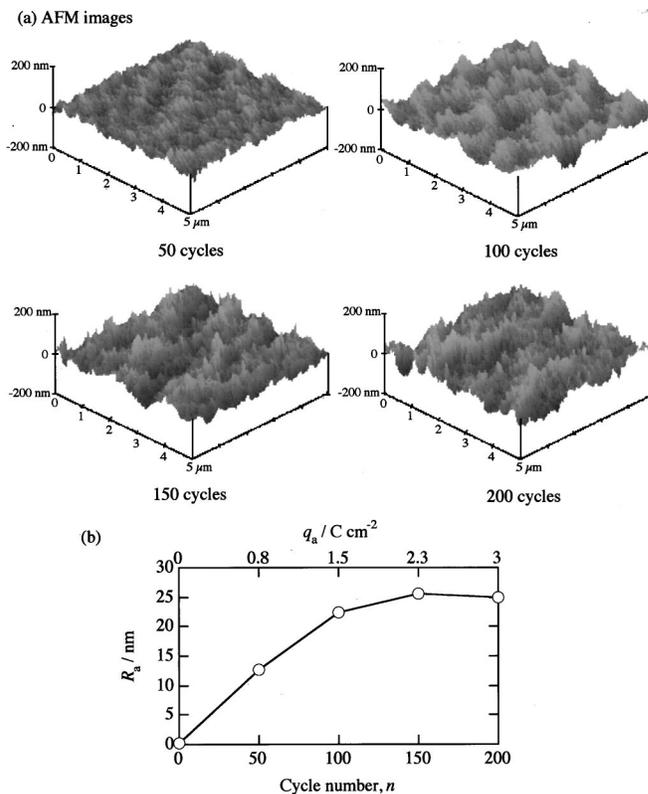


Figure 8. (a) AFM images of the n-type InP surfaces as a function of cycle number after the cyclic potential steps between $E_{c,1} = -0.75 \text{ V}$ for 30 s and $E_{a,1} = -0.3 \text{ V}$ for 30 s, and (b) the mean values of surface roughness, R_a , as a function of cycle number.

ever, the mean value of surface roughness, $R_a = 13.8 \text{ nm}$, at 100 mV s^{-1} is only 0.7% of the average decomposition depth of InP. The surface roughening due to electrode processes was reviewed and discussed elsewhere.^{19,20} The increase of potential sweep rate in CV enhances the delay in surface diffusion relative to surface reaction at local sites which would lead to surface roughening.

It is expected that cyclic potential step as well as CV contributes to surface roughening. Figure 7 shows the typical current responses to cyclic potential steps. The AFM images of the InP surfaces after the cyclic potential steps are shown as a function of cycle number in Fig. 8a. The mean values of surface roughness, R_a , are also shown in Fig. 8b, indicating that R_a increases with increasing cycle number up to 150 cycles and then attains to a steady state ($R_a = 25 \text{ nm}$). Figure 9 shows the AFM images of the InP surfaces after the cyclic potential steps between $E_{c,1} = -0.7, -0.75, -0.8, -0.85,$ or -0.9 V for 30 s and $E_{a,1} = -0.3 \text{ V}$ for 30 s. The cyclic number was adjusted in order to keep the total anodic charge, $q_a = 3 \text{ C cm}^{-2}$ for each experiment of the cyclic potential steps. It is seen from Fig. 8 that the surface roughness takes a maximum ($R_a = 28 \text{ nm}$) in case of $E_{c,1} = -0.75 \text{ V}$.

Although the surface roughening of the n-type InP was achieved to some extent with the repetition of cathodic decomposition and anodic dissolution of deposited indium, the degree of surface roughness was only several tens of nanometers. The formation of a porous InP layer with a thickness of several micrometers^{2,4} has not been achieved under the above experimental conditions. However, the repetition of cathodic decomposition and anodic dissolution of deposited indium after formation of a porous layer due to anodic or photoanodic etching may be effective in removal of stable surface films⁶ or surface states² which seem to suppress visible PL. The combination of anodic or photoanodic etching with the repeti-

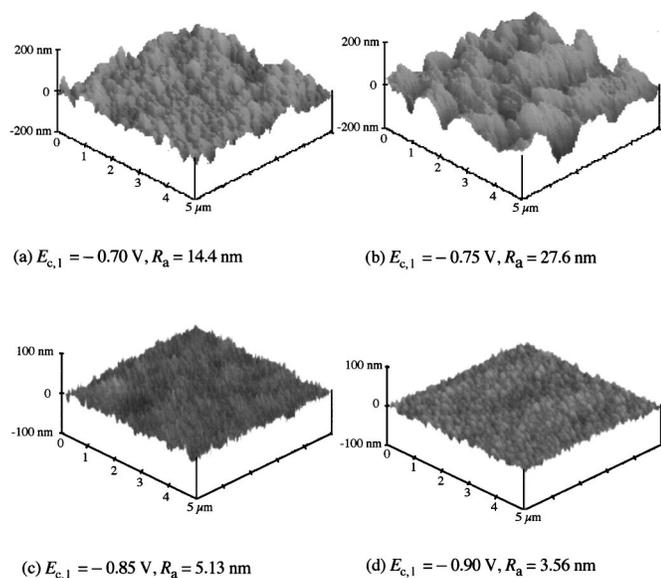


Figure 9. AFM images of the n-type InP surfaces after the cyclic potential steps between $E_{c,1} = -0.7$, -0.75 , -0.8 , -0.85 , or -0.9 V for 30 s and $E_{a,1} = -0.3$ V for 30 s. The cyclic numbers were adjusted in order to keep the total anodic charge, $q_a = 3 \text{ C cm}^{-2}$ for each experiment of the cyclic potential steps.

tion of cathodic decomposition and anodic dissolution will be proposed as our future work to improve the PL properties of porous InP layer.

Conclusions

The following conclusions were drawn from the cathodic decomposition of the n-type InP(100) plane in 1.0 M HCl and the subsequent anodic dissolution of deposited indium.

The reaction fraction of cathodic decomposition could be determined from the ratio of the charge, q_a , required for anodic dissolution of deposited indium to the total charge, q_c , for decomposition and hydrogen evolution, and took a maximum value of $x = 0.5$ for cathodic polarization at -0.75 V for 50 s. The cathodic decomposition of the n-type InP and anodic dissolution of the deposited indium could be explained by using the band model of the n-In-P/HCl or n-InP/In/HCl system.

The roughness of the InP surface increased with repeating the cathodic decomposition and anodic dissolution of deposited indium. When the cyclic potential steps between -0.75 V for 30 s and -0.3 V for 30 s were performed, the mean value of surface roughness, R_a , increased with increasing cycle number up to 150 cycles and then attained a steady state of $R_a = 25$ nm. However, the formation of a porous InP layer with a thickness of several micrometers could not be achieved with repetition of cathodic decomposition and anodic dissolution.

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