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Influence of Surface Treatment of the p-GaP Photocathode on the Photoelectrochemical Reduction of Carbon Dioxide

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Effects of the surface treatments of p-GaP electrodes with various etchants on the photoelectroreduction of CO_2 were investigated in 0.1 mol dm^{-3} $KHCO_3$ aqueous solution. The catalytic activities for CO_2 photoelectroreduction of p-GaP electrodes depended on the etchants and also their crystallographic orientations, (100) or (111) faces. The reduction products were only $HCOO^-$ and CO from CO_2, and H_2 as a by-product. Aqua regia was prefer to produce $HCOO^-$ on both faces. Conc. HCl was effective for $HCOO^-$ formation on the (111) face. Although the alkaline potassium hexacyanoferrate(III) solution was effective for reducing the overpotential and increase the photocurrent, the main product was H_2. Conc. HNO_3 was not effective.

Recently, the photoelectrochemical reduction (photoelectroreduction) of carbon dioxide (abbreviated as CO_2) on p-type semiconductor electrodes has been investigated by many authors, as reviewed recently.[1—3]

In the previous work, we have reported the influence of the light intensity for the photoelectroreduction of CO_2 at the p-GaP electrode in aqueous potassium hydrogen carbonate solution.[4]

The present report concerns the effect of the surface treatment with various etchants, such as aqua regia, concentrated hydrochloric acid, nitric acid, and alkaline potassium hexacyanoferrate(III) solution, on the photoelectrocatalytic properties of p-GaP photocathodes in photoelectroreduction of CO_2 in the aqueous electrolyte.

Experimental

Wafers of p-GaP single crystals with the (111); Zn doped 2.2—3.3$\times10^{17}$ cm^{-3}, and (100); Zn doped 2.0—4.8$\times10^{17}$ cm^{-3}, faces, respectively, were purchased from Electronics and Materials Corp., Ltd., and cut to 10×10 mm. The ohmic contacts were made with an In–Ga (1 : 1 by mole ratio) alloy. The procedures for the preparation of photocathodes were described previously.[2]

The surface of the photocathodes were firstly mechanically polished with 0.05 μm alumina powder. Next, they were etched with the individual ethcant, i.e. concentrated hydrochloric acid solution (about 12 M (M=mol dm^{-3}); concd HCl), concentrated nitric acid solution (about 16 M; concd HNO_3), aqua regia, and alkaline potassium hexacyanoferrate(III) solution (0.5 M KOH+1.0 M $K_3[Fe(CN)_6]$,)[5] for 2 min. After thoroughly washing with doubly distilled water, they were immediately served in the experiments. The etched surface of the p-GaP was analyzed by X-ray photoelectron spectroscopy (XPS) (SSX-100, Surface Science Instruments) immediately after drying with N_2 blow.

The photoelectrocatalytic properties for the CO_2 reduction of the surface treated p-GaP photocathodes were examined by linear sweep voltammetry and galvanostatic photoelectroreduction of CO_2 at the current density of 5 mA cm^{-2} where the mass transfer limitation of CO_2 to the electrode surface would occur.[1]

A bright Pt foil (6.0 cm^2) and an electrode of Ag/AgCl saturated with KCl served as the anode and the reference electrode, respectively. The potentials in this paper are represented with respect to this reference electrode. An aqueous solution of 1.0 M $KHCO_3$ which had been pre-electrolyzed for 12 h was used as the electrolyte. An H-type cell made of Pyrex equipped of a quartz window was employed. The catholyte, 40 cm^3, was separated from the anolyte, 40 cm^3, by a cation exchange membrane (Nafion® NX90209, Du Pont). The reacting gas was supplied from the same cyclic gas flow system as that shown previously.[2] The photoelectrolysis was mainly carried out galvanostatically by using a potentiostat (HA-301, Hokuto Denko), an electronic coulometer (HF-201, Hokuto Denko), and a Xe lamp (VX-300UV, Varian Corp.). The light intensity was controlled and measured with a thermopile (The Eppley Laboratory Inc.). The UV-cut filter (UV-37, Toshiba) and IR-cut filter (IRA-25S, Toshiba) were inserted between the light source and the cell which was immersed in a thermostated water bath. All the measurements were done at 298 K.

Products obtained by the photoelectroreduction of CO_2 were analyzed in the same manners as those described previously.[6]

Results

Surface Observation. The XPS spectra of O 1s, Ga 3d, and P 2p electrons in the surface treated p-GaP wafers having (111) and (100) faces are shown in Figs. 1 and 2, respectively. In the case of (111) face, the peak intensity of O 1s electron for all the etched surfaces became smaller than that of the untreated one, i.e. after mechanical polishing only, and the peak shifted to the lower binding energy. The spectrum of the Ga 3d electron has two peaks. The peak of lower binding energy, about 19 eV, is assigned to Ga binding to P, and that near at 21 eV to the oxide state of Ga.[7] The intensity of the lower peak has increased and that of the higher one has decreased by all the etching treatments. Consequently, it is found that the amount of Ga binding to P has increased by the etching corresponding to the decrease of the oxide on the surface. In the spectrum for P 2p, there are two peaks. One near at 129 eV is

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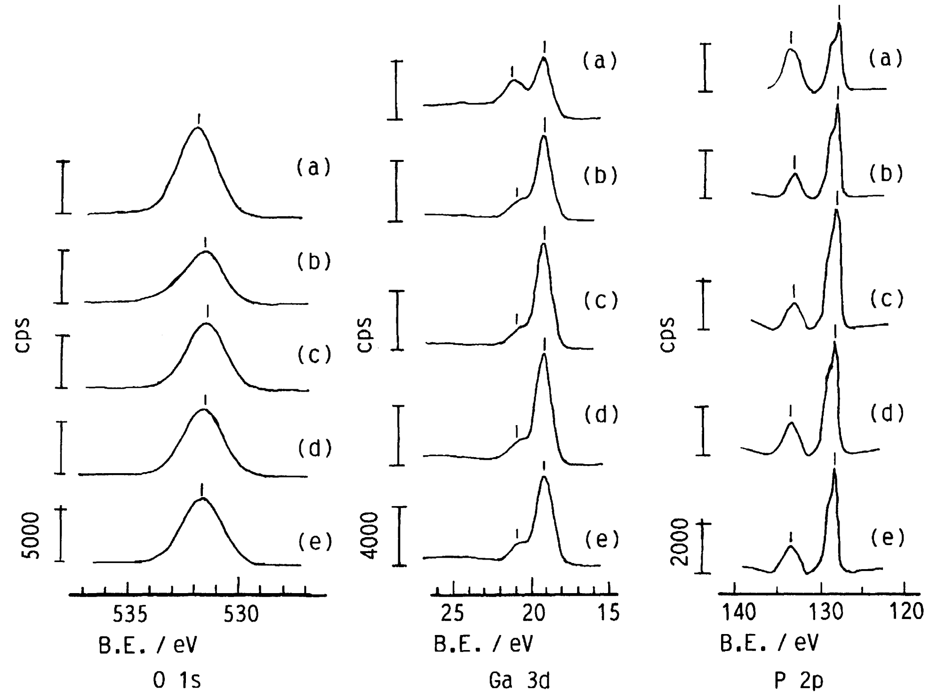

Fig. 1. XPS spectra of O 1s, Ga 3d, and P 2p measured at the p-GaP (111) wafers untreated (a), treated in concd HNO_3 solution (b), aqua regia (c), alkaline potassium hexacyanoferrate(III) solution (d), and concd HCl solution (e).

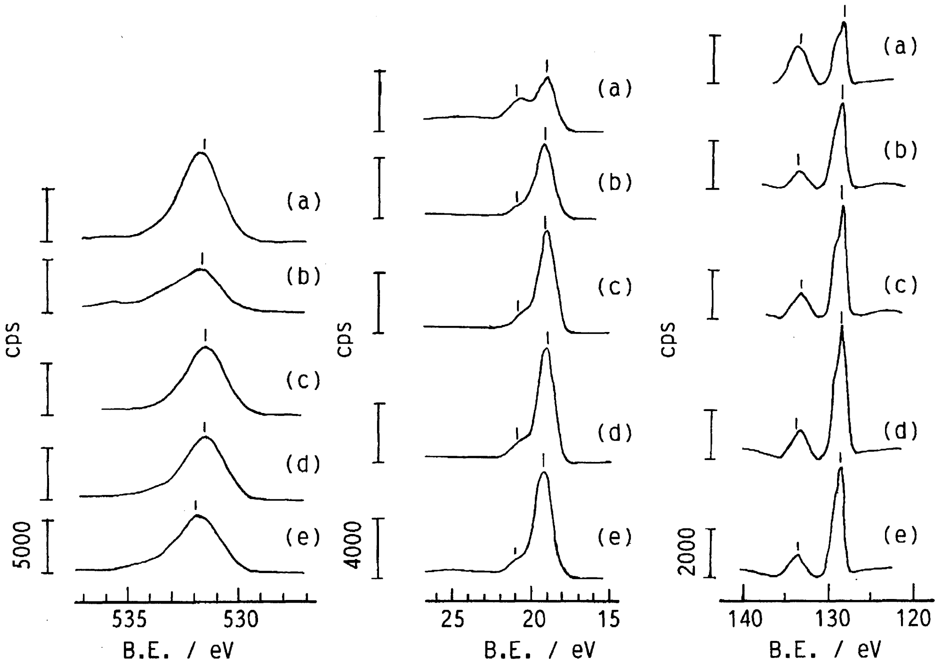

Fig. 2. XPS spectra of O 1s, Ga 3d, and P 2p measured at the p-GaP (100) wafers untreated (a), treated in concd HNO_3 solution (b), aqua regia (c), alkaline potassium hexacyanoferrate(III) solution (d), and concd HCl solution (e).

assigned to P binding to Ga and the other at 134 eV to the oxide state of P.[7] A similar interpretation on the spectrum of Ga 3d could be done. Analogous results have been obtained in the case of (100) face p-GaP.

Voltammetry. Photocurrent–potential curves on the p-GaP (111) electrode etched for 2 min in concd HNO_3, concd HCl, aqua regia, and alkaline potassium hexacyanoferrate(III) solution under the CO_2 atmosphere are shown in Fig. 3 with those under an inert atmosphere of N_2. Those on the (100) face are shown

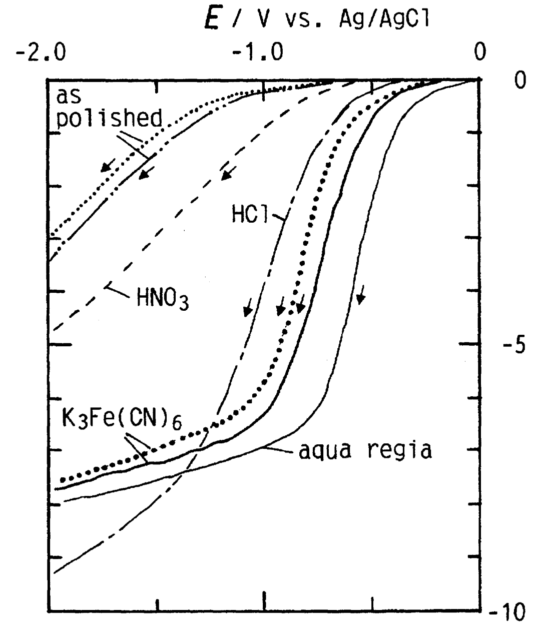

Fig. 3. Photocurrent–potential curves on the p-GaP (111) electrodes as polished and etched for 2 min in concd HNO_3 solution, aqua regia, alkaline potassium hexacyanoferrate(III) solution, and concd HCl solution under CO_2 or N_2 (····) atmosphere.

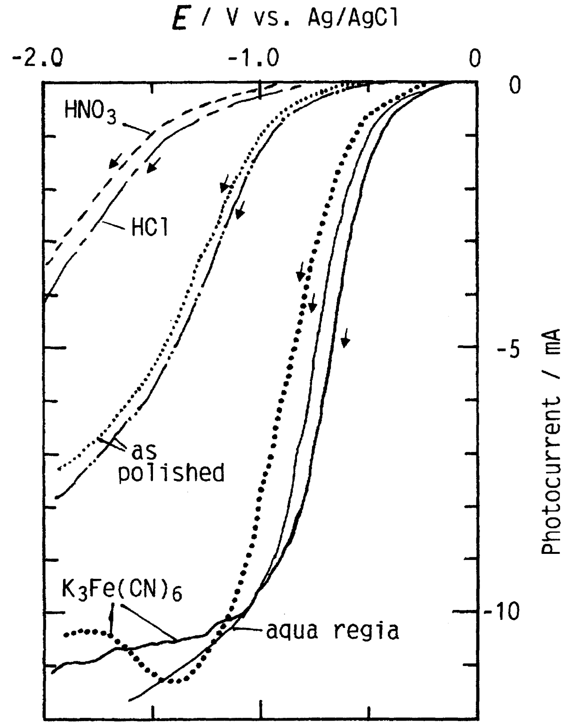

Fig. 4. Photocurrent–potential curves on the p-GaP (100) electrodes as polished and etched for 2 min in concd HNO_3 solution, aqua regia, alkaline potassium hexacyanoferrate(III) solution, and concd HCl solution under CO_2 or N_2 (····) atmosphere.

in Fig. 4. Photocurrents under CO_2 atmosphere flowed at the higher values than those under N_2 atmosphere indicating the significant occurrence of photoelectroreduction of CO_2, although the difference between these values was not so large.

In the case of (111) electrodes, the cathodic photocurrents on the electrodes treated with all the etchants examined flowed at the higher values than that on the as polished one. The onset potentials of the cathodic photocurrents on those treated with aqua regia and alkaline potassium hexacyanoferrate(III) solution were almost 0 V. The photocurrents exponentially increased with the potential until −1.0 V and thereafter saturated. That on the electrode treated with concd HCl rose at slightly negative potential than those on the formers and did not saturate in the potential range examined. On the other hand, the cathodic photocurrent began to flow at more negative potentials and was relatively small on the electrode treated with concd HNO_3. According to the value of photocurrent at −1.0 V, the surface treating etchant is effective in the order aqua regia>alkaline potassium hexacyanoferrate(III)>concd HCl>concd HNO_3>as polished.

In the case of the p-GaP having (100) face, the photocurrent on the as polished electrode began to flow at more positive potential than that on the (111) face one. The effectiveness of the etchants is different from the case of the (111) face. The electrodes etched with aqua regia and alkaline potassium hexacyanoferrate(III) solution showed the onset potential near at 0 V and almost the same profiles of photocurrents as those on the (111) electrodes. However, that treated with concd HCl did not show such the high photocurrent as the former, and the onset potential became lesser noble. These properties obtained on the electrode etched with concd HCl are almost same as those obtained on that with concd HNO_3. The ability of the etchant is in the order aqua regia=alkaline potassium hexacyanoferrate(III)≫as polished>concd HCl=concd HNO_3 considering the photocurrent at −1.0 V obtained on the p-GaP having (100) face.

Photoelectroreduction Products. The products detected were $HCOO^-$, CO, and H_2. Hydrocarbons, aldehydes, alcohols, and other carbolic acids were not found. The faradaic efficiencies for the products in the galvanostatic photoelectroreduction of CO_2 on the p-GaP (111) and p-GaP (100) at 5.0 mA cm^{-2} for 30 C are summarized in Table 1. In the case of (111) face, $HCOO^-$ was predominantly produced on the electrode treated with aqua regia and concd HCl. Whereas those treated with concd HNO_3 and alkaline potassium hexacyanoferrate(III) mainly produced H_2 rather than $HCOO^-$. The formation of CO, however, was not affected with the surface treatment, and the faradaic efficiency was less than 6% in each treatment.

In the case of (100) face, H_2 evolution became predominant instead of $HCOO^-$ formation by the concd

Table 1. Faradaic Efficiencies for the Products in the Photoelectroreduction of CO_2 on the Surface Treated p-GaP (111) and p-GaP (100) Electrodes in the Aqueous 0.1 M (M=mol dm^{-3}) $KHCO_3$ Solution[a)]

Surface orientation	Etchant	Potential V vs. Ag/AgCl		Faradaic efficiency/% $HCOO^-$	CO	H_2	Total
(111)	concd HCl (12 M)	−1.2	−1.4	43.2	4.1	33.6	81
	concd HNO_3 (16 M)	−2.4	−4.2	20.0	4.0	68.5	94
	Aqua regia	−0.8	−1.0	66.5	5.9	28.8	101
	Alkaline $K_3Fe(CN)_6$ (0.5 M KOH+1.0 M $K_3Fe(CN)_6$)	−0.8	−1.1	8.1	4.9	77.7	91
(100)	concd HCl (12 M)	−1.7	−1.8	30.6	12.8	57.9	101
	concd HNO_3 (16 M)	−1.6	−1.8	2.6	24.0	75.6	103
	Aqua regia	−0.9	−1.1	56.2	11.9	20.3	88
	Alkaline $K_3Fe(CN)_6$ (0.5 M KOH+1.0 M $K_3Fe(CN)_6$)	−0.9	−1.2	8.3	24.1	63.6	96

a) Current density: 5 mA cm^{-2}. Quantity of the electricity passed: 30 C.

HCl etching. The etching with aqua regia was favorable for $HCOO^-$ formation also on the (100) face. Although H_2 predominantly evolved on the electrodes treated with concd HNO_3 and alkaline potassium hexacyanoferrate(III) solution, the efficiency for CO formation was intensively affected by the etchants than the others and became 24%.

Discussion

Photo-generated electrons and holes in the illuminated semiconductor electrode recombine at lattice defects presenting near the surface of the semiconductor. In order to prevent the recombination and to move the electrons to the electrode surface and holes to the bulk rapidly, it is necessary to make a band vending steep by applying an external potential.

In the photoelectroreduction of CO_2 on a p-GaP photocathode, the photocurrent begins to flow at a considerably negative potential than the flat band potential. A large potential is necessary to apply a p-GaP electrode in order to move electrons to the surface and be allowed to be used for the electrode reaction,[8)] since in the vicinity of the surface of the p-GaP crystal, there are lots of lattice defects which become the recombination centers for the electron and hole pairs.[9,10)] On the other hand, the surface treatment by the chemical polishing to remove lattice defects from the electrode surface is also effective for improvement of the electrode activity. Therefore the more effective method of surface treatment is required to improve the electrode performance, namely the photocurrent rises at the positive potential.

From the observation by XPS, all four methods of the surface treatments employed in this paper have a certain effectiveness to remove the surface oxide layer. Therefore it is difficult to interpret that the onset potential of the photocurrent vary with the remained oxide layer. Consequently, the following consideration has been deduced from the variation of the catalytic activity for CO_2 reduction by the difference of affects on GaP among the etchants.

The faradaic efficiency for CO formation on (100) face of p-GaP photocathodes is greater than that on (111) face in all cases. This fact indicates that the (100) face originally has a larger activity of CO_2 reduction to CO (see Table 1). The difference in the activities for CO_2 reduction of both p-GaP electrodes would be caused by the differences between the ways in crystallographic stackings of the Ga and P planes in them. Namely, the Ga and P planes in the (100) face crystal, which shows the higher activity, have the same face-centered packings and are alternatively stacked with a constant interfacial spacing, i.e. $a/4$, where a is the lattice constant. On the other hand, those planes in the (111) face one are stacked with alternative spacings of $1:3$, i.e. $a\sqrt{3}/12$ and $a\sqrt{3}/4$. The difference in the packings would also cause the difference in the magnitudes of their photocurrents.

By the etching with concd HNO_3, the cathodic photocurrent can only flow under considerably higher polarization on both faces. This would be due to the lattice defect near the surface of the p-GaP which did not removed by the etching. It has been found that concd HNO_3 could can not dissolve the bulk InP,[11)] a III-V compound semiconductor same as the GaP. Namely, it may be conclude that concd HNO_3 has not a so high oxidizing power to dissolve the bulky GaP, although it can dissolve the oxide layer. Therefore, the lattice defects becoming the recombination center of electron-hole pairs by this etchant.

On the other hand, the electrodes treated with aqua regia or alkaline potassium hexacyanoferrate(III) solution, the photocurrents obtained on the both electrodes rise near at 0 V, and almost the similar profiles of their photocurrent–potential curves are obtained.

In the case of aqua regia, generated NOCl is concerning the dissolution of GaP. Immersing a GaP electrode in aqua regia, bubbles are violently evolved from the electrode surface. A lot of pits are observed after this treatment. Namely, GaP has been dissolved so large extent by aqua regia having a strong oxidizing power to reduce the lattice defects being present the electrode surface. As the results, the photocurrent becomes easy to flow with a small overvoltage. However, the face orientation of the surface of GaP becomes random due to rapid dissolution and is not controlled. Therefore the difference in the catalytic activities of CO_2 reduction between (100) and (111) faces of GaP electrodes becomes small and not clear. Namely, $HCOO^-$ formation becomes predominantly on both faces etched with aqua regia. It was suggested that the formation of $HCOO^-$ is the nature of the bulk p-GaP.

The electrode treated with the alkaline potassium hexacyanoferrate(III) solution has a metallic luster. This etchant selectively dissolves phosphorous plane of GaP wafer and the effect exerts into the deep portion of the crystal.[5] As the results, gallium plane remains on the electrode surface. Therefore, H_2 has been predominantly evolved on the alkaline treated electrode. This fact is similar to that obtained in the electrochemical reduction of CO_2 on metallic Ga electrode, which evolved H_2 predominantly and has a little activity for CO_2 reduction to produce CO (ca. 6%) but no $HCOO^-$.[12]

On the (111) face p-GaP electrode treated with concd HCl, the onset potential of the photocurrent becomes slightly negative than that on the electrode treated with aqua regia. Whereas on the (111) face, such a difference has not been observed. The electrode surface assume slightly golden color. Therefore, it has been estimated that the difference of dissolution speed between the crystal faces results in the different catalytic activity for CO_2 reduction in the case of concd HCl treatment. From Table 1, the fact that the catalytic activity of the (111) face electrode for $HCOO^-$ formation is higher than that of the (100) face indicates a significant effect of concd HCl treatment on the catalytic activity for CO_2 reduction.

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