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Mechanistic Study of Photoelectrochemical Reactions at a p-GaP Electrode

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ABSTRACT

The photocurrent-potential relations of a p-GaP electrode in various solutions are studied potentiostatically. Both the cathodic and anodic photocurrents are observed, i.e., the sign of photocurrent changes at a certain potential which we name the potential of zero photocurrent, $V_{zp}$. The potential of zero photocurrent is close but not equal to the flatband potential. The origin of the anodic photocurrent is presented. The log (photocurrent)-potential relations follow the Tafel line at medium bias potentials and deviate from it at large and small bias potentials. The mechanism of the cathodic reactions is proposed based on the experimental results. The rate-determining step is the supply of photoexcited electrons to the semiconductor surface at large bias potentials and is the electrochemical, i.e., surface, process at medium and small bias potentials. At the small bias potentials, the photocurrent is enhanced by the photoelectrochemical reduction of oxidized species created by holes in valence band.

Photoeffects on electrochemical reactions at semiconductor electrodes have been studied very actively (1-10), particularly after Fujishima and Honda drew attention to the possibility of direct hydrogen production by a photo-driven electrochemical cell without any external electrical energy (11). However, fundamental aspects of photoelectrochemical reactions such as reaction mechanism seem not to have been well understood. Most theoretical analyses neglected the potential drop in the electrochemical double (Helmholtz) layer (12) and the contribution of the charge transfer process to the overall reaction rate (13), although the importance of these contributions on the kinetics at semiconductor electrodes was pointed out by Green many years ago (14). We have been stressing the importance of the above contributions (15, 16) and have reported some supporting evidence (17). Recently, Bard et al. have used the word “Fermi-level pinning” to express the situation where the entire potential drop occurs within the Helmholtz layer and reported that this situation is not unusual (18).

In this work, we studied the photocurrent-potential relations at p-GaP, which is one of a few stable photoelectrodes (19), in various solutions to evaluate the reaction mechanism. The photoelectrochemical behavior of p-GaP has been studied very extensively (6, 15, 20-24) and it is reported that the flatband potential

Key words: semiconductor, photoelectrochemistry, energy conversion.

REFERENCES

determined by capacitance measurement differs from
the so-called critical potential or photocurrent onset
potential (20, 21). This difference is usually explained
by surface recombination without considering the
electrochemical steps (20). The main concern of this
paper is to analyze the photoelectrochemical behavior
of p-GaP at small potential biases which represent the
significant region for practical devices.

Experimental
A Zn-doped p-GaP single crystal wafer was used as
a working electrode. The carrier density and the spe-
cific resistance of the sample are $6.7 \times 10^{17}$ cm$^{-3}$ and
1.3 $\Omega \cdot$ cm, respectively. An ohmic contact was made by
using In-Zn alloy and a copper wire was attached onto
the ohmic contact by soldering. The semiconductor
electrode surface was covered with epoxy resin except
for (111) face (Ga) and was placed in a PTFE elec-
trode holder. The surface area of the electrode was
0.0315 cm$^2$. The electrode surface was etched in HNO$_3$-
HCl (1:1) solution before experiment. The electro-
chemical cell is similar to the one reported previously
(15). An Ag/AgCl electrode and a Pt wire were used
as a reference and a counter electrode, respectively. A
500W Xe lamp (Ritsu Oyo Kogaku) was used as a light
source and a potentiostat (Wenking Model 68 FRO.5)
was used to control the electrode potential. An IRA-20
(Toshiba) filter was placed between the light source
and the electrochemical cell to avoid a heat effect. Cur-
rent-time relations were recorded by using a Toa
Model CDR 11A recorder.

All solutions used in this work were prepared with
triply distilled water and reagent grade chemicals.
Purified helium gas was passed through the solutions
for at least 30 min before experiments. All experi-
ments were carried out at room temperature.

Results
The current-time relations of the p-GaP electrode in
1M NaOH at several electrode potentials illuminated
with pulsed light are shown in Fig. 1. Steady photo-
currents are observed at all potentials investigated,
even at potentials very close to the flatband potential,
$V_{FB}$, which is $\sim -0.04$V vs. Ag/AgCl (15). Further,
the anodic photocurrent, which has not been reported
at p-type semiconductor electrodes, is observed here at
relatively positive potentials. Thus, the sign of the
photocurrent changes at a certain potential. The steady
photocurrents of this electrode in various solutions are
plotted against the electrode potential in Fig. 2. In all
cases, both the cathodic and anodic photocurrents are
observed and the photocurrent-potential ($I_{ph} - V$)
relations shift towards more negative potentials when
the pH of the solution increases. The addition of methyl
viologen changes the shape of the $I_{ph} - V$ relation drasti-
cally.

The effect of time length kept in dark prior to the
illumination is also examined. The steady photocurrent
is not affected by changing the time length kept in
dark at all potentials but the longer the time kept in
the dark, the larger the initial photocurrent just after
the illumination at potentials close to the flatband po-
tential, as shown in Fig. 3.

Discussion
Origin of anodic photocurrent.—Usually, only a cath-
ocodic photocurrent is reported at p-type semiconductors
and only an anodic photocurrent is reported at n-type
semiconductors with the exception of a cathodic photo-
current observed at TiO$_2$ (n-type) (25). However, in
this work, we found both the cathodic and anodic photocurrents at p-GaP electrode. The origin of the
anodic photocurrent and the reason why it has not been reported are as follows.

The anodic currents at a semiconductor electrode in
the dark, $i_a$, and under illumination, $i_a^*$, are given by
Eq. [1] and [2], respectively, with the assumption that

\[ i_a \propto c d_0 W(E_v) G_R(E_v) \]

the electron transfer takes place in a narrow energy
range below the valence band energy, $E_v$. (1)
for a wide pH range. as shown in Table I. Anodic dissolution occurs at pH < 2.56 and pH > 11.7 and calculated the anodic decomposition potentials of GaP.

We reexamined the thermodynamic data (28-30) and calculated the anodic decomposition potentials of GaP for a wide pH range as shown in Table I. Anodic dissolution occurs at pH < 2.56 and pH > 11.7 and passive film is formed at 2.56 < pH < 11.7. The decomposition potentials are within the bandgap of GaP for all pH range concerned and the reactions expected from the calculation agree with experimental findings (28). The existence of the anodic (dark) currents even at the potentials more negative than VFB suggests that the reaction is very efficient in acid and alkaline solutions (6, 26).

### Table I. The anodic decomposition reactions of GaP and corresponding potentials at various pH

<table>
<thead>
<tr>
<th>pH range</th>
<th>Reaction</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 2</td>
<td>GaP + 6p⁺ + 3H₂O ⇌ Ga(OH)₃ + H²PO₄⁻ + 4H⁺</td>
<td>0.357 - 0.9295 pH + 0.00985 log [Ga⁺] + 0.00985 log [HPO₄²⁻]</td>
</tr>
<tr>
<td>2 &lt; pH &lt; 2.56</td>
<td>GaP + 6p⁺ + 3H₂O ⇌ Ga⁺⁺ + H²PO₄⁻ + 4H⁺</td>
<td>0.357 - 0.9394 pH + 0.00985 log [Ga⁺] + 0.00985 log [HPO₄²⁻]</td>
</tr>
<tr>
<td>2.56 &lt; pH &lt; 3.32</td>
<td>GaP + 6p⁺ + 9/2 H₂O ⇌ 1/2 Ga₂O₃ + 2H₂O + 7H⁺</td>
<td>0.253 - 0.0789 pH + 0.00985 log [HPO₄²⁻]</td>
</tr>
<tr>
<td>3.32 &lt; pH &lt; 11.7</td>
<td>GaP + 6p⁺ + 8 OH⁻ ⇌ 1/2 Ga₂O₃ + HPO₄⁻ + 7/2 H₂O</td>
<td>0.253 - 0.0789 pH + 0.00985 log [HPO₄²⁻]</td>
</tr>
<tr>
<td>pH &gt; 11.7</td>
<td>GaP + 6p⁺ + 11 OH⁻ ⇌ GaO₂⁺ + HPO₄²⁻ + 5H₂O</td>
<td>0.253 - 0.0789 pH + 0.00985 log [HPO₄²⁻]</td>
</tr>
</tbody>
</table>

The thermodynamic values used for calculation are all taken from Ref. (28) for phosphorous compounds and from Ref. (29) for gallium compounds except for ΔGₒ⁺V(Ga⁺) = 91.54 kJ·mol⁻¹ which is taken from Ref. (30).

...
energy $E_c$. Similarly, a cathodic photocurrent should be observed in the corresponding conditions. In other words, only when one of the conditions given in Eq. [8] and [9] is satisfied at $V_{FB}$, $V_{FB}$ should coincide with $V_{Spo}$

$$p_v^* - p_h = n_v^* - n_h = 0$$  \[8\]

$$j = | c_0 \left( n_v^* - n_h^* \right) W(E_c) G_0(E_c) |$$  \[9\]

In the present system, the existence of the anodic dark current even at the potential more negative than $V_{FB}$ (6, 26) suggests that the anodic reaction is considerably faster than the cathodic reaction near $V_{FB}$. Thus, from the above argument the presence of the anodic photocurrent is expected at $V_{FB}$ in this case as well as in other cases observed.

In the solution containing methyl viologen, the $V_{SP}$ is almost identical to the flatband potential. In this case, for the reaction $MV^{++} + e \rightarrow MV^{+}$ the condition given in Eq. [9] seems to be satisfied.

The photocurrent-potential relations and the reaction mechanism of photoelectrochemical reduction reactions.—The photoelectrochemical processes at cathodically polarized semiconductors are divided into two parts, namely, the bulk and the surface processes. The bulk processes are (i) absorption of photons and photoexcitation of electrons to the conduction band, (ii) photogeneration of electron-hole pairs, and (iii) deactivation of the photoexcited electrons to the valence band, in parallel with (i) i.e., recombination in the bulk including space charge layer of the semiconductor. The surface processes are (i) electron transfer to an oxidized species followed by chemical, electrochemical, and/or desorption processes in some cases, (ii) deactivation of the photoexcited electrons to the valence band at the surface directly or via surface states, i.e., surface recombination.

Equations [10]-[12] summarize the bulk processes

$$h_v \rightarrow p_v^+ + e^-$$  \[10\]

$$e^- \rightarrow \left( e^--_s \right)$$  \[11\]

$$e^- + p_v^+ \rightarrow \text{recombination}$$  \[12\]

where $p_v^+$ is the hole in the valence band and $(e^-)_s$ and $(e^-)_v$ are the electrons in the conduction band at the surface and at other places, respectively. The surface processes for hydrogen evolution reaction are

$$(e^-)_s + H_2O + S.C. \rightarrow H_2 + S.C.$$  \[13\]

$$(e^-)_s + H_2O + S.C. \rightarrow H_2 + S.C.$$  \[14\]

$$(e^-)_s + H_3O^+ + S.C. \rightarrow H_2O + S.C.$$  \[15\]

$$(e^-)_s + H_3O^+ + S.C. \rightarrow H_2O + S.C.$$.  \[16\]

and those for the recombination are

$$(e^-)_s + (p_v^+)_s \rightarrow \text{Surface recombination}$$  \[17\]

$$(e^-)_s + \square_{ss} \rightarrow \square_{ss}$$  \[18\]

$$(\square_{ss} + (p_v^+)) \rightarrow \square_{ss}$$

where S.C. is the semiconductor, S.C. - H represents hydrogen atom adsorbed on the semiconductor, $(p_v^+)_s$ is the hole in the valence band at the surface, $\square_s$ is the unoccupied surface state, and $\square_{ss}$ is the occupied surface state. The step expressed in Eq. [18] is the surface recombination via surface state. The combination of step [13] and step [16] could be called the surface recombination via adsorbed hydrogen state (31). For the reduction of methyl viologen, Eq. [19]-[16] should be replaced by the following

$$(e^-)_s + MV^{++} \rightarrow MV^{+}$$  \[19\]

The shape of log $(i_{ph}) - V$ relations at large cathodic potential biases suggests that the rate-determining step in this potential region is some transport-limited process. The deviation occurs at $ca. -0.7V vs. Ag/AgCl in 1M NaOH and ca. -0.05V vs. Ag/AgCl in 0.5M H_2SO_4.

Butler and Ginley proposed that step [18], i.e., surface recombination via surface state, is responsible for the discrepancy between $V_{FB}$ and the apparent photocurrent onset potential determined by $i_{ph} - V$ relation based on a simple Schottky barrier model with the assumption that electrochemical processes are fast and step [11] is the rate-determining process (20). Thus, the supply of the photogenerated electrons to the semiconductor surface seems to be the rate-determining step at the potentials more negative than $ca. -0.7V vs. Ag/AgCl in 1M NaOH and ca. -0.05V vs. Ag/AgCl in 0.5M H_2SO_4.

To elucidate the mechanism of the photoelectrochemical reduction reactions at the p-GaP electrode in a wide potential range, the photocurrents in logarithmic scale are plotted against the electrode potential in Fig. 4. The log $(i_{ph}) - V$ relations follow the Tafel line at medium biased potentials ($-0.4 \sim -0.7V$ in 1M NaOH and +0.2 $\sim -0.05V$ in 0.5M H_2SO_4) and deviate from it at large and small bias potentials. It is interesting to note that the slopes of the Tafel line are similar to those of hydrogen evolution reaction at metal (Ga) electrodes (32).

The shape of log $(i_{ph}) - V$ relations at large cathodic potential biases suggests that the rate-determining step in this potential region is some transport-limited process. The deviation occurs at $ca. -0.7V vs. Ag/AgCl in 1M NaOH and ca. -0.05V vs. Ag/AgCl in 0.5M H_2SO_4.

Butler and Ginley proposed that step [18], i.e., surface recombination via surface state, is responsible for the discrepancy between $V_{FB}$ and the apparent photocurrent onset potential determined by $i_{ph} - V$ relation (20). Thus, they concluded from IR photoresponse measurement that the localized state which is $\sim 0.7 eV$ above the valence band acts as the recombination center. According to their model, the photocurrent at steady state, $i_{ph}$ is given by

$$i_{ph} = k_r \left( j \left( e^- \right)_s \right) N_{ss} (1 - f_s)$$  \[21\]

where $j$ is the flux of the photogenerated electrons arriving at the surface, $k_r$ is the rate constant of the surface recombination reaction, $N_{ss}$ is the number of surface states, and $f_s$ is the Fermi distribution function.
for the surface states. For the present system, if all potential drop occurs within the semiconductor, \( f_t \) is given by

\[
f_t = 1 / [1 + \exp \{ E_t - E_F/kT \}]
\]

\[
= 1 / [1 + \exp \{ 0.7 - (V_{FB} - V)/kT \}]
\]

where \( E_t \) is the energy of the surface states and \( V \) is the electrode potential concerned. Since \( (1 - f_t) \) changes from 0 to 1 sharply around \(-0.7 V\) vs. \( V_{FB} \), one would expect sharp change in the photocurrent potential relation at that potential and not be able to explain the potential dependence of the photocurrent at relatively small bias potential (Tafel relation) where \( 1 - f_t = 1 \) by considering the surface recombination via surface states only. The effect of methyl viologen on \( i_{ph} - V \) relation gives some clue to evaluate the mechanism. In this case, the photocurrent is larger than that without \( MV^{++} \) at low bias potentials. This can be explained as follows.

The rate-determining step of the hydrogen evolution reaction at this potential range is one of the steps expressed by Eq. [13], [14], or [15], i.e., the electrochemical process. The electrochemical reaction rate of \( MV^{++} \) is faster than that of hydrogen evolution reaction and therefore much larger current is observed when \( MV^{++} \) is added. The fact that \( V_{FB} \) with \( MV^{++} \) is more positive than that without \( MV^{++} \) also supports the fact that the cathodic reaction of \( MV^{++} \) is faster than hydrogen evolution reaction. The \( i_{ph} \) with \( MV^{++} \) is smaller than that without \( MV^{++} \) at relatively negative potentials. It is due to absorption of light by \( MV^{++} \) created by photoelectrochemical reduction of \( MV^{++} \).

The \( \log (i_{ph}) - V \) relations deviate from the Tafel line again at the potentials near \( V_{FB} \), suggesting some faster reaction is involved. At this region, the initial photocurrent just after illumination depends on the length of time kept in the dark prior to illumination, as shown in Fig. 3. Also, the anodic dark current starts to flow at this potential region. Thus, this deviation should be due to the photoelectrochemical reduction of oxidized species created by dark oxidation reaction by holes in the valence band, as shown in Fig. 5. If the reduction of the oxidized species is faster than the hydrogen evolution reaction, much larger current is expected at a given potential. It is essentially the same effect as the addition of \( MV^{++} \). The effect of the time kept in the dark is explained as the accumulation of oxidized species in the dark.²

In the small bias potential region where \( \log (i_{ph}) - V \) relation deviates from the Tafel line, the stability

\[^{2}R. H. Wilson proposed a model which takes into account both the surface and bulk states, to explain the potential drop for n-type semiconductors (33, 34).

\[^{3}The height of the photocurrent spike just after illumination is much smaller when the solution is stirred supports this mechanism.

\[\text{CB} \quad \text{RED}' \quad \text{OX} \quad \text{RED} \]

\[\text{V} \quad \text{h} \nu \]

Fig. 5. Contribution of oxidized species created by hole to photocurrent enhancement at relatively small bias potential.

of p-GaP is in doubt even though the net cathodic photocurrent is observed, because the deviation is caused by the photoelectrochemical reduction of oxidized species which is the anodic decomposition product of GaP in this case. Since for practical devices, the potential bias would be small, the stability of p-GaP in this potential region should be studied more in detail.

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Semiconductor Electrodes

XXXVII. Photoelectrochemical Behavior of p-Type Cu2O in Acetonitrile Solutions

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ABSTRACT

The photoelectrochemical behavior of polycrystalline p-Cu2O in acetonitrile solutions containing a number of redox couples [e.g., phthalonitrile (0/−1), nitrobenzene (0/−1), methyl viologen (+2/+1)] was investigated. The p-Cu2O, grown by oxidation of Cu metal by thermal methods or anodization, showed stable behavior under optical irradiation in these solutions. The bandgap, estimated from photoacoustic spectroscopy (PAS) and the photocurrent action spectrum in solution, was ~2.0 eV and the flatband potential was ~ +0.16V vs. SCE. Scanning electron micrographs of the thermally grown samples reveal well-developed crystallites with distinct boundaries. A PEC cell of the form p-Cu2O/Ph(CN)2,MeCN/Pt was shown to have an overall optical-to-electrical energy conversion efficiency of only 0.05%. The low efficiency for such a cell is ascribed to rapid recombination processes in the bulk semiconductor and at the interface.

Cuprous oxide (Cu2O), which crystallizes in a cuprite structure is a catalyst of choice for a diverse variety of chemical reactions (1-4). The optical and electrical properties of p-Cu2O depend upon the conditions of preparation from Cu and O2, i.e., the temperature and oxygen pressure (5). Several workers (6-11) have studied the electrical properties of single crystals of this material and demonstrated that it is a p-type semiconductor whose hole conductivity can be attributed to copper ion vacancies which act as acceptors for electrons from the valence band. Recently, Trivich et al. (12) studied solid-state photovoltaic cells based on this material and reported an overall conversion efficiency of optical to electrical energy approaching 1% and stated that efficiencies of 6-12% should be possible. Aqueous photoelectrochemical (PEC) cells involving p-Cu2O have also been described (13-14). In these cells the p-Cu2O photocathode is unstable and under irradiation is reduced to Cu metal.

\[ \text{Cu}_2\text{O} + 2\text{H}^+ + 2e^- \rightarrow 2\text{Cu} + \text{H}_2\text{O} \]  \[1\]

Similar instability was observed with CuO electrodes (15). In an aprotic solvent such as acetonitrile (MeCN), however, such a reduction reaction is less favorable because of the unavailability of protons. Since the bandgap is 1.9-2.0 eV, and the reported efficiencies for photovoltaic devices appeared interesting and the material is inexpensive, abundant, and capable of being readily produced in thin film form, we undertook a study of the PEC properties of p-Cu2O prepared by thermal and anodic oxidation of metallic copper in MeCN. The polycrystalline compacts were prepared by heating a Cu plate in air to minimize the grain boundary effects encountered in the case of sintered powder compacts (10). Studies of the PEC behavior of p-Cu2O were carried out with MeCN containing several redox couples including phthalonitrile, Ph(CN)2(0/−1), nitrobenzene, PhNO2(0/−1), and methyl viologen MV (+2/+1). Photocathodes of p-Cu2O were shown to be stable in these solutions under intense optical irradiation. However, the overall optical-to-electrical energy conversion efficiencies in the PEC cells based on this material were low (< 0.1%).

Experimental

Chemicals.—The procedures for the purification of chemicals and solvent (MeCN) are given elsewhere (17). All compounds were stored inside a helium-filled Vacuum Atmosphere Corporation (Hawthorne, California) glove box. Polarographic grade, tetra-n-butyl ammonium perchlorate (TBAP), dissolved and recrystallized from ethanol thrice and dried under vacuum (< 10⁻⁵ Torr) for three days, was used as supporting electrolyte. The cell employed was a conventional two-compartment cell of 25 ml capacity containing the p-Cu2O, a Pt counterelectrode, and a quasi-reference electrode which was an Ag wire immersed in the solution and separated from the main compartment by a medium porosity glass frit. The potential of the electrode was checked against an aqueous saturated calomel electrode (SCE) at regular intervals and was found to be constant. All potentials reported here, unless specified otherwise, are given in V vs. SCE.

P-Cu2O was prepared by the method of Trivich et al. (12, 18). A Cu plate, 0.8 mm thick (Alfa Ventron), was cut to a 2 x 2 cm square, polished with Al2O3 (0.5 μm), washed with acetone, and rinsed thoroughly with double distilled water. The plates were dried and heated in a muffle furnace at about 600°C for 24 hr. Subsequently, the furnace temperature was raised to 1050°C and the samples were heated for an additional 160 hr. The furnace temperature was then reduced to 500°C and at this temperature, the samples were annealed for a day, before quenching them in air at room temperature.

* Electrochemical Society Active Member.

Key words: solar energy conversion, photovoltaics, nonaqueous electrolytes.