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Mechanistic Study of Photoelectrochemical Reactions at a p? –?GaP Electrode

Kohei Uosaki and Hideaki Kita

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Summary

The surface photovoltage of the red and green forms of lutetium diphthalocyanine have photovoltage spectra which are characteristically different and are related to the optical absorptions of these two electrochromic forms. Dynamical measurements indicate that the green form has an electron depletion layer, while the red form has an electron accumulation layer. Both films have a photovoltage which is linearly dependent on light intensity, which implies that the photovoltaic change in the band bending is small compared to the total amount of energy band bending at the surface. The photovoltaic relaxation is linearly dependent on light intensity for the red form and inversely dependent for the green form, and this is shown that this is consistent with the presence of long-lived traps which make the band bending and/or flatband mobility dependent on light intensity.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1982 JOURNAL. All discussions for the June 1982 Discussion Section should be submitted by Feb. 1, 1982.

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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 contribution (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 photocathodes (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.

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 specific resistance of the sample are 6.7×10^{17} cm^{-3} and 1.3 Ω · 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 electrode 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 electrochemical cell is similar to the one reported previously (15). An Ag/AgCl electrode and a Pt wire were used as a reference and a counterelectrode, 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. Current-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 experiments 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 photocurrents are observed at all potentials investigated, even at potentials very close to the flatband potential, V_{FB}, which is ~ -0.04V *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 *p*H of the solution increases. The addition of methyl viologen changes the shape of the I_{ph}-V relation drastically.

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 potential, as shown in Fig. 3.

Discussion

Origin of anodic photocurrent.—Usually, only a cathodic photocurrent is reported at p-type semiconductors and only an anodic photocurrent is reported at n-type semiconductors with the exception of a cathodic photocurrent 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

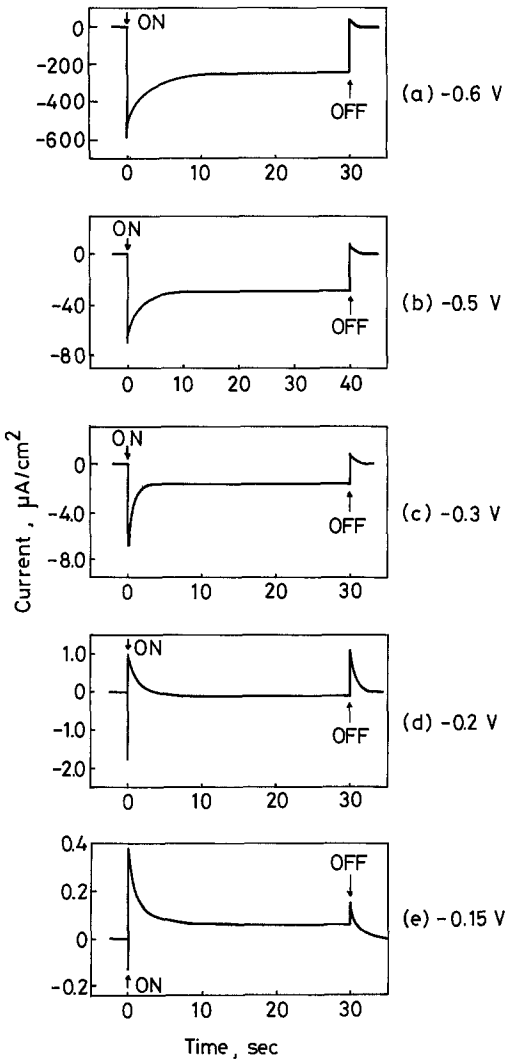

Fig. 1. Current-time relations of p-GaP in 1M NaOH at several potentials illuminated with pulsed light. Currents before illumination were taken as zero. Electrode potentials are with respect to Ag/AgCl.

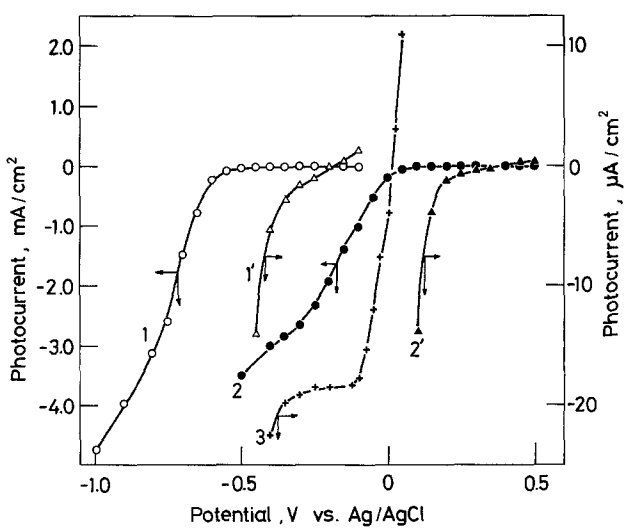

Fig. 2. The photocurrent-potential relation of p-GaP in various solutions with two current scales. 1,1' in 1M NaOH, 2,2' in 0.5M H_2SO_4, 3 in 1M NaOH + 1.7 mM methyl viologen.

the electron transfer takes place in a narrow energy range below the valence band energy, E_v (1)

$$i_a \propto c_R p_s W(E_v)\, G_R(E_v) \qquad [1]$$

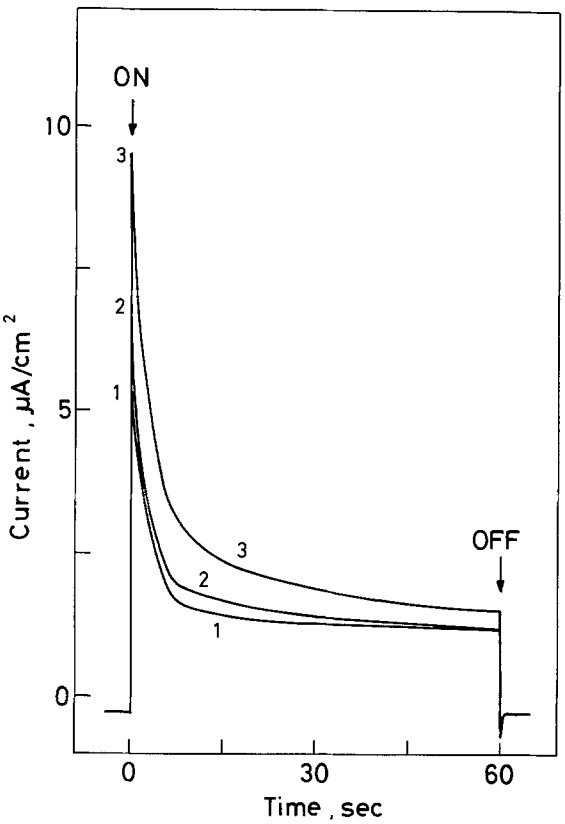

Fig. 3. The current-time relations of p-GaP in 0.5M H_2SO_4 at 0.2V *vs.* Ag/AgCl, for various lengths of time kept in the dark before illumination. Curve 1, 30 sec; curve 2, 2 min; curve 3, 10 min.

$$i_a^* \propto c_R p_s^* W(E_v) G_R(E_v) \quad [2]$$

where c_R is the concentration of reduced species and p_s and p_s^* are the number of holes at the semiconductor surface in dark and under illumination, respectively, $W(E_v)$ is the tunneling probability at the valence bandedge and $G_R(E_v)$ is the distribution function for finding the reduced species at the energy E_v. Thus, the anodic photocurrent, $i_{a,ph}$, is given by

$$i_{a,ph} = i_a^* - i_a \propto c_R(p_s^* - p_s) W(E_v) G_R(E_v) \quad [3]$$

Therefore, when $p_s^* - p_s > 0$, the anodic photocurrent should be observed at both n-type and p-type semiconductor electrodes. Since holes are the majority carriers of p-type semiconductors, p_s is large and, therefore, anodic dark current is large at the potentials where the anodic photocurrent is expected. Usually $p_s >> p_s^* - p_s$ and hence $i_a \simeq i_a^*$. This is why anodic photocurrent has not been reported at p-type semiconductor electrodes. For example, in the present work, $i_a = 8.54$ μA/cm^2 and $i_a^* = 10.0$ μA/cm^2 at -0.1V *vs.* Ag/AgCl in 1M NaOH. The small difference between the two could be measured by the potentiostatic method employed in this work but is not possible to be detected by the sweep method which is usually employed in studying the current-potential relations at semiconductor electrodes.

In this system, the anodic reaction is the decomposition of the electrode itself, since no redox reagent is added (6, 26). The anodic decomposition potential of GaP has been calculated only at $pH = 7$ by assuming the following reaction (24, 27)

$$GaP + 6p^+ + 6H_2O \rightleftarrows Ga(OH)_3 + H_3PO_3 + 6H^+ \quad [4]$$

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 (26). The existence of the anodic (dark) currents even at the potentials more negative than V_{FB} 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

$pH < 2$
$GaP + 6p^+ + 3H_2O \rightleftarrows H_3PO_3 + 3H^+$
$E = -0.357 - 0.0295\ pH + 0.00985 \log [Ga^{3+}] + 0.000985 \log [H_3PO_3]$
$2 < pH < 2.56$
$GaP + 6p^+ + 3H_2O \rightleftarrows Ga^{3+} + H_2PO_3^- + 4H^+$
$E = -0.337 - 0.0394\ pH + 0.00985 \log [Ga^{3+}] + 0.00985 \log [H_2PO_3^-]$
$2.56 < pH < 8.32$
$GaP + 6p^+ + 9/2\ H_2O \rightleftarrows 1/2\ Ga_2O_3 + H_2PO_3^- + 7H^+$
$E = -0.315 - 0.0690\ pH + 0.00985 \log [H_2PO_3^-]$
$8.32 < pH < 11.7$
$GaP + 6p^+ + 8\ OH^- \rightleftarrows 1/2\ Ga_2O_3 + HPO_3^{2-} + 7/2\ H_2O$
$E = -0.233 - 0.0788\ pH + 0.00985 \log [HPO_3^{2-}]$
$pH > 11.7$
$GaP + 6p^+ + 11\ OH^- \rightleftarrows GaO_3^{3-} + HPO_3^{2-} + 5H_2O$
$E = 0.170 - 0.108\ pH + 0.00985 \log [GaO_3^{3-}] + 0.0985 \log [HPO_3^{2-}]$

The thermodynamic values used for calculation are all taken from Ref. (28) for phosphorous compounds and from Ref. (29) for gallium compounds except for $\Delta G°_f(GaP) = 91.54$ kJ · mol^{-1} which is taken from Ref. (30).

Photocurrent onset potential and flatband potential. —The photocurrent onset potential has a practical importance in a solar energy conversion. However, it is usually defined very vaguely (20, 21) in a similar way to the decomposition potential in electrode processes at metal electrodes which has no theoretical significance. In fact, the value of the photocurrent onset potential varies depending on the current scale chosen, as shown in Fig. 2. We propose here the definition of the photocurrent onset potential as the potential at which the sign of the photocurrent changes. By doing so, no ambiguity is introduced in determining the photocurrent onset potential. To distinguish this potential from the apparent photocurrent onset potential formerly used, we name it the "potential of zero photocurrent," V_{zp}. At V_{zp}

$$i_{ph} = |i_{ph,c}| - |i_{ph,a}| = 0 \quad [5]$$

$$i.e., \quad |i_{ph,c}| = |i_{ph,a}| \quad [6]$$

Butler and Ginley reported that the difference between V_{FB} and the photocurrent onset potential is 0.7V for p-GaP (20). However, V_{zp} determined in this work are much closer to V_{FB} in various solutions, although there still exists some difference between them up to *ca.* 200 mV. It is usually believed that one would expect no photocurrent at V_{FB}, because holes and electrons created by illumination recombine easily under the absence of a potential gradient in the semiconductor. However, this is not necessarily true. If the diffusion length of holes is large and the anodic reaction at the valence band is faster than both the cathodic reaction at the conduction band and the surface recombination reaction, the photogenerated hole accepts either an electron from a reduced species in solution or a valence electron of the semiconductor before deactivation. Thus, an anodic photocurrent should be observed at V_{FB}, because the photocurrent observed, i_{ph}, is given by

$$i_{ph} = |i_{ph,a}| - |i_{ph,c}| \propto |c_R(p_s^* - p_s)W(E_v)G_R(E_v)| - |c_o(n_s^* - n_s)W(E_c)G_o(E_c)| \quad [7]$$

where c_o is the concentration of the oxidized species, n_s^* and n_s are the concentration of the electrons at the surface under illumination and in the dark, respectively, $W(E_c)$ is the tunneling probability for the cathodic reaction at the conduction bandedge, and $G_o(E_c)$ is the distribution function of oxidized species at the

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_{zp}

$$p_s^* - p_s = n_s^* - n_s = 0 \quad [8]$$

$$|c_R(p_s^* - p_s)W(E_v)G_R(E_v)| = |c_o(n_s^* - n_s)W(E_c)G_o(E_c)| \quad [9]$$

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 experimentally observed.

In the solution containing methyl viologen, the V_{zp} is almost identical to the flatband potential. In this case, for the reaction $MV^{++} + e \rightleftarrows MV^{+\cdot}$ 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, *i.e.*, photogeneration of electron-hole pairs, (*ii*) migration of the photoexcited electrons to the semiconductor surface, and (*iii*) deactivation of the photoexcited electrons to the valence band, in parallel with (*ii*), *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

$$h\nu \rightarrow p_v^+ + e_c^- \quad [10]$$

$$e_c^- \rightarrow (e_c^-)_s \quad [11]$$

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

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

$$(e_c^-)_s + H_3O^+ + \text{S.C.} \rightarrow H_2O + \text{S.C.} - H \quad [13]$$

$$(e_c^-)_s + H_3O^+ + \text{S.C.} - H \rightarrow H_2 + H_2O + \text{S.C.} \quad [14]$$

$$\text{S.C.} - H + \text{S.C.} - H \rightarrow H_2 + 2\text{S.C.} \quad [15]$$

$$p_v^+ + H_2O + \text{S.C.} - H \rightarrow \text{S.C.} + H_3O^+ \quad [16]$$

and those for the recombination are

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

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

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

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, $\square_{ss}$ 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. [13]-[16] should be replaced by the following

$$(e_c^-)_s + MV^{++} \rightarrow MV^{+\cdot} \quad [19]$$

$$MV^{+\cdot} + (p_v^+)_s \rightarrow MV^{++} \quad [20]$$

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 ~ −0.7V in 1M NaOH and +0.2 ~ −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 both with and without methyl viologen. This potential coincides with the apparent photocurrent onset potential determined by $i_{ph}^2 - V$ 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.

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 $i_{ph}^2 - V$ relation (20). They concluded from *IR* photoresponse measurement that the localized state which is ~0.7 eV above the top of the valence band acts as the recombination center. According to their model, the photocurrent at steady state, i_{ph}, is given by

$$i_{ph} \propto j - k_r[e_c^-]_s N_{ss}(1 - f_t) \quad [21]$$

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_t is the Fermi distribution function

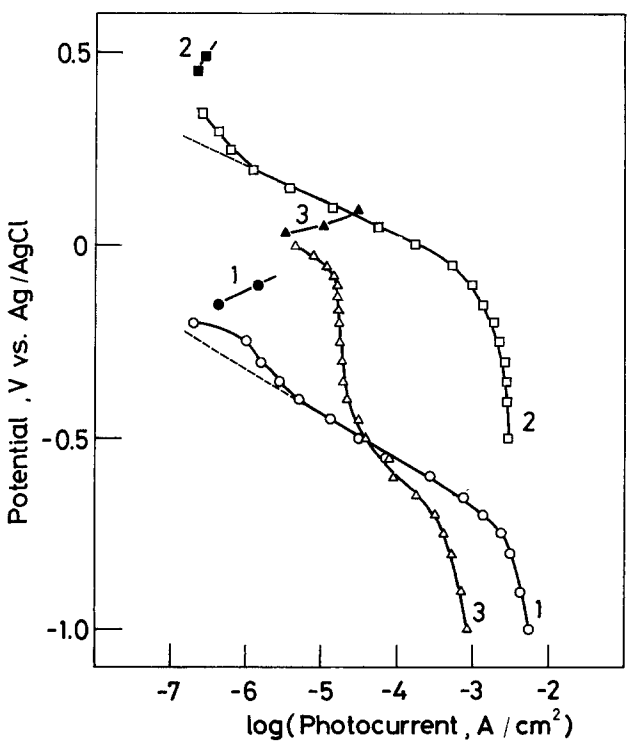

Fig. 4. Tafel plots of the photocurrents of p-GaP in various solutions. Curve 1, 1M NaOH; curve 2, 0.5M H_2SO_4; curve 3, 1M NaOH + 1.7 mM methyl viologen.

for the surface states. For the present system, if all potential drop occurs within the semiconductor, f_t is given by

$$f_t = 1/[1 + \exp\{E_t - E_F/kT\}]$$
$$= 1/[1 + \exp\{0.7 - (V_{FB} - V)/kT\}] \quad [22]$$

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 -0.7V *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.[1] 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_{zp} 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 $MV^{+\cdot}$ 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 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.

[1] R. H. Wilson proposed a model which takes into account both the surface recombination rate and charge transfer rate for n-type semiconductors (33, 34).

[2] The fact that the height of the photocurrent spike just after illumination is much smaller when the solution is stirred supports this mechanism.

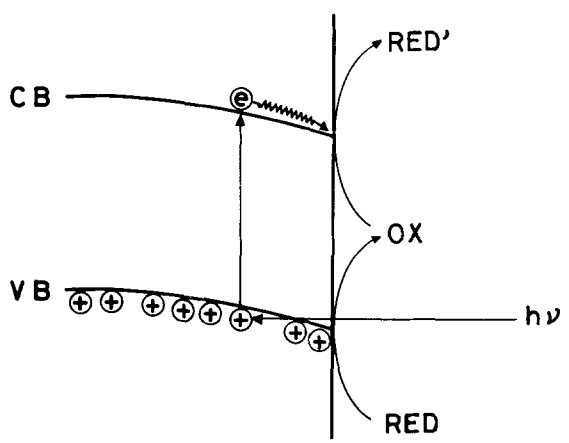

Fig. 5. Contribution of oxidized species created by hole to photocurrent enhancement at relatively small bias potential.

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Semiconductor Electrodes

XXXVII. Photoelectrochemical Behavior of p-Type Cu_2O in Acetonitrile Solutions

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ABSTRACT

The photoelectrochemical behavior of polycrystalline p-Cu_2O 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-Cu_2O, 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-Cu_2O/$Ph(CN)_2$,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 (Cu_2O), 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-Cu_2O depend upon the conditions of preparation from Cu and O_2, *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-Cu_2O have also been described (13-14). In these cells the p-Cu_2O photocathode is unstable and under irradiation is reduced to Cu metal

$$Cu_2O + 2H^+ + 2e \rightarrow 2Cu + H_2O \qquad [1]$$

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-Cu_2O 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 (16). Studies of the PEC behavior of p-Cu_2O were carried out with MeCN containing several redox couples including phthalonitrile, $Ph(CN)_2$(0/−1), nitrobenzene, $PhNO_2$(0/−1), and methyl viologen MV (+2/+1). Photocathodes of p-Cu_2O 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-Cu_2O, 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-Cu_2O 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 × 2 cm square, polished with Al_2O_3 (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 900°C for 24 hr. Subsequently, the furnace temperature was raised to 1030°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. Upon quenching, the CuO layer formed

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