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SOLAR CELLS OF METAL-FREE PHTHALOCYANINE
DISPERSED IN POLYVINYL CARBAZOLE

(I) EFFECTS OF THE RECRYSTALLIZATION OF
H_2PC ON CELL CHARACTERISTICS

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16. Abstract

For the purpose of developing an organic semiconductor solar cell, the effects of the recrystallization of metal-free phthalocyanine (H_2PC) on the characteristics of NESA/H_2PC-PVK/Au sandwich cells have been investigated. Alfa-H_2PC sandwich cells showed photovoltage and photocurrent in a direction opposite to that shown by as-supplied H_2PC cells, which consisted mainly of beta-H_2PC. Some difference was observed in the response times of the two cells. It was considered that photocharacteristics change with the specific resistance of the H_2PC, which is related to its crystal forms. In the cells with low-resistance H_2PC (i.e., alfa-H_2PC), carriers were generated in H_2PC by illumination, while in high resistance H_2PC (i.e., beta-H_2PC) cells, carriers were generated in PVK which was sensitized with H_2PC.

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SOLAR CELLS OF METAL-FREE PHTHALOCYANINE DISPERSED IN POLYVINYL CARBAZOLE
(I) EFFECTS OF THE RECRYSTALLIZATION OF H_2PC ON CELL CHARACTERISTICS

M. Shimura[x]), H. Baba[x])

1. Introduction

Among various methods of energy conversion solar cells are the most clean and noiseless. There is a problem of cost, which, however, is reduced from year to year[*1]. A coefficient of conversion in the case of tandem cells can be as high as 50 and more [1]. In the last few years more and more investigations are carried out with regard to utilization of organic semiconductors for the manufacture of solar cells[*2]. Organic materials are not so restrictive from the point of view of resources as inorganic materials. Furthermore, their advantage is that they can be easily produced in the form of thin films for lower cost. Manufacturing of thin films is performed by dripping an organic material dispersed in a slurry-type high-molecular binder onto the surface of a substrate [4]. This method may be very promising for the future as it is free of disadvantages in ~ent in evaporation methods, i.e. it does not require the use ~f thermally decomposable materi？~s and prevents losses due to scattering.

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[*1] In 1970 the cost was $500/watt, whereas in 1980 it was reduced down to $10/watt. In 1986 the cost may be as low as ¢70/watt[1].

[*2] It has been reported that phthalocyanine [2-4] ,chlorophyll [5], merocyanine, hydroxy-squalilium compounds [6] are used for this purpose.

[*] Numbers in the margin indicate pagination in the foreign text.

However, under conditions of high light intensity,solar cells in-
corporating organic materials reveal a disadvantage consisting
of an extremely small coefficient of conversion. This stems from
the low quantum efficiency of carrier generation in the case of or-
ganic materials, low mobility of carrier and high trap density [7].
Furthermore, in this case one cannot neglect the light-retaining
effect caused by a metal film existing on the path of light due to
application of the Schottky barier on the plane of interface.

An object of the present investigation was to measure "p-n
junctionness" of an organic material per se in order to reduce its
specific resistance by changing carriers. due to various additives.
As a first step for investigating the effect of purification, phtha-
locyanine, which is known as a chemically-stable cosmetic has been
chosen. Metal-free phthalocyanine (hereinafter referred to simply
as H_2PC) , which is advantageous from the point of view of light ab-
sorbance,was selected for experiments. Susceptibility to the effect
of purification of H_2PC also has been considered in a sandwich-cell
structure,in view of a weak barrier action on both sides of the
interface between NESA/H_2PC/Au used as electrodes.

2. Experiment

2.1. Preparation of H_2PC-PVK Film

H_2PC was used as-supplied,by purchasing this high-purity ma-
terial from Eastman Kodak or,after purification,by recrystalliza-
tion from concentrated sulfuric acid. Finely divided powder of
H_2PC in agate mortar (with an average size of particles equal to
47 μm) was added to a slurry-type polyvinyl carbazole(the product
of Tokyo Kaseisei, hereinafter referred to as PVK) solution (the
solvent comprised monochlor benzene and dichlor ethane taken in

1:1 ratio). Apart from special cases, an amount of additives comprised about 40% by weight. Experiments which have been conducted by the authors [8] confirmed that this proportion is the most advantageous from the point of view of the photovoltaic power and stability of the film (resistance to cracking and peeling-off from the substrate). The H_2PC-PVK solution was stirred for several hours in a magnetic stirrer until uniform distribution had been reached. Following this, the solution was dripped onto the surface of the substrate, and then dried, first naturally and then by keeping it for a day in a vacuum-type desiccator.

2.2. Preparation of Sandwich Cell

NESA glass was used as a substrate (SnO_2 film, $N_D \approx 2 \times 10^{19}$ cm^{-3}, a product of ·Matsuzaki Shinkusei Co.) the surface of which was covered with a film of H_2PC-PVK (an average thickness of the film was about 48μm)*3 and then an electrode of Au (with a thickness of about 300Å) was applied onto the film by a spattering method. Lead wires from the electrode were formed by sticking copper foil pieces to one end of the Au electrode with the use of an Ag paste (a product of Du Pont, No. 4922). Tapping of the·lead wires from the NESA film was performed first by vacuum depositing indium onto the end of the NESA film and then by sticking a copper foil piece onto said layer with the Ag paste.

2.3. Measurement of Photovoltaic Power and Photocurrent

In order to exclude the effect of atmospheric humidity and electric noise on the results of measurements, the latter were conducted in

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*3 Electric-type film thickness gage (a product of Tokyo Seimitsu Sei K.K., Minicom, EDM-M306) was used for measurements

in a vacuometer (a product of Pirex Co., .10^{-2} Torr capacity) which in turn was installed inside a metal shield box (with a small opening for the optical path). An electrometer (a product of Tageta Rikensei K.K., mod. TR-8651[4]) also was used for measuring circuit interruption voltage V_{oc} and short-circuit current I_{sc}.

A 500W Xenon lamp was used as a light source and monochromatic light of various wavelength between 700 and 400 nm was selected by means of color glass filters (Toshiba Garasu K.K., Y-48)passing the light with $\lambda > 480$ nm (light intensity[5]: 32.4 mW·cm^{-2})[6] and interference filters (interference filters manufactured by Mitsunobu Kogaku K.K., $\lambda_{1/2}$: about 10 nm; light intensity: about 0.3 mW·cm^{-2}).

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[4] Input impedance of the electrometer during the measurement of V_{oc} was $10^{14}\Omega$ and the following impedances were applied during the measurement of I_{sc}: input impedance for the range of 10^{-11}A was $10^9 \sim 10^8$ Ω; input impedance for the range of 10^{-10}A was $10^8 \sim 10^7$ Ω; and input impedance for the range of 10^{-6}A was $10^4 \sim 10^3$ Ω . The response time of the electrometer (the time of oscillation of the indicator until it shows 99% of the rated input signal current) for currents above 10^{-10}A was within the limits of 0.5 sec.

[5] Measurements were conducted with the use of a compressor-type thermopile (a product of Eppley Co., 16-junction Bi-Ag).

[6] Emission of light with $\lambda > 480$ nm was selected in order to hinder the light absorption by PVK and to reveal the light absorption effect from the side of H_2PC itself.

3. Results of Experiments

3.1. Variation of H_2PC under Effect of Purification

Under the effect of recrystallization from concentrated sulfuric acid H_2PC changes its color (from blue tinged with green to blue) and increases in volume. However, X-ray diffraction patterns (Figure 1) differ only by wider peaks at 6.8~7.2, 13.5~16.7 and 24.7~27.3°.
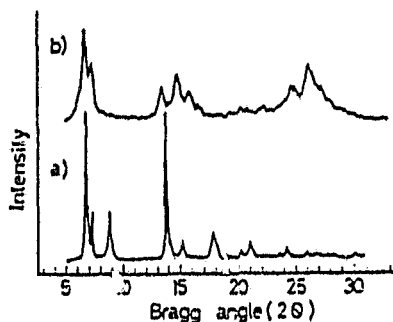

Fig.1. X-ray diffraction pattern of H_2PC: (a) as-supplied; (b) recrystallized.

This material was established as α-H_2PC [9-11]. On the other hand, an unpurified material was recognized as β-H_2PC[9-11] and it was impossible to detect the impurities by means of X-ray diffraction. However, it proved to be possible to determine the absorption caused by impurities (the absorption maximum at 644 nm and shoulder at 633 nm),apart from the absorption from H_2PC (695, 657 nm) in the unpurified material, by resolving said H_2PC in monochlor benzene[7] and subsequntly determining the visual absorption spectrum.

Figure 2 illustrates an IR absorption spectrum of H_2PC (KBr disk method). All absorption spectrums obtained from the purified H_2PC belonged to α-H_2PC, whereas almost all absorption spectra from unpurified material turned out to be β-H_2PC with a small quantity of particles in the range of 1570, 1520 and 1360 cm^{-1}, which, however, cannot belong to α-H_2PC.

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[7] Monochlor benzene was chosen as a solvent because it possesses low solubility with respect to H_2PC whereby without interfering with the absorption of H_2PC per se it allows detection also of the absorption of impurities.

The results given above show the way for exclusion of impurities and the manner of conversion from β to α-modification of H_2PC by means of recrystallization from concentrated sulfuric acid.

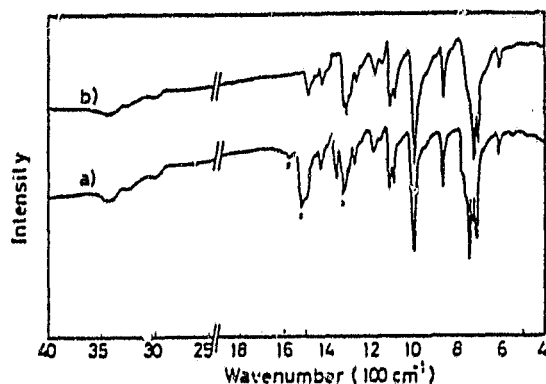Furthermore, although it is not shown in the drawings, H_2SO_4 hardly shows any residual activity [8] (due to adsorption and formation of electric charge-transfer complexes[9]) in the recrystallized material. The following description relates to the effect of purification of H_2PC when it is dispersed in a PVK film.

Fig.2. IR spectra of H_2PC by KBr disk method: (a) as-supplied; (b) recrystallized

3.2. Photovoltaic Power

Under conditions of illumination by 480 nm light the purification of H_2PC considerably changes the photovoltaic power generated in H_2PC-PVK film sandwich cells (Figure 3). As an ordinate in this drawing, the voltage of the NESA-pole is plotted with an Au-pole taken as a criterion. About +200 mV voltage (however, with the illumination of the Au-pole side) was obtained for purified H_2PC cells as compared to -180 mV for the unpurified H_2PC (with the illumination of the NESA-pole) in the case of measurement of a steady photovoltaic power. The same symbols are maintained with the change of the planes of illumination and only the photovoltaic power is reduced. In the

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[8] The absorption of SO_4^{2-} cannot be detected by means of IR.

[9] When ESR measurements of H_2PC powder are carried out at room temperature, a strong signal is obtained in the vicinity of g= 2.002 [12]. Because this is not related with the recrystallization, the results are the same both for unpurified and purified H_2PC. It has been assumed that in this case electrons are trapped
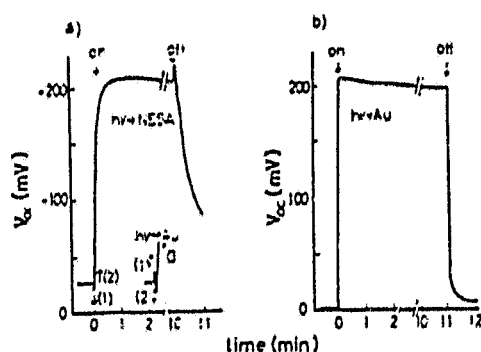
Fig.3. Typical time pro-
files of open circuit
voltage of H_2PC-PVK sand-
wich cells by the illu-
mination of $\lambda > 480$ nm
light:
(a) as-supplied H_2PC;
(b) recrystallized

determination of working spectrums
with regard to the steady photovoltaic
power, the absorption spectrum of a
film with the illumination of the NESA-
pole in an unpurified H_2PC cell and
that of a film with the illumination
of the Au-pole in a purified H_2PC cell
are close to each other.

Complicated transient phenome-
na*[10] take place in an unpurified
H_2PC cell until conditions of steady
photovoltaic power are reached. In
other words,when the NESA-pole side
is illuminated, the photovoltaic power
is first shifted towards a positive
side,then is converted into a negative
value, amplified and at last reaches
a steady value (Figure 3a). Also in
the case of illumination of the Au-
pole side the voltage is shifted to-
wards a nagative value, then towards a positive value, then again
becomes negative and reaches a steady value (Figure 3a). Detailed
explanations for these phenomena are given further in Chapter 3.3.

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in structural cracks of H_2PC. However, at the present time this
question is again under investigation. On the other hand, Calvin
[13] has published the information on H_2PC and chloranil in connec-
tion with the ESR absorption due to electric charge-transfer comp-
lexes of H_2PC.

*[10]
The regeneration ability of the transient phenomena is very
strong and it does . not change even with cyclically repeated illu-
mination or after heat treatment (30 min at $80^\circ C$ under 10^{-2} Torr).

On the other hand, in purified H₂PC cells, along with the illumination, the photovoltaic power is shifted towards a positive side and quickly reaches steady conditions (Figure 3b).

Time necessary to achieve steady conditions comprises in unpurified H₂PC cells about 7 sec and in purified H₂PC about 1.6 sec. Also the time required to restore the initial voltage after stopping illumination in unpurified H₂PC cells is equal to 2 min and in purified H₂PC is equal to 35 sec. The difference in speeds of optical response is determined mainly by difference in the usual trap density. However, it may be supposed that divergence of carries generated in the films, i.e. the question where the majority of carries takes place--in H_2PC or in PVK, stems from differences in planes of separation of charges, which has been mentioned above, and from differences in directions of generation of the photovoltaic power associated with this phenomenon. This is the final source of deviations in the form of crystals of H_2PC. According to the results of measurements of the specific resistance, in a dark room of tablet forming facilities, in the present investigation of H_2PC powder, [14] *11 3.3 x $10^{12}\Omega \cdot cm$ was obtained for an unpurified material, i.e. for $\beta-H_2PC$, whereas a value of 1.0 x $10^7\Omega \cdot cm$ was obtained for a purified material, i.e. for $\alpha-H_2PC$. The reason for which the specific resistance is different in various modifications of crystals is known [15], however some deviations may be introduced due to difference in methods of measurements and conditions of H_2PC (tablets, vacuum deposited film, monocrystal). It is supposed that $\alpha-H_2PC$ has a small value of specific resistance due to the irregular chrystalline structure and small activation energy of dark current generation, and also due to the fact that wavelength limits in the generation of photoelectric current are longer than the wavelength in β-modification [16] *12. Apart from this, multiple states of the carrier may be

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*11 100 mɑ of H_2PC was treated in än IR tablet-forming machine under vacuum conditions (400 kg cm^{-2}). By means of spattering, Au was applied onto both sides of the thus formed tablet. Measurements were conducted by applying a stable voltage at 15°C in a vacuometer (10^{-2} Torr).

*12 According to Liang [16] the activation energy of dark conduction of

8

caused by a disordered state leading to incompleteness in the crystal= line structure in band gaps of α-H_2PC. Due to considerable differences in the specific resistance of various crystalline modifications, H_2PC has a smaller specific resistance than PVK. Therefore in the case of application of H_2PC with high carrier concentration, the Fermi level is determined by means of the carrier in H_2PC. On the other hand, in the case of high specific resistance , which is equal or higher than that of PVK, i.e. when H_2PC is dispersed in the film with low concentration of the carrier, the Fermi level is determined by the carrier in PVK. Thus, in this case H_2PC in the film plays the role of a sensitization pigment with respect to PVK. Such a concept is supported by the behavior of photoelectric current described in the subsequent chapters.

3.3. Short-Circuit Photovoltaic Current

The following remarkable effect of purification of H_2PC has been observed in measuring the short-circuit photovoltaic current $I_{sc,ph}$. when a sandwich cell is connected to the direct electrometer and illuminated with $\lambda > 480nm$. In other words, there are no special dis- tinctions in the direction [13] and generation efficiency of current $I_{sc,ph}$, when, in an unpurified H_2PC cell, this current reaches its steady value equal to -1.2×10^{10} $A \cdot cm^{-2}$ (however, when the NESA pole side is illuminated, apart from the light penetration factor of NESA pole equal to 0.82, this value has to be conpensated with regard to the in- cident light illuminous intensity) and when, in a purified H_2PC cell, it reaches its steady value at $+9.7 \times 10^{-8} A \cdot cm^{-2}$ (however, when the Au pole side is illuminated, apart from the Au pole penetration factor of 0.38, this value has to be compensated with regard to the incident light/illiminous intensity). Also, in this case, complicated transient

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H_2PC has been determined as follows: α-H_2PC: 1.4eV, β-H_2PC: 1.9eV. Also the wavelength limits in generation of the photovoltaic current were the following: α-H_2PC: 0.68eV, β-H_2PC: 0.79eV.

[13] Symbol $\oplus$ means that current is flowing from the NESA pole to the outside circuit.

phenomena take place. Although these phenomena are almost the same as have been described in the previous chapter with regard to photovoltaic power, the following details may be added. In the case when the NESA pole side is illuminated, the photoelectric current has $\oplus$ sign, i.e. it flows from the NESA pole towards an outside circuit. Then after 0.1 sec the current is reversed to $\ominus$ sign, i.e. the current $I_{sc,ph}$ flows towards the NESA pole. This $\ominus$ $I_{sc,ph}$ current immediately (in 0.3 sec after reversing) reaches its maximum, and following this, it is slowly reduced until the steady state is achieved. Figure 4(a) illustrates active spectra of $\oplus$ and $\ominus$ $I_{sc,ph}$ in the transient area. One can see that both are very close to the absorption spectra of the film. Therefore it can be supposed that both are formed under the effect of light absoption in H_2PC ajoining the NESA pole.
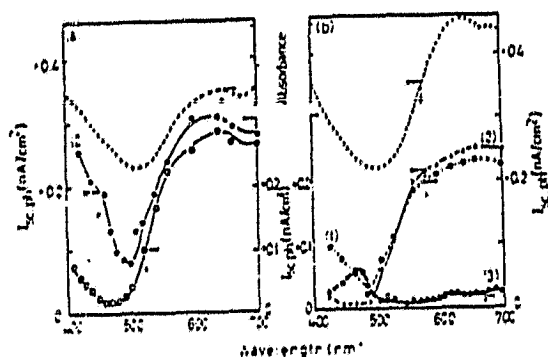

Fig. 4. Action spectra of transient short-circuit photovoltaic current of as-supplied H_2PC-PVK sandwich cell: Illuminated (a) though NESA and (b) through Au. The currents are corrected for transmittances of NESA, Au, and interference filters. The absorption spectra of (a) as-supplied H_2PC in thin PVK film and (b) as-supplied H_2PC powder: ....

Among them the best efficiency was shown (in the area of the wavelength exceeding 520 nm) by $\oplus$ $I_{sc.ph}$ (curve (1)) which has a very quick speed of response. Comparison of these results with the behavior of cells (curve (1)) in the case of illumination on the Au pole, side shown in Figure 4(b), suggests that on the basis of holes formed in H_2PC the Dember effect's photoelectric current takes place.*14. With regard to $\ominus$ $I_{sc,ph}$ (curve (2)), the generation of which is slightly delayed, it should be noted that the best efficiency occurs within the wavelength range below 500 nm. This suggests that, in the case when H_2PC acts with respect to PVK as a sensitizer, one can assume that carriers are generated in PVK [18]. (Figure 4(b), cirve (3)). When the Au-pole side is illuminated in an unpurified H_2PC cell, first a $\ominus$

10.

negative current $I_{sc,ph}$, i.e. the current flowing from the Au pole towards the outer circuit , occurs, and then immediately (in 0.1 sec) after this it reverses to a $\oplus$ positive value and flows from the outer circuit towards the Au-pole . In 0.5 sec the current reverses again to a $\ominus$ negative value which increases and at last reaches its steady value. Thus, in the case of illuminating the Au-pole side the current passes through complicated transient phenomena and its direction experiences complicated variations. Figure 4 (b) shows action spectra of each $I_{sc,ph}$. One can see that both, $\ominus I_{sc,ph}$ (curve (1)),having quick response,and $\oplus I_{sc,ph}$ (curve (2)), approach the absorption spectrum of $\beta-H_2PC$. It confirms the fact that these currents are generated under the effect of light absorption in H_2PC adjoining to the Au-pole. The quick-responsive $\ominus I_{sc,ph}$ current flows from the il-lumination plane (the Au-pole) towards the outer circuit. First of all, when the NESA-pole side is illuminated, the positive $\oplus$ photovol-taic current $I_{sc,ph}$ is observed flowing from the illumination plane (the NESA pole) towards the outer circuit. It is suggested that in this case the photovoltaic current can be associated with the Dember effect of electron holes formed in H_2PC under the action of illumination. However, it is supposed that the quick-responsive negative $\ominus$ current $I_{sc,ph}$ also occurs under the Dember effect.

As far as the positive $\oplus$ current $I_{sc,ph}$ (curve (2)) is concerned, it should be noted that, referring to the behavior (Figure 5(a)) in the purified H_2PC cell, which is considered below, the photovoltaic

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*14 The following experiments were conducted to verify the existence of the Dember effect in a H_2PC-PVK film. A sandwich cell was formed by placing a thick $\alpha-H_2PC$-PVK film between two NESA films (NESA/ αH_2PC-PVK/NESA sandwich), and following this, the $I_{sc,ph}$ current was observed along with $V_{oc,ph}$ by illuminating one side of the sand-wich with the $\lambda > 480$ nm light. As a result, generally the potential on the illuminated surface was increased and the outer circuit was formed by the photovoltaic current which flowed from the illuminated surface to the dark surface. Holes were formed in H_2PC.

current can be considered, with the use of the potential gradient on the interface plane between H_2PC and Au, as the motion of excited electrons in the optically excited H_2PC. The $\ominus$ negative $I_{sc,ph}$ current (curve (3)), which has the most delayed response, by configuration of its spectrum approaches that of the transmission spectrum of the film. Therefore, this corresponds to separation of charge on the back surface of the film (NESA-pole side). Its current $I_{sc,ph}$ has a delayed response but is generated under steady conditions. This suggests that in cells produced on the basis of an unpurified H_2PC the electric charge separation dominates on the boundary surface of the NESA pole, and current flows from the film towards the NESA pole, i.e. the negative $\ominus$ $I_{sc,ph}$ current flows under steady conditions. Consideration of the interface plane between H_2PC and PVK shows that in view of high concentration of carriers (as in the case of the present investigation), the NESA-
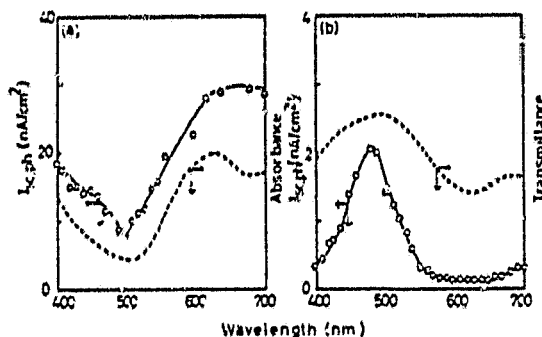
Fig. 5. Action spectra of transient short-circuit photovoltaic current of recrystallized H_2PC-PVK sandwich cells: Illuminated (a) through Au and (b) through NESA. The currents are corrected for transmittance of NESA, Au and interference filters. The absoption (a) and transmission (b) spectra of recrystallized H_2PC in PVK film:
·········

pole has a Fermi level of about 4.9eV [4]. On the other hand, with regard to PVK, it was revealed that its ionization potential is equal to 6.1 eV, and electronic affinity takes place at 1.5 eV. Therefore with a relatively high concentration of carriers, as in the present investigation, the Fermi level exists near the band of valence electrons. For this reason a barrier is formed on the interface plane*[15]

*[15] A similar barrier is formed on the interface with Au. Therefore the energy band of PVK decreases on both boundary planes of NESA and Au, and a protrusion should be formed due to the bulk activity. However, in reality

It should be noted with regard to this interface plane that if
the illumination performed excites PVK per se, then the transfer
of electrons starts in the direction from the excited PVK towards the
NESA-pole and photoelectric current is generated ($I_{sc,ph}$ has a negative
$\ominus$ value because it flows from the outside circuit towards the NESA-
pole). Furthermore, when illumination is carried out by means of light
having a long wavelength, the light is absorbed by H_2PC adjoining PVK.
Perhaps the photovoltaic current is generated due to charge transfer,
when the excitation level of H_2PC and that in PVC have superimposed wave
functions.

There have been many reports [18, 19] on the photoconductivity
effect of PVK, when sensitivity was increased by means of a pigment.
Okado et al. 19 *[16] observed the initial spike in a system composed
of a pigment applied by means of vacuum deposition onto the surface of
a PVK film. The phenomenon took place under the effect of a charge
transfer between the PVK and pigment. The conclusion can be drawn on
the basis of the above results, that in cells produced with the use of
an unpurified H_2PC, the photovoltaic current is induced by carriers in
PVK and that H_2PC acts as a sensitivity increasing pigment for PVK.

Action spectra shown in Figure 5 were obtained for cells manu-
factured on the basis of a purified H_2PC. In the case of illumination
on the Au-pole side, these spectra approach the absorption spectrum
of α-H_2PC (Figure 5(a)) and in the case of illumination on the side of
the NESA pole, the configuration approaches the transmission spectrum
of α-H_2PC (Figure 5(b)). This clarifies the fact that the plane of se-
paration of the electric charge in a purified H_2PC cell is a boundary
plane between H_2PC and Au and that the photovoltaic current is genera-
ted due to excitation of H_2PC. *[17]

the charge separation on the boundary surface of NESA is dominant.
At the present time this phenomena is under investigation.
*16
The initial spike of the photovoltaic current is induced by electrons,
in the case of an n-type pigment, and by traps formed by holes in PVK,
in the case of a p-type pigment.

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A similar behavior has been observed by Sharp [4]·in a NESA/
X-H₂PC-PVA/Al sandwich cell. However, in this case the Schottky
barier is formed on the interface between X-H_2PC (E_F: about 5.09
eV[4]) and Al (about 4.2eV[4]), which has.- a low work function. In the
present investigation an apparent barrier of this type appears in the
case of conjugation with Au having a high work function *[18]. How-
ever this is a topic of the next report.

3.4. Behavior of PVK Film Sensitized by H₂PC

The previous chapter described observation of   ·behavior in
the case of pigment sensitization, with regard to PVK and the use of
unpurified H_2PC. Probably this is related to the high specific re-
sistance of unpurified H_2PC and low mobility and high concentration of
carriers in H_2PC.

In this chapter a subject of discussion comprises   behavior of   /683
PVK sensitized with H_2PC, in the case of α -H_2PC of low specific
resistance dispersed in small quantities in PVK.

The results showed that, when the quantity of α-H_2PC in the film
is less than 5% by weight, the behavior is the same as in cells produced
with unpurified H_2PC. In other words, the current $I_{sc,ph}$ changes
from the outer circuit towards the NESA-pole, and the action spect-
rum shows that the charge separation plane is transferred to the
NESA/film boundary plane (Fig. 6). The speed of optical response
also is delayed, behind the value of that in unpurified H_2PC cells.
This confirms the previously mentioned facts about sensitizing action
in unpurified H_2PC cells. With regard to H_2PC , the carrier concent-
ration depends essentially on the type of crystals. With high concen-

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*17 Typical rectifying characteristics (the direction is assumed as
forward when the NESA pole is polarized as a positive one) were ob-
tained in determining V-I relationship on the dark side with appli-
cation of voltage to the NESA/purified H_2PC-PVK/Au cell from the·outer
side. On the other hand, the rectifying char   eristics were defini-
tely absent in cells based on unpurified H_2PC.

'tration of carriers, p-type occurs, whereas low concentration pro-
duces an intrinsic type, both having different Fermi levels. Thus,
a barrier of a certain type is formed on the interface plane, which :
suggests that it can act as a charge separation plane. However, this
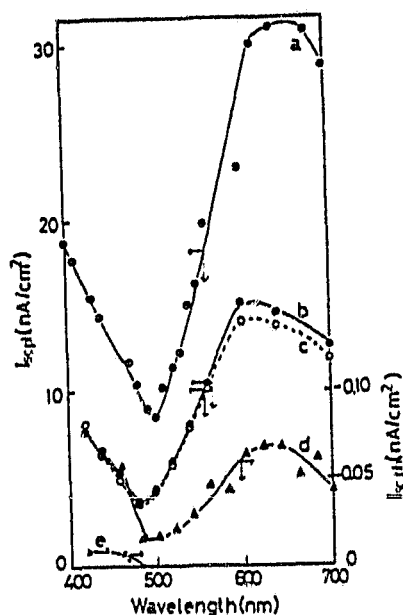question is still under investigation.
Figure 6 illustrates action spectra,
when a sandwich cell is made only of
a PVK film. For PVK used in the
cells, optical characteristics are shown
from the minimum values to 460 nm.
These characteristics were analyzed on
the basis of excitation correlated with
the level of impurities in PVK.

Thus, the present experiment cla-
rifies an effect of impurities con-
tained in unpurified H_2PC.

Fig. 6 Action spectra of
short-circuit photovoltaic
current of $\alpha-H_2PC-PVK$ sand-
wich cells, concentrations
of $\alpha-H_2PC$ are 40(a), 20(b),
15(c),5(d), and 0 wt%(e) :
a,b and c were illiminated
through Au; d and e were
through NESA. The currents
are corrected for transmit-
tance of NESA,Au and inter-
ference filters.

4. Conclusions

The following conclusions can be
drawn on the basis of investigations of
the effect of H_2PC purification on cha-
racteristics of a SA/H_2PC-PVK/Au cell,
the investigation being conducted for
the purpose of developing semiconductor
so...r cells:

(1) Cells formed by dispersing
in a PVK film, $\alpha-H_2PC$, obtained by re-
crystallization from concentrated sul-
furic acid, along with the photovoltaic

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*18
The same phenomenon has been observed when, apart from Au, other
materials such as Ag and In were used as poles.

power, which is opposite in its direction to that in an unpurified H_2PC cell, produce a photoelectric current (the main component of unpurified H_2PC is β-H_2PC). The speed of optical response also is different.

(2) It is suggested that the distinctions of cell characteristics mentioned above stem from differences in specific resistances, which in turn depend on the type of H_2PC crystals. In the case when α-H_2PC of low specific resistance is used, carriers in a film approach holes of H_2PC, and when β-H_2PC is used, they approach holes in PVK. In the last case, H_2PC acts as a sensitizing pigment for PVK.

(3) In order to improve characteristics of cells it is necessary either to reduce resistance of H_2PC or to choose another high molecular binder apart from PVK.

REFERENCES

1) IEEE Spectrum, 17, 26 (1980).
2) A.K. Ghosh, D.L. Morel, T. Feng, R.F. Shaw and C.A. Rowe Jr., *J. Appl. Phys.* 45, 230 (1974).
3) F-R. Fan and L.R. Faulkner, *J. Chem. Phys.* 69, 3334, 3341 (1978).
4) R.O. Loutfy and J.H. Sharp, *J. Chem. Phys.* 71, 1211 (1979).
5) C.W. Tang and A.C. Albrecht, *J. Chem. Phys.* 62, 2139 (1975).
6) V.Y. Merritt, *I.B.M. J. Res. Develop.* 22, 353 (1978).
7) 小門 宏, 電気化学 28, 647 (1960).
8) 志村英知子, 上保賢治, 馬場英夫, 電子デバイス, 新・省エネルギー合同研究会資料, p. 37 (1981).
9) A.A. Ebert, Jr. and H.B. Gottlieb, *J. Amer. Chem. Soc.* 74, 2806 (1952).
10) F.W. Karasek and J.C. Decius, *J. Amer. Chem. Soc.* 74, 4716 (1952).
11) J.F. Byrne and P.F. Kurz, U.S. Patent, No. 3357989 (1967).
12) 志村英知子, 馬場英夫, 電気化学協会秋季大会要旨集, p. 161 (1981).
13) D.R. Kearns, G. Tollin and M. Calvin, *J. Chem. Phys.* 32, 1020 (1960).
14) 志村英知子, 馬場英夫, 未発表.
15) F. Gutmann and L.E. Lyons, "Organic Semiconductors", p. 713~14 (1967), John Wiley and Sons.
16) C.Y. Liang and E.G. Scalco, *J. Electrochem. Soc.* 110, 779 (1963).
17) K. Okamoto, S. Kusabayashi and H. Mikawa, *Bull. Chem. Soc. Japan* 46, 1948, 1953 (1973).
18) M. Ikeda, K. Morimoto, Y. Murakami and H. Sato, *Japan J. Appl. Phys.* 8, 759 (1969).
19) 小門 宏, 岡 裕, 井上英一, 電子写真 12, 30 (1963).

7. Hiroshi Okado. <u>Denki Kagaku</u> (Journal of the Electrochemical Society of Japan), <u>28</u>, 647 (1960).

8. Michiko Shimura et al. <u>Denshi Debaisu</u> (Electronic Devices). New and Economical Kinds of Energy, Materials of Joint Research, p. 37 (1981).

12. Michiko Shimura, et al. Summary of the Autumn Meeting of the Japanese Society of Electrochemical Engineers, p. 161 (1981).

14. Michiko Shimura,et al. (Prepared for Publication).

19. Hiroshi Okado, et al. <u>Denshi Shashin</u> (Electrophotography), <u>12,</u> 30 (1963)