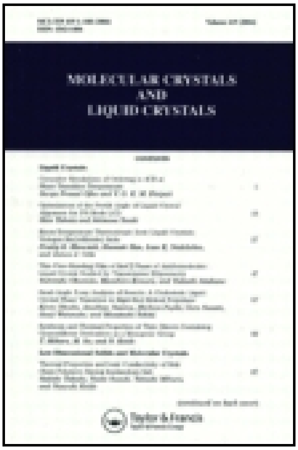

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Photoelectric Effect in Single and Double Layers of Metal-Free and Lead Phthalocyanines Evapolated films

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ABSTRACT Photoelectric properties of evapolated metal-free phthalocyanine (H_2Pc) and lead phthalocyanine (PbPc) films were investigated in the sandwich type cells using three kinds of metal electrodes (Au, Al, Pb). Current-voltage (I-V) characteristics and short circuit photo current (I_{sc}) spectra strongly depended on metal electrodes. It is indicated that a charge separation of photo generated carriers occurred at the interface between H_2Pc and PbPc from I_{sc} spectra of double layered (H_2Pc/PbPc and PbPc/H_2Pc) cells.

INTRODUCTION

Recently optical and electrical properties of phthalocyanine (Pc) derivatives have intensively been investigated because of their high stability and various new functions. The various properties of Pcs come from different metal ions in the center of the molecules, and various crystallographic phases of the Pcs films. Lead phthalocyanine (PbPc) has been expected to be a one-dimensional electronic conductor because non-planar molecules of PbPc, that is called a shuttle cock shape, co-facially stack to form a molecular column parallel to the c axis in a monoclinic form [1,2]. The electrical conductivity of PbPc has also been known to be sensitive to atmosphere or adsorbed gases. Dark conductivity is strongly influenced by adsorbed gases such as thermally diffused oxygen [3,4] and NO_2 [5] molecules. Rectifying properties of an Al/PbPc/Au structure are quite different for air and vacuum atmospheres [6].

Au/PbPc/Au sandwich type cells have shown an electrical switching phenomenon [7,8]. For this switching phenomenon, PbPc/Au electrode interfaces probably have strong contribution. For asymmetric barriers in symmetric structure, movements of lead metal ions and other impurities and so on have been suggested. For analysis of the interfaces, photoelectric properties are studied. A layered structure using "metal-free" phthalocyanine (H_2Pc) is substantial to investigate which interface, upper or lower one, contributes to the electrical switching phenomenon.

In this paper, we report photoelectric effects in metal 1/Pcs/metal 2 cells with single and double layered Pcs structures. We studied I_{sc} spectra and I-V characteristics and compared I_{sc} spectra with optical absorption spectra of Pcs thin films.

EXPERIMENTAL

Figure 1 shows chemical structures of PbPc and H_2Pc molecules, used material of PbPc was purified by repeated vacuum sublimations. PbPc and H_2Pc were deposited onto precleaned glass substrates by thermal evaporation in high-vacuum evaporater at pressures around 10^{-5} Torr. Three kinds of organic layers, PbPc single and two kinds of double layers (H_2Pc/PbPc and PbPc/H_2Pc), were fabricated without breaking the vacuum.

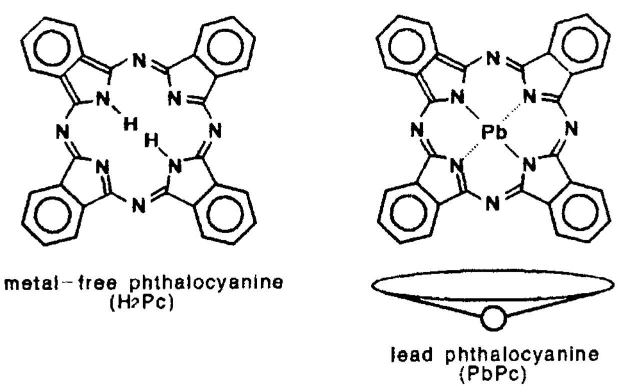

Figure 1. Chemical structure of H_2Pc and PbPc molecules used in this study. A PbPc molecule has the shuttle cock shape.

The sandwich type cells of glass/metal 1/organic layer/metal 2 configurations were prepared through three kinds of metals (gold, aluminum and lead) evaporation as the electrodes. All combinations of metal 1, 2 were examined in the cells as shown in Figure 2. In all cells the metal 1 is the bottom electrode as shown in Figure 2.

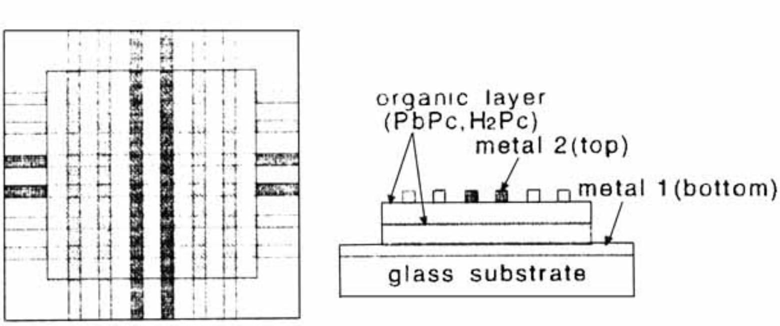

Figure 2. Schematic diagram of the glass/metal 1/Pcs layer/ metal 2 cell used in this study.

The temperatures of crucibles were controlled at 430 to 480 °C for PbPc, and 420 to 460 °C for H_2Pc respectively. The PbPc films were about 1 μm thick, and the H_2Pc films were about 0.5 μm thick respectively.

The optical absorption spectra of the films were measured with a Hitachi U-2000 spectrophotometer. I_{sc} spectra were measured by irradiation of Xenon light source with diffraction grating monochromator through the top or bottom electrodes. Those spectra were compared with the optical absorption spectra of both Pcs films.

In I-V measurements of the sandwich type cells, the top electrode (metal 2) was grounded and the voltage was applied to the bottom electrode (metal 1). In the circuit, a 20 kΩ load resister was connected as a series resistance.

RESULTS AND DISCUSSION

The dependence of I-V characteristics and I_{sc} spectra on metal electrodes is summerized in table 1. This table shows I-V characteristics and degrees of agreement between I_{sc} spectra and optical absorption spectra. For example, I-V characteristics of a glass/Au/PbPc/Au cell show ohmic properties in whole measurement voltage range. Thus 'Linear' is used in the table. It is well known that a thin film of phthalocyanine derivatives behaves like a p-type semiconductor at room temperature. Then, at the interface of Pcs/Al or Pb, a potential barrier is formed. As I-V characteristics of those cells showed rectifying properties, 'Block' is used in this table. This barrier is attributable to a charge separation of photo generated carriers.

Table 1 : Dependence of I−V and I_{sc} on metal electrodes. In column "I_{sc}", degrees of agreement between I_{sc} spectra and the optical absorption spectra of Pcs are expressed by marks (◎○△▲×).
◎ : In good agreement.
○ : Almost agree.
△ : Intensity ratio of peaks is differnt.
▲ : Pcs layers behave like an optical filter.
× : Disagree.

	PbPc		PbPc/H2Pc		H2Pc/PbPc	
	I−V	I_{sc}	I−V	I_{sc}	I−V	I_{sc}
Au/Au	Linear	——	Non−Line	×	Non−Line	×
Au/Al	Block	◎	Block	◎	Block	◎
Au/Pb	Block	△	Block	△	Block	△
Al/Al	Block	▲	Block	▲	Block	▲
Al/Au	Block	◎	Block	◎	Block	◎
Al/Pb	Block	△	Block	▲	Block	▲
Pb/Pb	Block	△	Block	△	Block	△
Pb/Au	Block	△	Block	△	Block	△
Pb/Al	Block	△	Block	○	Block	○

Using Al or Pb as the top and bottom electrodes, the potential barriers are formed at both Pcs/metal interfaces. Thus I_{sc} spectra partly coincide with the absorption spectra. Using Au as the top or bottom electrode, I_{sc} properties correspond to the optical absorption of Pcs.

Figure 3 shows optical absorption spectra of PbPc and H_2Pc thin films. Figure 4 shows I_{sc} spectra of a glass/Au/PbPc/Al cell. The curve (A) in Figure 4 shows the I_{sc} spectrum in which the light was incident through the top Al electrode and the curve (B) shows that through the bottom Au electrode. The curve (A) is in good agreement with the optical absorption spectrum of PbPc film in Figure 3. However, the curve (B) does not coincide with the optical absorption. Where the optical absorption is at a minimum, the photocurrent is at a maximum. This tendency can be explained as follows [9]. First, the light irradiated through the Au electrodes generates excitons in organic layer. Then only those excitons that diffuse to the PbPc/Al interface results in free carriers. When the absorption constant is higher, the excitons will be generated very close to the Au electrode. Therefore, fewer numbers of excitons will reach the PbPc/Al interface. As a consequence, the I_{sc} will be less. However, if the absorption constant is lower, the excitons are generated much closer to the PbPc/Al interface and a correspondingly larger photocurrent is measured. Consequently the organic layer behaves like an optical filter. A potential barrier exists at the PbPc/Al interface of the glass/Au/PbPc/Al cell, so the I_{sc} spectrum irradiated through the top Al electrode corresponds to the optical absorption.

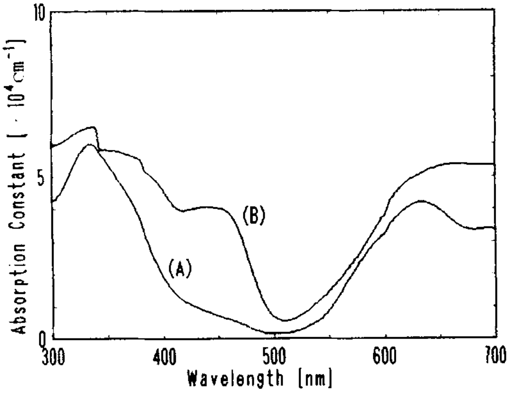

Figure 3. Optical absorption spectra of H_2Pc and PbPc thin films. Curves (A) and (B) show the spectra of H_2Pc and PbPc respectively.

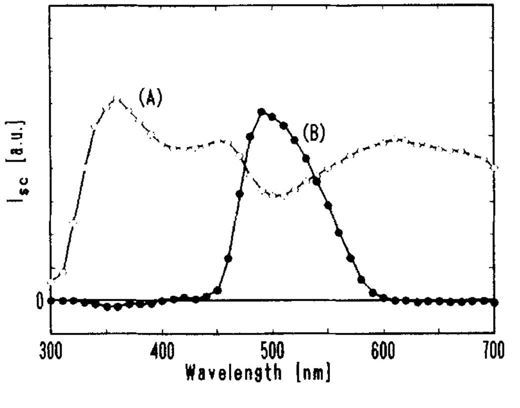

Figure 4. I_{sc} spectra of a glass/Au/PbPc/Al cell. Curves (A) and (B) show spectra of the cell irradiated through the top Al electrode and the bottom Au electrode respectively.

I_{sc} spectra of double layered cells using Au as the top and bottom electrodes show different spectra from Figure 4. Neither ohmic property nor rectifying property was shown in I-V characteristics. Figure 5 shows I_{sc} spectra of a glass/Au/H_2Pc/PbPc/Au double layered cell.

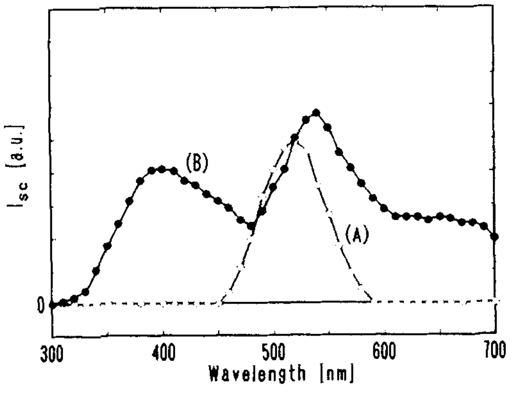

Figure 5. I_{sc} spectra of a glass/Au/PbPc/H_2Pc/Au cell. Curves (A) and (B) show spectra of the cell irradiated through the top and the bottom Au electrodes respectively.

As can be seen by comparing them with the optical absorption spectra shown in Figure 3, both I_{sc} spectra irradiated through the top (curve (A)) and bottom (curve (B)) electrodes are out of phase. Especially curve (B) has two peaks at different wavelength from the absorption spectra. I_{sc} spectrum of a glass/Au/PbPc/H_2Pc/Au cell irradiated through the top Au electrode also shows almost same result. Further, it is probable that Pcs/Au interfaces make ohmic contact, because electrical resistance of Au/PbPc/Au cells is relatively low to other cells using Al or Pb electrodes, and most of I_{sc} spectra irradiated through Au electrode show the optical filter effects. In other words, the Pcs/Au interface does not make a potential barrier that is attributable to the charge separation. From these results, it is suggested that the charge separation of photo generated carriers are occurred at the organic-organic (H_2Pc/PbPc) interface.

To verify that the charge separation occurred at the organic-organic interface, we calculated photocurrent spectrum from amount of the absorbed light. This absorbed light was calculated from incident light intensity, film thickness and absorption constant. Figure 6 shows the calculated I_{sc} spectrum of H_2Pc/PbPc double layers. A new peak appears at 460 nm in the calculated spectrum results from incident light peak. As can be seen by comparing it with the curve (B) shown in Figure 5, the curves correspond each other in whole range of wavelength, but peaks slightly shift from the experimental results. These disagreements are probably caused by insufficiency of parameters, such as charge transport efficiency, charge separation efficiency, absorption of Au electrode, etc.

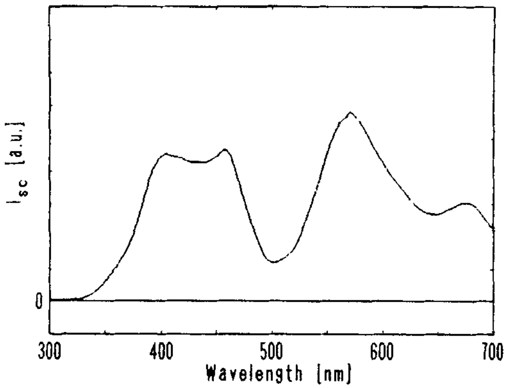

Figure 6. I_{sc} spectrum of the H_2Pc/PbPc double layer calculated from the amount of absorbed light. Assuming that the light is irradiated from the H_2Pc side.

CONCLUSION

We investigated photoelectric properties of single and double layered Pcs evapolated films using various combinations of metal electrodes. From I-V and I_{sc} measurements, it is shown that potential barriers at the Pcs/metal (Al or Pb) interfaces were made. We found that I_{sc} spectra of H_2Pc and PbPc double layered cells sandwiched by Au electrodes do not coincide with absorption spectra of Pcs. As the Pcs/Au interfaces do not make potential barriers attributable to the charge separation, the existence of a potential barrier at the organic-organic (H_2Pc/PbPc) interface was suggested. The calculation of the I_{sc} spectrum also supported the charge separation of photo generated carriers occurred at the organic-organic interface.

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