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Photoelectric Cells of Organic Dye Thin Films Utilizing Surface Plasmon Excitations

Keizo Kato[1,2], Masaru Hirano[3], Futoshi Takahashi[3], Kazunari Shinbo[1,2], Futao Kaneko[1,2] and Takashi Wakamatsu[4]
[1]Department of Electrical and Electronic Engineering, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan
Fax: +81-25-262-6724, e-mail: keikato@eng.niigata-u.ac.jp
[2]Center for Transdisciplinary Research, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan
[3]Graduate School of Science and Technology, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan
[4]Department of Electrical Engineering, Ibaraki National College of Technology, 866 Nakane, Hitachinaka 312-8508, Japan

Short-circuit photocurrent (I_{SC}) due to surface plasmon (SP) excitation has been investigated for the photoelectric cells using copper phtalocyanine (CuPc). The CuPc molecule exhibits p-type conduction, and the Schottky and Ohmic contacts are obtained at the interfaces between CuPc and Al thin films and between CuPc and Ag thin films, respectively. Since the Schottky diodes show the photoelectric effects, the Schottky photoelectric cells have been constructed. The cells had a prism/Al/CuPc/Ag structure of the Kretschmann configuration in the attenuated total reflection (ATR) method. SP has been resonantly excited at the interface between Ag and air. The ATR and the I_{SC} properties have been simultaneously measured as a function of the incident angles of the laser beams. The peaks of the I_{SC} have corresponded to the resonant angles of the ATR curves. The electric fields and optical absorptions in the cells have been also calculated using the complex dielectric constants and the film thicknesses obtained from the ATR measurements. The calculated absorptions in the CuPc thin film as a function of the incident angles have corresponded to the results of I_{SC}. It has been estimated that the I_{SC} could be enhanced by the excitations of SP in the ATR configuration.

Keywords: photoelectric cell, organic dye, copper phtalocyanine, surface plasmon excitation, Kretschmann configuration, attenuated total reflection, short-circuit photocurrent

1. INTRODUCTION

Recently, organic thin films have been attracting much attention for their variety of functions, such as gas sensing, non-liner optics, luminescence, photoelectric effect. Various studies on the organic thin films have been carried out so far [1,2]. Several studies of the organic photoelectric devices have been reported [3]. For the conventional photoelectric devices, high efficiency has not been obtained because of light transmission through organic thin layers, light reflection at the metal electrodes in the cells and so on. In the attenuated total reflection (ATR) configuration utilizing the surface plasmon (SP) excitation [4-8], remarkably strong optical absorption is expected for organic dye ultrathin films in photoelectric cells [9-11]. For the development of photoelectric devices with high efficiency, it is important to evaluate the structure and the optical and electrical properties of the devices.

The ATR method is one of useful measurements of evaluating ultrathin films. The SP resonance properties, that is, ATR curves are measured as a function of the incident angle at a constant wavelength, utilizing the SP resonantly excited at the interface between metal and dielectrics in a configuration of dielectric ultrathin films on metal thin films [4-8]. The complex dielectric constants and/or the thickness of the ultrathin films on the metal thin films can be obtained in high accuracy from the ATR curves. In the ATR method, the SP are resonantly excited on surface of metal electrodes by the incident light, and evanescent fields, that is, strong electromagnetic fields, are induced and localized at the surface. In addition to that, strong absorption of the incident light can be observed in the sample during the SP excitation. It is expected that strong photoelectric effects will occur due to the strong absorption.

In this paper, short-circuit photocurrents (I_{SC}) due to SP excitation have been investigated for the photoelectric cells using copper phtalocyanine (CuPc). The CuPc exhibits p-type conduction, and the Schottky diode has been constructed. The ATR and the I_{SC} properties have been investigated.

2. EXPERIMENTAL

The chemical structure of CuPc used in this work is shown in Fig. 1. The CuPc exhibits p-type conduction, and the Schottky and Ohmic contacts are obtained at the interfaces between CuPc and Al thin films and between CuPc and Ag thin films, respectively. Since the Schottky diodes show the photoelectric effects, the Schottky photoelectric cells have been constructed.

Figure 2 shows the structure of the photoelectric cells fabricated in this work. The cells had a prism/Al/CuPc/Ag structure of the Kretschmann configuration [4] in the ATR method. The depositions of all the films were carried out using a vacuum evaporation method under a pressure of 5.0×10^{-6} Torr. The Al thin film (thickness: about 30 nm) was evaporated onto a cover glass as the lower electrode at first. Then, the CuPc film (thickness: about 35 nm) was deposited. Finally, the Ag thin film (thickness: about 45 nm) was evaporated as the upper electrode. The effective junction area of the cell was about 0.13 cm^2. The cover glass was brought into optical contact with a half-cylindrical glass prism using an index matching fluid. Both the cover glass and the prism were made of BK-7 glass. In the ATR measurements, SP was resonantly excited at the interface between Ag and air.

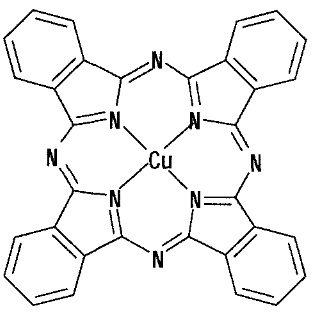

Fig. 1. Structure of copper phtalocyanine (CuPc) dye used in this work.

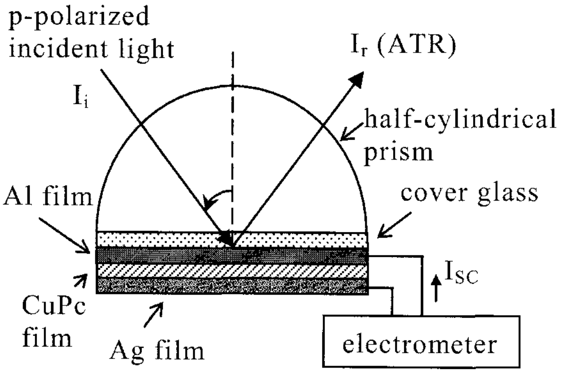

Fig. 2. Structure of the photoelectric cells fabricated in this work and arrangement for ATR and I_{SC} measurements based on the Kretschmann configuration.

The ATR properties and the short-circuit photocurrent (I_{SC}) in the photoelectric cells were measured simultaneously. Using He-Ne lasers with the wavelengths at 594.1 nm and 632.8 nm, p-polarized laser beams were directed onto the back surface of the cell through the prism. The cell on the prism was mounted on a rotating stage and the incident angle θ_i of the laser beams was scanned using a pulse motor. In the ATR measurements, the intensities I_i of the incident beams were monitored by a photodiode. The reflected intensities I_r of the beams, that is, the ATR curves were detected at an interval of 0.01° as a function of the incident angle θ_i using another photodiode. In the I_{SC} measurements, the currents were measured using an electrometer. The current I_{SC} was observed in the direction shown in Fig. 2.

3. RESULTS AND DISCUSSION

Figure 3 shows the optical absorption spectrum of the CuPc thin film with the thickness of about 35 nm evaporated on a glass substrate. It is known that the absorption peak of the isolated monomer state is located around 670 nm [12]. The CuPC film has a strong optical absorption at about 630 nm. The shift of the absorption peak to 630 nm indicates that the CuPc molecules form typical α-type microcrystals [13] in the film. The laser beams of 632.8 nm near the absorption peak and 594.1 nm were used in this measurement.

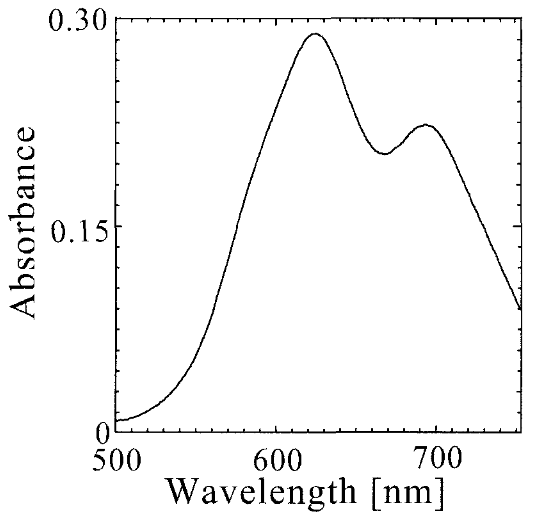

Fig. 3. Optical absorption spectrum of the CuPc thin film evaporated on a glass substrate.

Figures 4(a) and 4(b) show the ATR properties of the photoelectric cells measured at 594.1 nm and 632.8 nm, respectively. For the ATR curve at 594.1 nm, a small dip was observed at 43.5° due to the SP excitation at the Ag/air interface. On the contrary, for the ATR curve at 632.8 nm, a small dip was observed at 43.5° due to the SP excitation at the Ag/air interface and a large dip was also observed at around 75°. The theoretical ATR curves were calculated and are also shown in Figs. 4(a) and 4(b). It is found that the calculated curves agree well with the experimental results. Both the calculated ATR curves at 594.1 nm and 632.8 nm had small dips at 43.5° due to SP excitation and large dips at around 75°.

In order to investigate the effect of the SP excitation, the electric field amplitudes in the cells were calculated using a transfer matrix method [14-16]. The thicknesses and complex dielectric constants of Al, Al_2O_3, CuPc and Ag thin films were obtained from the theoretical ATR curves in Figs. 4(a) and 4(b) and were used for the calculation. The results are exhibited in Figs. 5(a) and 5(b) as a function of the distance from the interface between the prism and Al thin film for the beams at 594.1 nm and at 632.8 nm, respectively. The calculations were carried out for the electric field amplitudes at the incident angles of 0°, 43.5°, 50° 60°

and 70°. It is found that the electric field at 43.5° is strong at the Ag/air interface and that the electric field in the CuPc thin film with the SP excitation is much stronger than those without the SP excitation.

The I_{SC} curves in the photoelectric cells measured at 594.1 nm and 632.8 nm are shown as a function of the incident angle in Figs. 6(a) and 6(b). The I_{SC} pofiles in Figs. 6(a) and 6(b) almost correspond to the ATR curves in Fig. 4(a) and 4(b), respectively. In the I_{SC} curves measured at 594.1 nm and 632.8 nm, the sharp peaks are observed at 43.5° and are considered to be due to the SP excitation at the Ag/air interface. From the results, it is estimated that the SP excitation caused the I_{SC} in the cell. The peaks of the I_{SC} at the resonant incident angles may be caused by some enhancement of optical absorptions in the cells or photoemissions [16] from the metal electrodes due to the SP excitations. The I_{SC} at 632.8 nm is much larger than that at 594.1 nm and this is related to the optical absorption of CuPc thin film shown in Fig. 3.

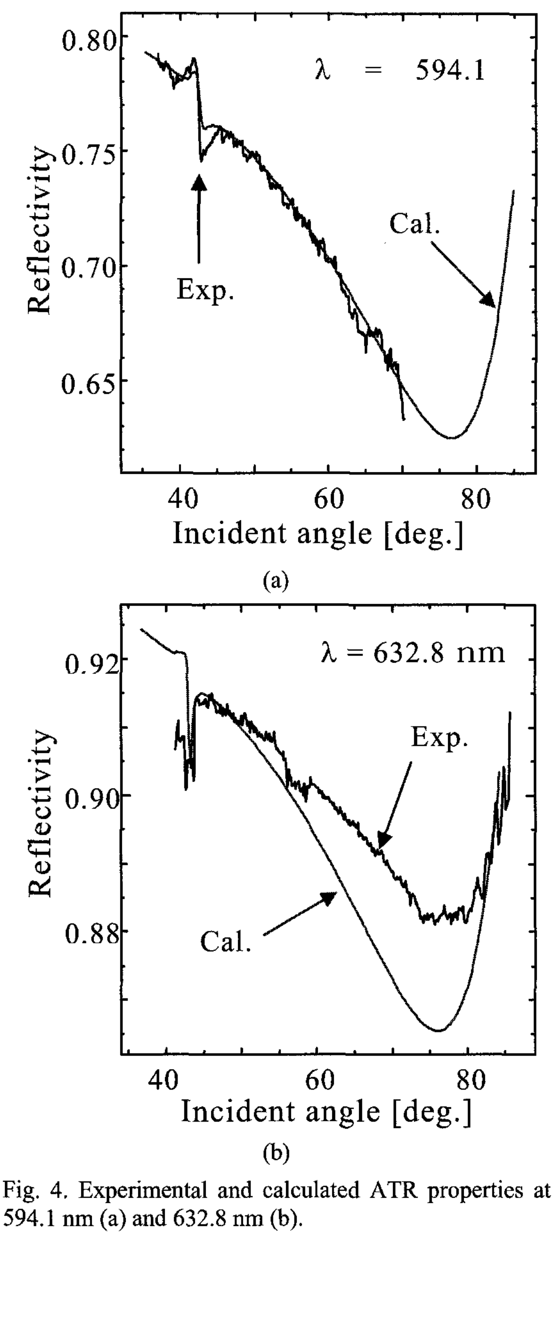

Fig. 4. Experimental and calculated ATR properties at 594.1 nm (a) and 632.8 nm (b).

To investigate the peaks of I_{SC} at the resonant incident angle, the optical absorption in the photoelectric cells was also calculated using a transfer matrix method [14-16]. The calculated total absorptions as a function of the incident angle in the CuPc thin films of the cells are also shown in Figs. 6(a) and 6(b). The calculated profiles for 594.1 nm and 632.8 nm almost correspond to the I_{SC} curves. From the results, it was estimated that the absorption due to the SP excitation in the CuPc thin film dominated the I_{SC}. Figure 7 shows the same absorptions in the CuPc layer as those in Figs. 6(a) and 6(b). From Fig. 7, it is found that the absorption in the CuPc layer for 632.8 nm is much larger than that for 594.1 nm.

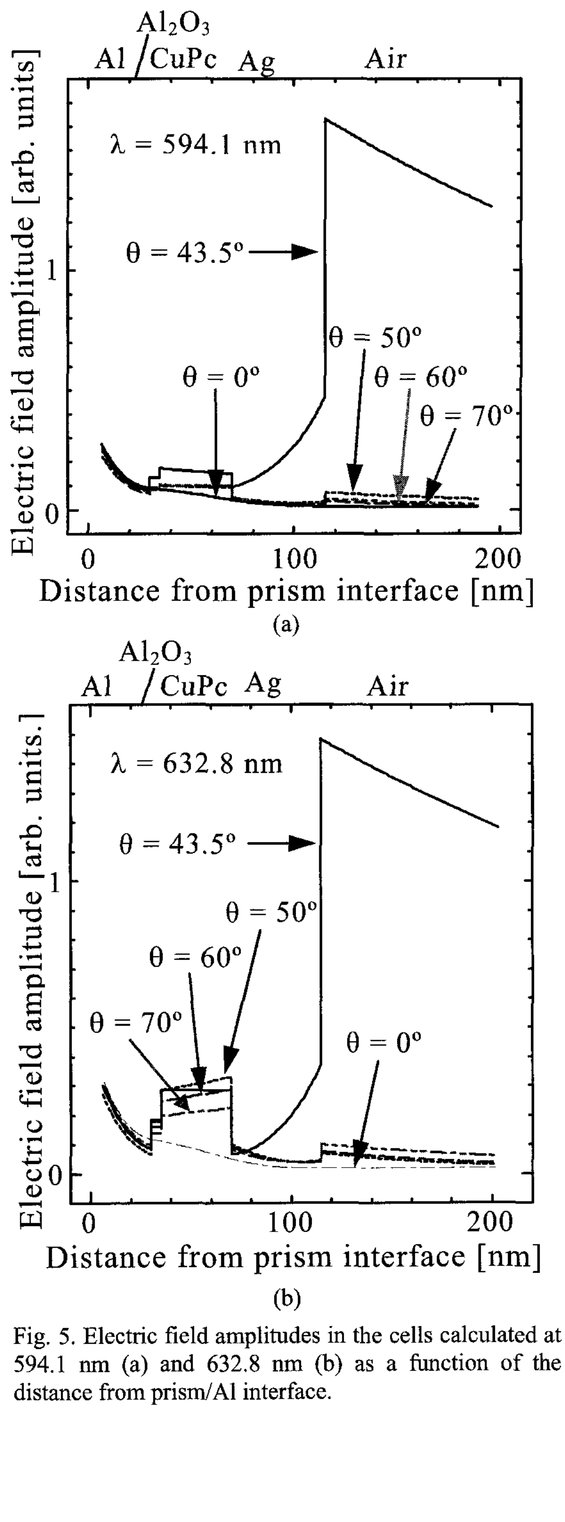

Fig. 5. Electric field amplitudes in the cells calculated at 594.1 nm (a) and 632.8 nm (b) as a function of the distance from prism/Al interface.

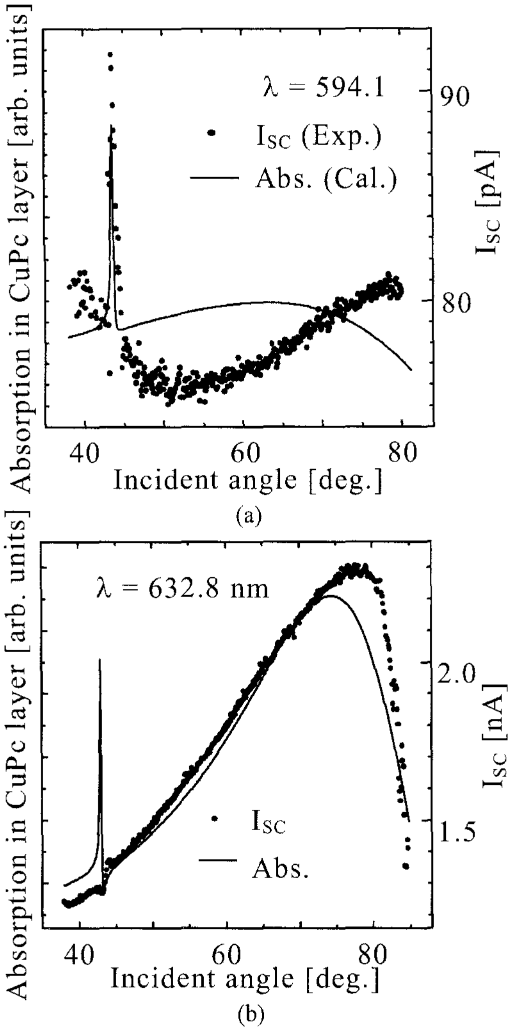

Fig. 6. Experiemtal results of I_{SC} and calculated optical absorptions in the CuPc layer at 594.1 nm (a) and 632.8 nm (b) as a function of the incident angle.

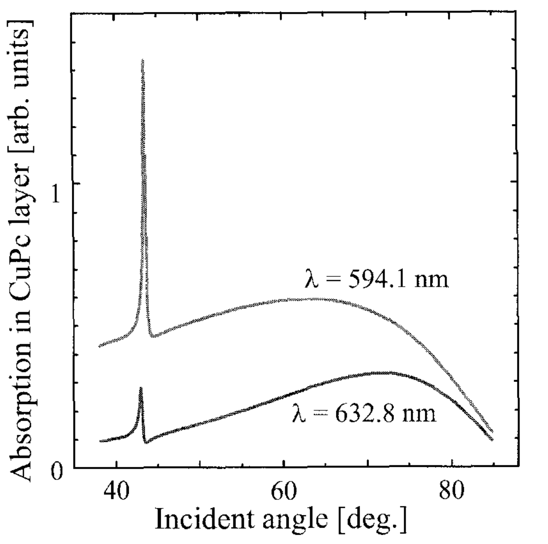

Fig. 7. Calculated optical absorptions in the CuPc layer at 594.1nm and 632.8 nm which are the same as those in Figs. 6(a) and 6(b).

4. CONCLUSIONS

The CuPc photoelectric cells in the ATR configuration were investigated. The I_{SC} profiles as a function of the incident angle corresponded to the ATR curves in the cells. The electric fields and optical absorptions in the cell were calculated. It was estimated that the I_{SC} was caused by the strong optical absorptions in the cells related to the SP excitation. It is expected that the I_{SC} can be enhanced utilizing the SP excitations. This is a great advantage for developing solar cell, sensing device, light switch and so on.

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