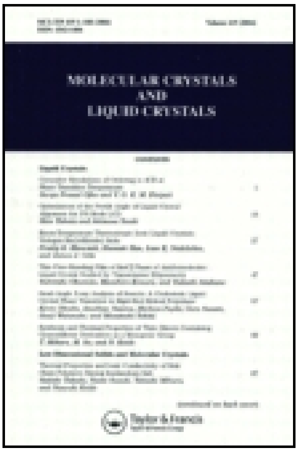

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Photovoltaic Effects in Polymer Thin Films

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Photovoltaic Effects in Polymer Thin Films

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Electroactive polymers such as conducting polymers, ferroelectric polymers and natural proteins show photovoltaic effects when used in the ultrathin film state. The junction type, the internal field type and/or the proton pump type photovoltaic cells have been prepared by using those polymer thin films in our laboratory and the results are reviewed.

INTRODUCTION

In the physics of photovoltaics in materials, the following two steps are required: (1) the carrier generation by photoexcitation and the carrier separation without applying field, that is, the spontaneous electron-hole separation or the liberation of ionic carriers, and (2) their movement in the opposite direction or the spontaneous proton transfer. Therefore in order to get photovoltaic effects in polymers we should design the polymer structure as semiconductors (the small band gap and the wide band width) and/or select native proteins which have a function of "proton pump" such as bacteriorhodopsin.[1]

According to the band theory of semiconductors, electrons in the valence band or in the local levels can be excited to the conduction band under the illumination of light whose energy is larger than the band gap and/or activation energies. (The same process is considered for holes.) These photogenerated carriers move along the applied field because of the band inclination, which is called "photoconduction." In the case of "photovoltaics," they must move spontaneously in the materials, and hence it is required to form a band inclination without applying external electric field. There are a couple of techniques to accomplish this requirement; i.e., (1) the junction type structures such as *p-n* junction and Schottky barrier, and (2) the internal field type structure formed in ferroelectric materials.[2,3]

A completely different mechanism to create electrical potential under the photoexcitation is introduced from the living systems, that is, the active transport of protons in biomembrane and/or proteins.

In this paper we will review our works on photovoltaics and show examples of these three mechanisms observed in polymer thin films: a *p-n* junction formed in conducting polymers[4] and a Schottky barrier formed in hetero-structure of the metal/polymer/metal sandwiched cell,[5] the anomalous photovoltaic effect in ferroelectric polymers[6] such as polyvinylidene fluoride and copoly(vinylidene/trifluoroethylene), and the purple membrane[7] which is composed of bacteriorhodopsin (bR) and lipids.

EXPERIMENTAL

Sample preparation

p-n junction. Many kinds of conducting polymers (*e.g.*, polyacetylene, poly-p-phenylene etc.) can be doped with donors and/or acceptors to form *n*- and/or *p*-type semiconductors. The usual doping technique such as chemical or electrochemical doping is based on the diffusion process of dopant molecules, and hence the dopants distribute in the film in an exponential fashion from the surface of film. This means that the surface is the most active region. In case of an ion implantation, on the other hand, the distribution of implanted atoms is Gaussian[8] and the most active region lies inside of the material, which depends on the ion species, acceleration energy of ions and the density of matrix material. Therefore the implanted region can be protected from the attack of oxygen or humidity.[9]

We used the ion implantation technique to get a stable *p-n* junction of polyacetylene (CH)x, that is, the electron donating sodium ions were implanted into the *p*-type (CH)x film.[4] Figure 1 shows an example of the depth profile of sodium atoms implanted into high density (CH)x film at 150 keV and the fluence of 10^{17} ions/cm^2, which was determined by means of SIMS (secondary ion mass spectroscopy).[9] The high density (CH)x film was prepared by the hot press of (CH)x gel. The density of the film was ca. 1.0 g/cm^3. The pristine (CH)x film was slightly doped with iodine by the chemical technique

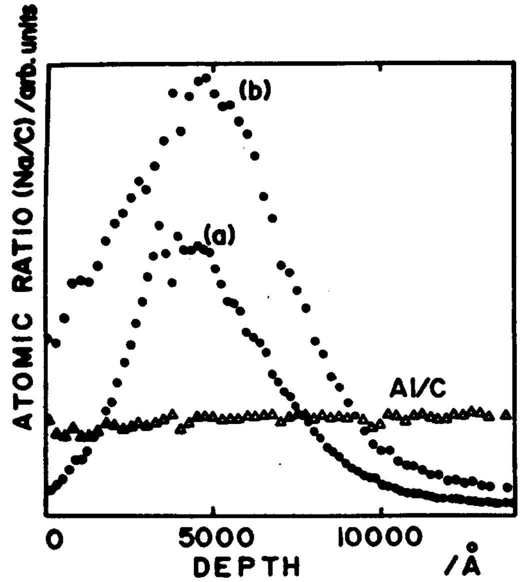

FIGURE 1 Depth profile of implanted Na atoms in high density (CH)x film at 150 keV. The fluence is (a) 1 × 10^{16} ions/cm^2 and (b) 1 × 10^{17} ions/cm^2, respectively. Al atoms (residual catalyst) distribute uniformly in the film.

to make a *p*-type semiconductor (conductivity is ca. 3.8 × 10^{-2} S/cm).

Schottky Barrier Type MIM Cell. In general the thickness of depletion layer formed at the interface of metal/insulator is less than 100 Å, hence it is required to prepare an ultrathin film of polymers as the insulator layer of which thickness is desirably less than 200 Å. There are a variety of techniques to make a polymeric ultrathin film as shown in Table I.[10] In our laboratory we applied several techniques as indicated with asterisks in Table I.

In the case of vacuum deposition of polymers the vacuum system shown in Figure 2 was used.[5] Powders of polymer were put in Mo boat and heated up to 10 degrees higher than the melting point under the vacuum of 10^{-5} Torr. The substrate was a metal-deposited glass and/or ITO (indium-tin-oxide) glass, and its temperature was controlled around 30 degrees lower than the melting point. We obtained quite good polymer crystals of polyethylene (PE), poly-p-phenylene sulfide (PPS), polyvinylidene fluoride (PVDF) and so forth, whose c-axis is almost perpendicular to the substrate.[11] The thickness of the polymer film can be easily controlled by the deposition rate and time

TABLE I

Methods for polymeric ultrathin film preparation.

During polymerization	After polymerization
Catalyst coating	Adsorption technique
	Gas phase
Polymerizable LB techniques*	Liquid phase
	Monolayers (LB)*
	Co-Drawing
Electrochemical polymerization*	Vacuum evaporation (PVD)
	Thermal evaporation*
	Molecular beam epitaxy (MBE)*
	Ionized cluster beam (ICB)
Chemical vapor deposition (CVD)	Sputtering
Thermal CVD	DC, AC Sputtering*
Laser CVD	Magnetron sputtering
Plasma CVD*	Ion Beam sputtering*

in the range from 100 Å to several 1000 Å. The counter electrode was also deposited *in vacuo* semitransparently. Several kinds of metals with different work function such as aluminum, copper, gold, silver, indium and so forth were used as materials for heteroelectrode.

The conventional RF sputtering equipment (ANELVA SPF-210A) was also used for the preparation of MIM cell. Bulk or powders of polymer were set on the target electrode and sputtered by Ar^+ under the vacuum of 10^{-3} Torr onto the substrate at a certain temperature.[12] In order to eliminate pin-holes, the sputtered film was annealed at about 30 degrees below the melting temperature *in vacuo*. The film thickness was controlled by the gas flow rate, sputtering power and time. Usually the sputtered film is highly crosslinked and hardly dissolved in any organic solvents. Once, however, we determine the sputtering conditions, then the reproducibility of film is quite good. Polymers used were PPS, PVDF, PE, polyvinylcarbazole (PVK) and polycarbonate (PC).

Internal Field-type Cell. As a ferroelectric polymer we used a poled PVDF film which was supplied by KUREHA Chemical Industries. Gold electrodes were deposited on both sides of the film, one side thick and the other side semitransparent. The internal electric field E_s caused by a spontaneous polarization of poled PVDF is estimated as 4.3 MV/cm.[6] Another cell was formed by the sputtering of PVDF powders as mentioned above.[12] In this case the dipole orientation of polymer chain was not so complete as the bulk poled PVDF film,

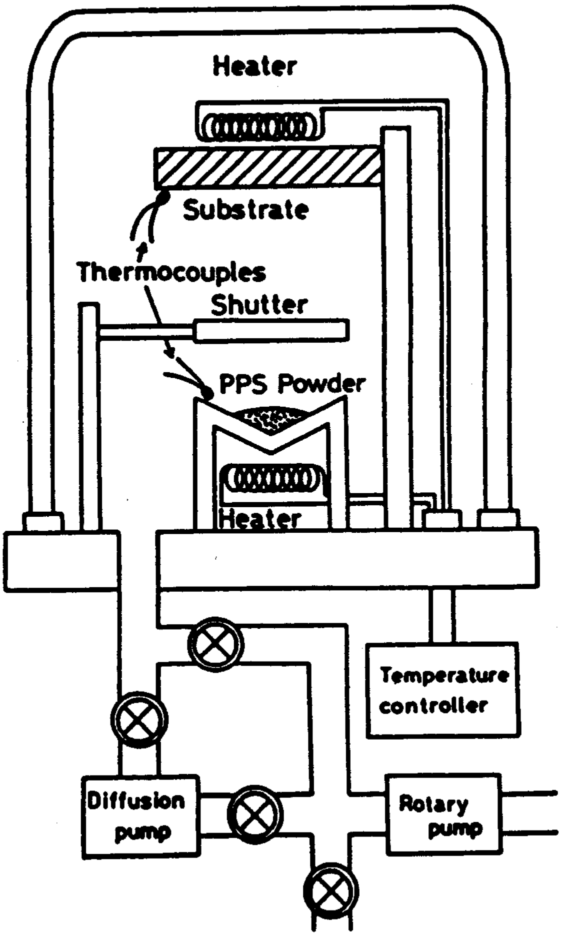

FIGURE 2 The vacuum deposition aparatus for polymeric powders. After Misoh *et al.*[5]

but the dipoles might be partly aligned due to the dc bias applied during the sputtering.

The macroscopic mixture of PZT fine powders and PVK was also examined as a model compound for the internal field-type cell. The finely ground PZT powders (diameter ca. 10 microns) were dispersed into the dense solution of PVK-chlorobenzene up to the PZT:PVK ratio of 1:2.5 in weight, and then the film was formed on the glass substrate by means of solvent casting. The thickness of the free stand-

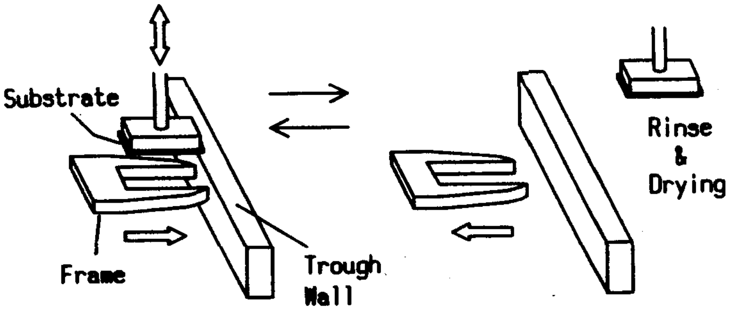

FIGURE 3 Schematic representation of horizontal transfer technique for Langmuir-Blodgett films.

ing film ranges from 50 to 100 microns. After depositing Au electrodes on both sides of the film, we poled the film at 200°C and 6 MV/cm.

Purple Membrane LB Films. The purple membrane (PM) of *Halo bacterium halobium* is a simple system for conversion of light energy into pH gradient across the cell membrane.[1] The single protein, bacteriorhodopsin (bR), which exists as two dimensional crystal in PM[13] translocates protons upon illumination with light. To obtain an ultrathin film of PM the Langmuir-Blodgett technique was used.[7] We spread the suspension of PM fragments in dimethylformamide of 25% concentration on the surface of a subphase containing 0.2–0.4 mM $CaCl_2$, then after one hour started the compression to form a monolayer and deposited it on a substrate at 15–20 dyn/cm by the horizontal transfer technique as shown in Figure 3. After every transfer of a layer the film was rinsed with pure water and dried under streaming nitrogen gas.

The building up of films was checked by transfer ratio and optical density measurements. The morphology of the PM interface film transferred onto a chip of silicon wafer was investigated by a scanning electron microscope (HITACHI S-900). The samples for photoelectric measurements were prepared onto ITO or Al electrodes. The counter Al electrode was deposited *in vacuo*.

Photovoltaic measurement

A photocurrent I_{ph} across the MIM type sandwiched cell can be observed under the light excitation through the transparent electrode when the external electric field is applied. If the external field is absent, on the other hand, a short circuited photovoltaic current I_{pv}

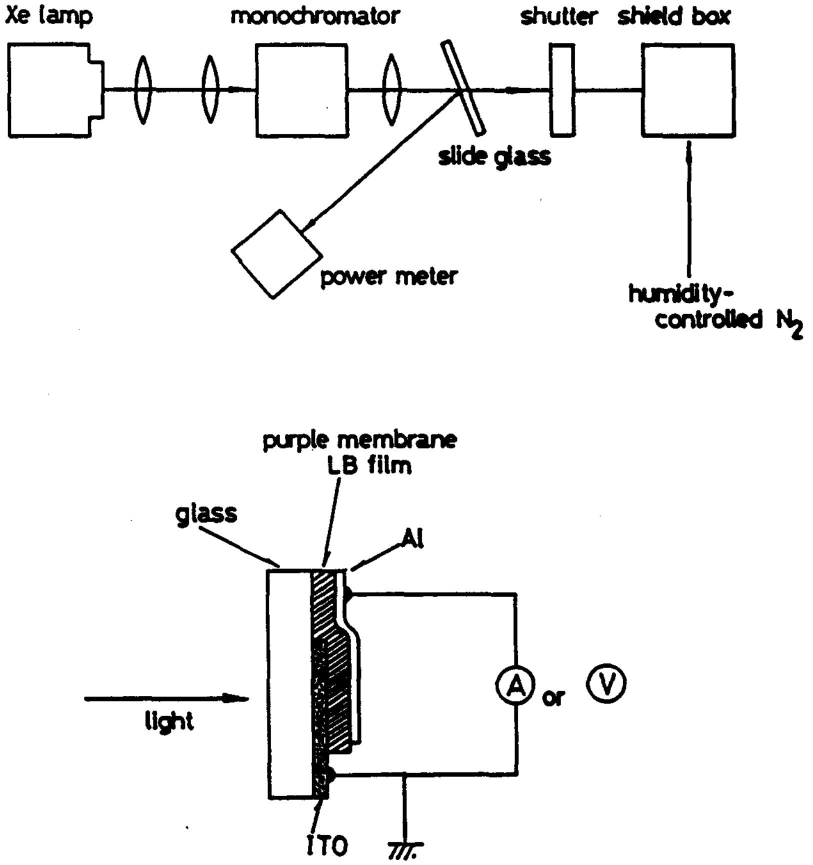

FIGURE 4 Schematic diagram of photovoltaic measuring system for purple membranes and the structure of ITO/PM/Al cell.

can be observed in the same geometry. The same measuring system reported in the previous paper[6] was mostly used for the Schottky barrier type and the internal field type cells. Another type of measuring system was designed for the purple membrane cell as shown in Figure 4. The sample chamber was filled with humidity-controlled nitrogen gas, and the specimen was equilibrated longer than half a day before measurement. Light induced absorption changes of PM LB film were measured with a crossed-illumination spectrophotometer capable of measuring absorption spectra in the presence of actinic light.

RESULTS AND DISCUSSION

p-n Junction

Several research groups have observed[14–17] the rectifying properties and photovoltaic effect in the *p-n* junction of n-Si/p-(CH)x. For example Shirakawa *et al*[14] developed a solar cell of this type and obtained the open circuit voltage V_{oc} = 0.445 V, short circuit current I_{sc} = 9.70 mA/cm^2 and conversion efficiency of 2.51% under the illumination of AM1 (input power P_{in} of 72.37 mW/cm^2). However the photovoltaic effect owed strongly to n-Si, not to p-(CH)x. No all polymer and stable *p-n* junction, *e.g.*, n-(CH)x/p-(CH)x, has been succeeded so far. Wachi *et al.*[8] observed a rectification in the I-V curve of Na/K doped (CH)x and I_2 doped (CH)x junction, but it disappeared quickly, say in two hours, due to the compensation effect of dopants. On the other hand, the *p-n* junction formed by Na$^+$ implantation to p-(CH)x has a beautiful rectifying property as shown in Figure 5 and has been stable in the open air for more than two months.[4,9]

We tried to illuminate the junction with Xe lamp (500 W), but

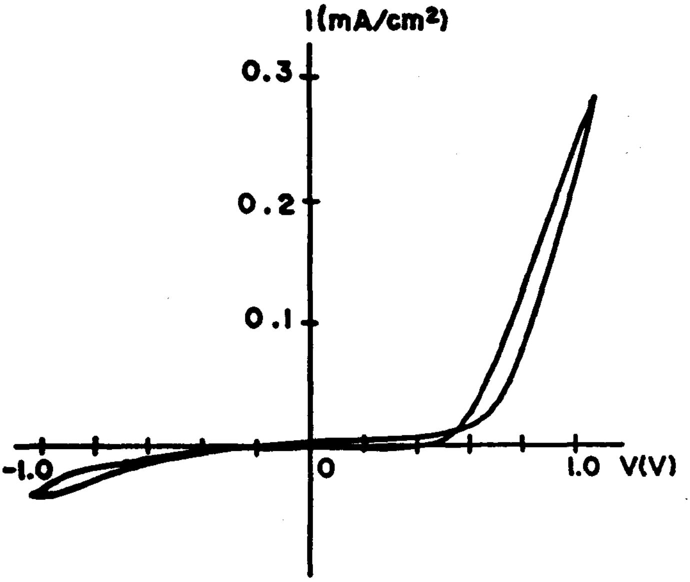

FIGURE 5 The current-voltage (*I-V*) characteristics of Na-implanted (CH)x (*n*)/ (CHI$_{0.05}$)x (*p*). Na ions were implanted at 50 keV and fluence of 3 × 10^{17} ions/cm^2. After Wada *et al.*[4]

unfortunately little photovoltaic effect was observed because of the absorption at the surface layer. As discussed in the previous paper,[9] the surface layer of the ion-implanted (CH)x film was carbonized due to the degradation of polymer, which was checked by the depth profile of resonant Raman spectra and the gas evolution. The thickness of carbonized layer depends on the ion species, fluence and accelerating voltage, ranging in several 100 Å. We will sputter out the carbonized layer by the same technique as the depth profile measurement in the near future.

Schottky barrier type MIM cell

Figure 6 indicates the photovoltaic behavior of Al/PPS/Cu cell.[5] Here PPS film was prepared by means of vacuum deposition (500 Å thick). Under the excitation with 400 nm light (P_{in} = 1.29 mW/cm^2) we obtained V_{oc} = 0.24 V and I_{sc} = 83.9 nA/cm^2 with the conversion efficiency of 0.005%. The efficiency is quite poor, but if the thickness of PPS and/or P_{in} is reduced, then it can be improved; *e.g.*, for PPS

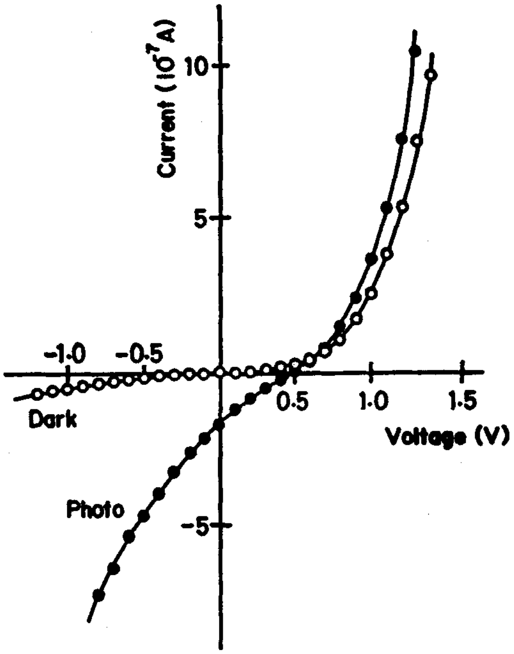

FIGURE 6 *I-V* characteristics of Cu/PPS (500 A)/Al cell in the dark (open circles) and under the photoexcitation (solid circles). After Misoh *et al.*[5]

TABLE II

Photovoltaic properties of Schottky barrier type polymer cells.

Configuration (M/polymer/M)	Preparation	Thickness (A)	P_{in} (mW/cm^2)	I_{sc} (nA/cm^2)	V_{oc} (V)	ff
Cu/PPS/Al	Evaporation	150	0.012	1.8	0.5	0.28
Cu/PPS/Al	Evaporation	500	1.29	83.9	0.24	0.29
Au/PVDF/Al	Evaporation	300	12.3	234	0.8	0.31
Au/PBz/Al	Plasma CVD	150	7.8	0.27	0.2	0.21
Au/PAn/Al	Electrochem	5000	0.012	210	0.38	0.33
Au/(CH)x/Al	Vapor Polym.	50 μm	7	35000	0.32	0.26
Al/PE/NiPc/ITO	Evaporation	100	0.08	0.04	0.83	0.30

ff: Fill factor, PBz: polybenzene, PAn: polyaniline, NiPc:Ni-phthalocyanine.

of 150 Å thick with $P_{in} = 12.3\ \mu W/cm^2$, $V_{oc} = 0.5$ V and $I_{sc} = 1.8$ nA/cm² with the efficiency of 0.21%. This tendency can be observed for almost all kinds of polymer thin films. Table II summarizes the results of MIM cells using polymer thin films as an insulator.

In order to improve I_{sc} and the conversion efficiency we should reduce the bulk resistance (perpendicular direction to the film) and increase the quantum efficiency of the polymer film. Firstly to reduce the bulk resistance, the polymer structure should be modified such as highly conjugated system and/or charge transfer complex formation, or the thickness of the film must be reduced. In the latter case the most important point is to make an ultrathin layer without pinholes. As mentioned in Sample Preparation Section, the RF sputtering technique is promising in this sense, though thermal degradation or crosslinking might occur during the sputtering of polymers. The mechanism of polymeric film formation by means of sputtering may be the same as the plasma polymerization process of monomer gas, that is, the polymer chains are scissored by plasma ions into fragments with radicals, which are re-polymerized on the substrate. Secondly to increase the quantum efficiency, photoactive polymers such as PVK and dye sensitized polymers are desirable. However in case of the sputtered PVK films the degradation and/or crosslinking of polymer chains were so definitely occured, then the activity of photocarrier generation was strongly suppressed.

Internal field type cell

When ferroelectric polymers (or polymer electrets) are illuminated by light, two types of current flow across the film; that is, an anomalous photovoltaic current I_{apv} due to the photogenerated carrier transport along the internal field and a pyroelectric current I_{pyro} due to the temperature gradient caused by the absorbed light energy. Figure 7 is a typical example of the photovoltaic response (that is, the time evolution of short-circuited photocurrent I_{sc}) observed in the ferroelectric polymer PVDF.[6] The sharp rise of I_{sc} followed by slow decay corresponds to the pyroelectric effect. At the thermal equilibrium state of the film under steady illumination, I_{sc} reaches a steady state current corresponding to I_{apv}. The reversal current observed after light OFF shows the same shape and absolute value (but opposite polarity) as I_{pyro}, and hence it corresponds to the pyroelectric current.

I_{apv} observed in the poled PVDF film (30 micron thick) is apparently independent of the exciting wavelength and equal to ca. 1.5

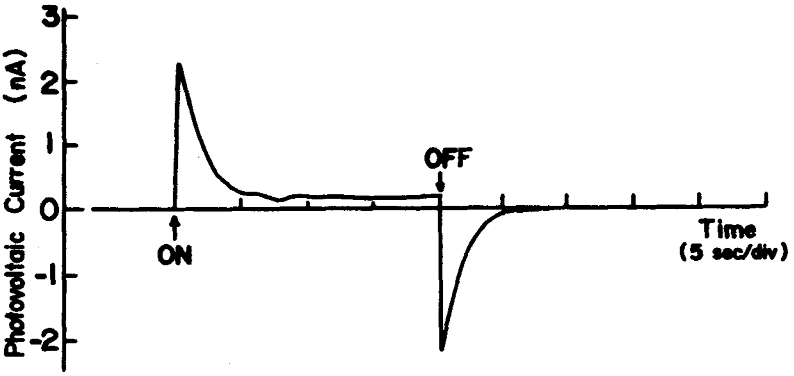

FIGURE 7 Time evolution of photovoltaic current observed in ferroelectric PVDF film. The time-dependent current correspond to the pyroelectric current, whereas the steady state current under photoexcitation corresponds to the anomalous photovoltaic current. After Sasabe *et al.*[6]

nA/W. Taking the high dc resistance of the film (2.5×10^{13} ohm) into consideration, we could estimate the open circuit voltage V_{oc} to be 4×10^4 V. This value is much higher than the band gap potential of PVDF (ca. 9 eV) by three decades, and suggests the existence of anomalous photovoltaic effect in PVDF. The conversion efficiency was estimated to be 0.25%. Recently Matsushige[19] observed a similar photovoltaic response as Figure 7 in copoly(VDF/TrFE). He also

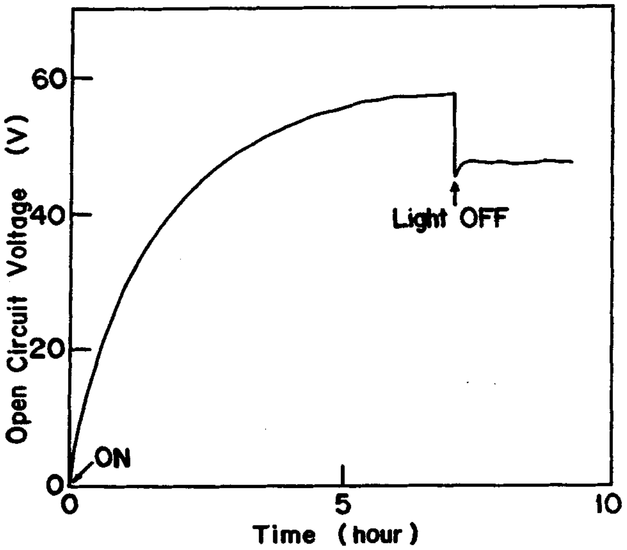

FIGURE 8 Time evolution of open circuit voltage observed in ferroelectric copoly(VDF/TrFE). After Matsushige.[19]

measured the time evolution of V_{oc} as shown in Figure 8. The observed value is smaller than that estimated by two decades in magnitude, but it is much larger than the band gap potential.

In case of the composite film of PZT-PVK, we obtained I_{apv} = 20 nA/W under the excitation of high pressure mercury lamp, or I_{sc} = 2.9 μA/W and V_{oc} = 2.1 V under the monochromatic light excitation (P_{in} = 1 mW/cm^2, λ = 370 nm). It should be noted that the action spectrum of I_{apv} is symbatic to the absorption spectrum of PVK, which indicates the carriers are generated in PVK and move along the internal field formed by PZT.

As shown in Figure 9,[12] the MIM cell of PVDF ultrathin film prepared by RF sputtering generates I_{apv}, which is larger than I_{pv} generated by the Schottky barrier effect (MIM of evaporated PVDF film) by the magnitude of 2 decades. For Al/PVDF(300 Å)/Au cell the open circuit voltage and short circuit current are 0.8 V and 19 μA/W respectively. The conversion efficiency was 0.04% (with the correction for reflection). The quite poor efficiency may be caused

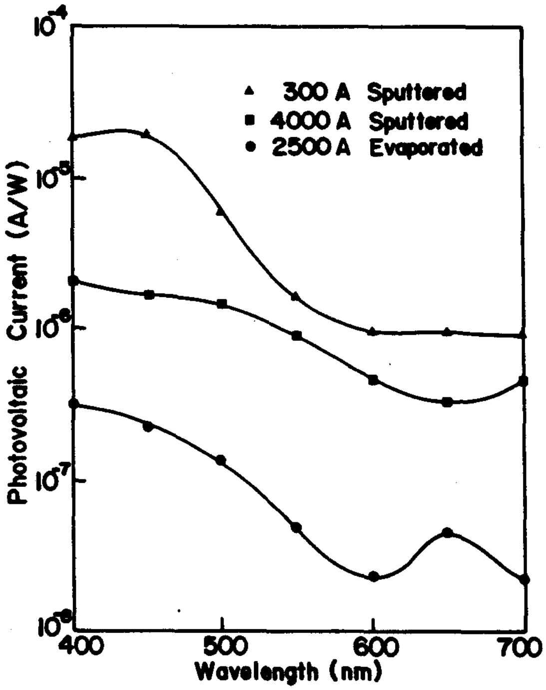

FIGURE 9 Action spectra of photovoltaic current in Al/PVDF/Au cells. PVDF ultrathin films were prepared by RF sputtering and/or vacuum deposition techniques as indicated in the figure. After Hanzawa *et al.*[12]

by the small internal field (0.13 MV/cm) in the sputtered PVDF film, which is 1/30 of the internal field in poled bulk PVDF film.

Purple membrane LB films

Figure 10 shows the typical photoresponses of 50 layers of purple membrane (PM) sandwiched with ITO and Al electrodes.[7] The direction of photovoltaic current was from Al-top to ITO-bottom electrode of the cell. This result was reasonable because the multilayer of PM is *z*-type construction whose hydrophobic side faces to the ITO substrate. It is well known that in PM the protons released from the end group of bacteriorhodopsin (bR), —COOH, by photoexcitation move across the membrane from inside (cytoplasmic side of PM fragment) to outside and hence the PM monolayer at the air/subphase interface statistically faces down its cytoplasmic side towards the subphase. When the light was turned off, the current of opposite polarity appeared, and it decayed and reached at a level slightly lower than the dark current (ca. 1 pA) which might be caused by the chemical battery due to the electrochemical reaction of metal electrode with residual humidity and salts. Actually the current and polarity of

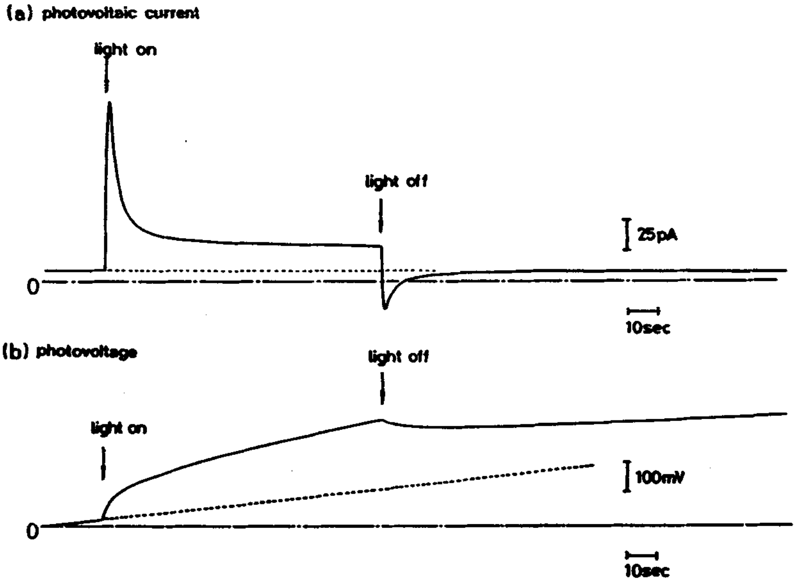

FIGURE 10 Typical photoresponses of ITO/purple membrane LBF (50 layers)/Al cell under the illumination of Xe lamp (75 W). (a) Represents the photovoltaic current and (b) the photovoltage. After Furuno *et al.*[7]

the dark current are dependent on relative humidity (RH), electrode materials (especially in the case of hetero-electrodes) and resistivity of the LB film. The resistance of ITO/PM/Al cell (area of electrode 0.28 cm^2) was higher than 7×10^{11} ohm below 15% RH, and approximately 2×10^{10} ohm at 70% RH. These values are exceedingly high compared to those obtained by Hwang *et al.*[20] where the PM LB films were prepared by vertical dipping method. We found that the salt added to the subphase recrystallized on the substrate as small granules by vertical dipping method, whereas the salt recrystallization was not observed for the horizontally transferred and rinsed film.

Both photovoltaic current and photovoltage at 1 second after excitation depend on the light intensity in a linear fashion, and their action spectra are symbatic with the absorption spectrum of PM suspension. It is also cleared from the crossed-illumination spectrophotometry that the photovoltaic response of PM cell comes from the formation of M intermediate during the photocycle of bR.

CONCLUDING REMARKS

We have reviewed some techniques for polymeric ultrathin film preparation and their application to photovoltaic cells. From the viewpoint of the energy conversion efficiency any type of cells using polymer layers has quite poor efficiency compared to the crystalline and/or amorphous semiconductor junction devices and it is almost impossible to use it as a solar battery. If we take, however, the quality of photoresponse (*i.e.*, S/N ratio) and the response time into consideration, these polymeric cells may be available for the photosensors.

Acknowledgments

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References

1. W. Stoeckenius, R. H. Lozier and R. A. Bogomolni, *Biochim. Biophys. Acta.*, **505**, 215 (1979).
2. V. M. Fridkin, *Photoferroelectrics*, Springer Verlag, Berlin-N.Y., 1979, Chapter 6.
3. A. M. Glass, D. von der Linde and T. J. Negran, *Appl. Phys. Lett.*, **25**, 233 (1974).

4. T. Wada, A. Takeno, M. Iwaki, H. Sasabe and Y. Kobayashi, *J. C. S. Chem. Comm.*, 1194 (1985).
5. K. Misoh, S. Tasaka, S. Miyata and H. Sasabe, *Nippon Kagakukai-shi* (*Chem. Soc. Jpn.*), 763 (1983) (in Japanese).
6. H. Sasabe, T. Nakayama, K. Kumazawa, S. Miyata and E. Fukada, *Polym. J.*, **13**, 967 (1981).
7. T. Furuno, K. Takimoto, T. Kouyama, A. Ikegami and H. Sasabe, *Thin Solid Films*, in press (1988).
8. J. Lindhard, M. Scharff and H. F. Schiott, *K. Danske Vidensk. Selsk. Mat.-Fis. Medd.*, **33**, 14 (1963).
9. T. Wada, A. Takeno, M. Iwaki and H. Sasabe, *Synthetic Metals*, **18**, 585 (1987).
10. H. Sasabe, *Oyo Butsuri* (*Appl. Phys. Jpn.*), **56**, 146 (1987) (in Japanese).
11. S. Miyata, K. Misoh, S. Tasaka and H. Sasabe, *Proc. IUPAC 28th Macromol. Symp.* (Macro 82), p. 408 (1982).
12. Y. Hanzawa, Y. Wachi, K. Kamisako and H. Sasabe, *Repts. Progr. Polym. Phys. Jpn.*, **26**, 393 (1983).
13. P. N. T. Unwin and R. Henderson, *J. Mol. Biol.*, **94**, 425 (1975).
14. H. Shirakawa, Y. Kobayashi, A. Nagai, S. Ikeda, I. Shijime, M. Konagai and K. Takahashi, *Polym. Preprints*, Jpn., **28**, 467 (1979) (in Japanese).
15. M. Ozaki, D. L. Peebles, B. R. Weinberger, C. K. Chiang, S. C. Gau, A. J. Heeger and A. G. MacDiarmid, *Appl. Phys. Lett.*, **35**, 83 (1979).
16. S. C. Gau, Ph.D. Thesis, 1982, Univ. Pennsylvania, U.S.A.
17. J. Tsukamoto and K. Ohigashi, *Jpn. J. Appl. Phys.*, **20**, L 127 (1981).
18. Y. Wachi and A. G. MacDiarmid, private communication.
19. K. Matsushige, Repts. Organic Thin Films for Information Conversion, Ministry of Education, Jpn., p. 5 (1987) (in Japanese).
20. S.-B. Hwang, J. I. Korenbrol and W. Stoeckenius, *Biochim. Biophys. Acta*, **509**, 300 (1978).