

Photo-responsible polarization switching in TiOPc/P(VDF-TrFE) stacking films

Yasuko Koshiba¹, Hiroshi Horii¹, Masahiro Morimoto^{1,2}, Masahiro Misaki^{1,3}, Tatsuya Fukushima¹, and Kenji Ishida¹

¹ Kobe Univ.

¹ Department of Chemical Science & Engineering, Graduate School of Engineering,

1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan

Phone: +81-78-803-6150 E-mail: kishida@crystal.kobe-u.ac.jp

² Univ. of Toyama

Graduate School of Science & Engineering for Research,

3190 Gofuku, Toyama, 930-8555, Japan

³ Kindai Univ. Tech. Col.

Electrical and Electronic Systems Course, Department of Comprehensive Engineering,

7-1 kasugaoka, Nabari, 518-0459, Japan

Abstract

Titanyl phthalocyanine (TiOPc)/Poly(vinylidene fluoride-trifluoroethylene)(P(VDF-TrFE)) stacking films were fabricated; and electrical properties were investigated under light irradiation and dark condition. The polarization switching behavior of TiOPc/P(VDF-TrFE) films was changed with 650 nm light irradiation, because of photoconductivity of TiOPc. Under applying threshold electric field, the polarization switching current was observed with light irradiation; thus the photo-responsible polarization switching was suggested.

1. Introduction

Ferroelectric materials have two stable spontaneous polarization states, hence, these materials has been used for non-volatile memory. Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene [P(VDF-TrFE)] are well known to be ferroelectric polymers with large electric dipole moments[1-4]. Generally, reversible switching of ferroelectric polarization could be achieved under the electrodes in electrode/ferroelectric/electrode capacitor structure, therefore, these devices are controlled with the electric-field. On the other hand, titanyl phthalocyanine (TiOPc) is widely used in organic electronics for its good stability, optical properties and charge mobility [5-7]. In this study, we focused photoconductivity of TiOPc for control of polarization switching in P(VDF-TrFE) thin films. Therefore, we fabricated the organic photoconductor /organic ferroelectric stacked devices, and investigated the photo-responsive ferroelectric properties.

2. Experimental methods

A P(VDF-TrFE) copolymer consisting of a 75/25 VDF/TrFE molar content ratio was dissolved in methylethylketone and spin-coated onto a ITO coated glass substrate. Then, TiOPc was deposited on P(VDF-TrFE) layer at room temperature under a vacuum condition of 5×10^{-4} Pa. Finally, 100 nm Al as a top electrode was deposited. The optical properties of TiOPc were investigated by ultraviolet-visible (UV-Vis) spectroscopy; and the absorption spectrum of the TiOPc film exhibited a Q-band in the wavelength region between

600 and 800 nm, thus, we used red laser (650nm) for irradiation. The current density electric field (J - E) curves of TiOPc/P(VDF-TrFE) films were measured under dark and light irradiation of red laser (650nm). Time dependence of current density of these films was also measured.

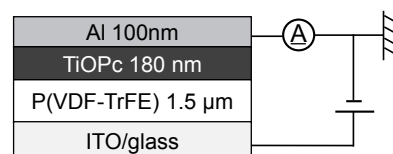


Fig. 1 Schematic structure of TiOPc /P(VDF-TrFE) stacked device.

3. Results and discussions

Figure 2 shows J - E characteristic of TiOPc/P(VDF/TrFE) film under dark condition and irradiation with red laser light (5.1 mW/cm^2). In the dark condition, a strong peak at approximately -50 V , originated from polarization switching, was observed in negative electric field, however, the split peaks between 40 and 70 [MV/m] , were observed in positive electric field.

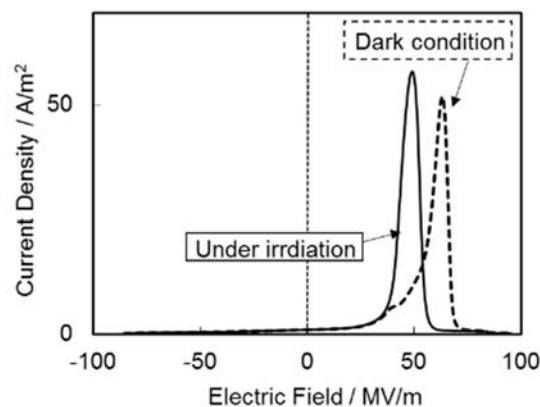


Fig.2 J - E curves of TiOPc/P(VDF-TrFE) film. Solid line: under irradiation with red laser; dotted line: dark condition.

The peak splitting in positive electric field is due to the distinct behavior of charge compensation for the electric dipole in P(VDF-TrFE) layer between metal/ferroelectric and organic semiconductor/ferroelectric interfaces. Although, P_r of the TiOPc/P(VDF-TrFE) film were 77 mC/m^2 (in the positive electric field) and 79 mC/m^2 (in the negative electric field); these value were approximately equal to that of P(VDF-TrFE) film, thus, the dipole moment of the P(VDF-TrFE) in TiOPc/P(VDF-TrFE) films reversed completely.

On the other hand, under irradiation with 650 nm light, the peak splitting was not observed in positive electric field; and the peak of polarization switching was shifted to low voltage side, thus, the coercive electric field of the TiOPc/P(VDF-TrFE) film decreased from 62 MV/m to 50 MV/m. These results indicated that the TiOPc layer has photocarrier generation under red laser irradiation; and the polarization switching behavior of TiOPc/P(VDF-TrFE) film was changed by photoconductivity of TiOPc layer.

Therefore, based on the decrease of E_c of TiOPc/P(VDF-TrFE) film with light irradiation, we fixed threshold electric field to 53 MV/m; and measured J - E curves between -53 MV/m and 53 MV/m, as shown Fig. 3.

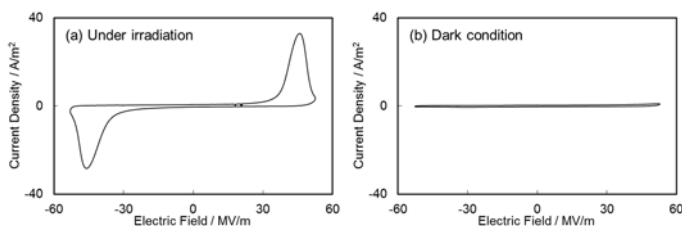


Fig. 3 J - E characteristic of TiOPc/P(VDF-TrFE) film measured between threshold electric field. (a) under irradiation, (b) dark condition.

Under irradiation, the two peaks observed indicated polarization switching, and P_r of the film were 75 mC/m^2 (in positive electric field) and 71 mC/m^2 (in negative electric field), that are ten times larger, approximately, than P_r measured in the dark condition (6 mC/m^2 : in positive, 7 mC/m^2 in negative). Thus, under 650 nm light irradiation, the dipole moment of the P(VDF-TrFE) reversed by applying the threshold electric field.

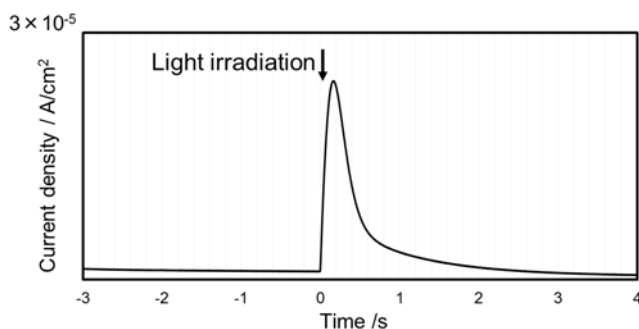


Fig. 4 J - t characteristic of TiOPc/P(VDF-TrFE) film with light irradiation.

Moreover, under applying the threshold electric field to the Al/TiOPc/P(VDF-TrFE)/ITO device, we irradiated the device with the red laser. Figure 4 shows the time dependence of current density with light irradiation.

With 650 nm light irradiation at 0 s, the current increased sharply to maximum and decreased. The total charge calculated from this current peak was 136 mC/m^2 , this value is comparable to the P_r of P(VDF-TrFE), hence, this photore-sponse current suggested polarization switching. The dipole moment of the TiOPc/P(VDF-TrFE) stacked film could reverse by light irradiation under threshold electric field.

The interaction between the photocarrier of TiOPc layer and the polarization electric field in the TiOPc/P(VDF-TrFE) stacked devices will be discussed.

4. Conclusions

In this study, the polarization switching behavior of TiOPc/P(VDF-TrFE) stacking films was investigated. In the dark condition, in positive electric field, splitting of polarization switching peak was observed. Under irradiation of red laser light (650nm), the peak splitting was not observed, and the coercive electric field of the TiOPc/P(VDF-TrFE) film decreased from 62 MV/m to 50 MV/m. Under applying the threshold electric field, polarization switching current was observed with 650nm light irradiation, thus, the photo-responsible polarization switching was suggested.

Acknowledgements

This work was partially supported by CREST, JST, and JSPS KAKENHI.

References

- [1] T. Fulukawa, M. Date and E. Fukuda, *J. Appl. Phys.* **151** (1980) 1135.
- [2] K. Takahiro, K. Takano, M. Kobayashi, Y. Chatani and H. Tadokoro, *Polymer*, **124** (1983) 199.
- [3] G. Zhu, J. Zhaug, X. Luo and X. Yan, *Organic Electron.* **10** (2009) 753.
- [4] Y. Kuroda, Y. Koshiba, M. Misaki, K. Ishida and Y. Ueda, *Appl. Phys. Express*, **6** (2013) 021601.
- [5] Y. Fujimaki, H. Tadokoro, Y. Oda, H. Yoshioka, T. Homma, H. Moriguchi, K. Watanabe, A. Kinoshita, N. Hirose, A. Itami and S. Ikeuchi, *SPSE Proc., The Fifth International Congress on Advances in Non-Impact Printing Technologies* (1989) 37.
- [6] Y. Oda, T. Homma, Y. Fujimaki, *Electrophotography* **29** (1990) 250.
- [7] K. Y. Law, *Chem. Rev.* **93**, (1993) 449.