

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

**ScienceDirect**

Progress in Natural Science: Materials International 20(2010) 27–30

---

**Progress in  
Natural Science:  
Materials  
International**


---

[www.elsevier.com/locate/pnsc](http://www.elsevier.com/locate/pnsc)

## Formation and characterization of phthalocyanine dimer/C<sub>60</sub> solar cells

Akihiro TAKEDA<sup>1</sup>, Akira MINOWA<sup>1</sup>, Takeo OKU<sup>1</sup>, Atsushi SUZUKI<sup>1</sup>,  
Kenji KIKUCHI<sup>1</sup>, Yasuhiro YAMASAKI<sup>2</sup>

1. Department of Materials Science, The University of Shiga Prefecture, 2500, Hassaka, Hikone, Shiga 522-8533, Japan;
2. Orient Chemical Industries, Co. Ltd., Department of New Business, 8-1, Sanra-Higashi-Machi, Neyagawa, Osaka 572-8581, Japan

Received 18 October 2010; accepted 23 December 2010

**Abstract:** Organic solar cells with  $\mu$ -oxo-bridged gallium phthalocyanine dimer (GaPc dimer) and fullerene were produced by an evaporation method. A device based on the GaPc dimer provided a conversion efficiency of  $4.2 \times 10^{-3}\%$ , which is better compared to a device based on phthalocyanine monomer. Dimerization effect was discussed with a molecular orbital calculation, and the crystalline phases of the present solar cells were investigated by X-ray diffraction. Further improvement of the efficiency was discussed on the basis of the experimental results.

**Key words:** phthalocyanine dimer; fullerene; solar cell

### 1 Introduction

Silicon solar cells are mainstream in the world because of their high performance, long life and high reliability. However, silicon solar cells have some problems. For example, silicon raw materials are close to the supply limit, and the production energy is high due to the complicated process, and energy payback time is long. Therefore, development of new solar cells instead of silicon solar cells is mandatory.

Recently, organic solar cells have been studied due to their low cost and easy processing. Phthalocyanines which have a photovoltaic property, heat-resistance, light-stability, chemical stability, and high optical absorption at visible range are used for an oxidation catalyst, catalyst of fuel cells and solar cells. Organic solar cell efficiency of  $\sim 5\%$  was achieved by employing small molecular such as copper phthalocyanine and fullerene[1–3]. Many studies on the phthalocyanine monomer have been performed, and the properties are different by changing central metal and chemical substitution. However, few phthalocyanine dimers have been studied.

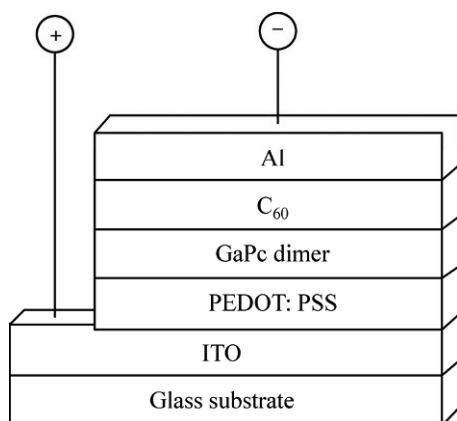
The purpose of the present work is to fabricate and characterize phthalocyanine dimer/fullerene hetero-

junction solar cells. In the present work,  $\mu$ -oxo-bridged gallium phthalocyanine (GaPc) dimer is used for p-type semiconductors, and fullerene with excellent electron affinity is used for n-type one[4–5].

### 2 Experimental

A thin layer of polyethylenedioxythiophen doped with polystyrenesulfonic acid (PEDOT:PSS) (Sigma Aldrich Corp.) was spin-coated on pre-cleaned indium tin oxide (ITO) glass plate (Geomatec Co., Ltd.,  $\sim 10\Omega/\square$ ). The PEDOT:PSS has a role as an electron blocking layer for hole transport. After annealing at 100 °C for 20 min in N<sub>2</sub> atmosphere,  $\mu$ -oxo-bridged GaPc dimer (Orient Chemical Industries, Co. Ltd.) and fullerene (C<sub>60</sub>) (Material Technologies Research, 99.98%) layer were prepared on a PEDOT:PSS layer by evaporation ( $1.8 \times 10^{-3}$  Pa). Finally, aluminium metal contacts were evaporated as a top electrode and annealed at 140 °C for 20 min in N<sub>2</sub> atmosphere[4–6]. The active area of the solar cells was 4 mm×4 mm. A schematic diagram of the present solar cells is shown in Fig.1. GaPc monomer with axial Cl ligand was also used for the comparison.

Current density-voltage (J-V) characteristics (Hokuto Denko Corp., HSV-100) of the solar cells were measured both in the dark and under illumination at 100



**Fig.1** Structure of GaPc dimer/ $C_{60}$  heterojunction solar cell

$\text{mW}/\text{cm}^2$  by using an AM 1.5 solar simulator (San-ei Electric, XES-301S) in  $N_2$  atmosphere. The solar cells were illuminated through the side of ITO substrates, and the illuminated area was  $0.16 \text{ cm}^2$ . Optical absorption of solar cells was investigated by means of UV-visible spectroscopy (Hitachi Ltd., U-4100). Crystalline phases of the present solar cells were investigated by X-ray diffraction (XRD, Philips X'pert-MPD System).

The isolated molecular structures were optimized by ab-initio molecular orbital calculations using Gaussian 03. Conditions in the present calculation were as follows: calculation method (density functional theory, DFT) and basis set (LANL2DZ). Electronic structures such as energy gaps between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and electronic densities were investigated.

### 3 Results and discussion

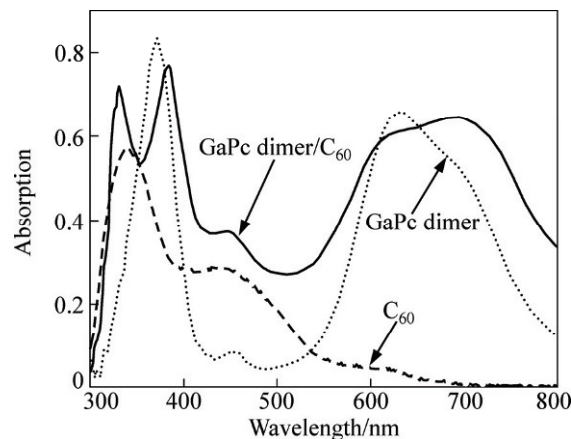
The measured J-V characteristic parameters of ITO/PEDOT:PSS/GaPc dimer/ $C_{60}$ /Al solar cell and ITO/PEDOT:PSS/GaPc/ $C_{60}$ /Al are summarized in Table 1. Each structure shows a characteristic curve for open circuit voltage and short-circuit current density. A solar cell using GaPc dimer provided power conversion efficiency ( $\eta$ ) of  $4.2 \times 10^{-3}\%$ , fill factor (FF) of 0.27, open-circuit voltage ( $V_{oc}$ ) of 0.14 V and short-circuit current density ( $J_{sc}$ ) of  $0.11 \text{ mA}/\text{cm}^2$ . All parameters were improved by using GaPc dimer compared to GaPc monomer, as listed in Table 1.

**Table 1** Measured parameters of solar cells

Sample	$V_{oc}/V$	$J_{sc}/(\text{mA}\cdot\text{cm}^{-2})$	FF	$\eta/\%$
GaPc-dimer	0.14	0.11	0.27	$4.2 \times 10^{-3}$
GaPc-monomer	$1.4 \times 10^{-4}$	0.15	0.25	$5.3 \times 10^{-6}$

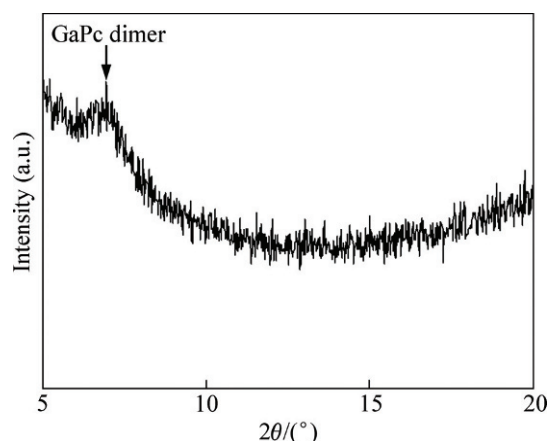
Figure 2 show a measured optical absorption of GaPc dimer,  $C_{60}$  and GaPc dimer/ $C_{60}$  cells. The solar cells show a wide optical absorption ranging from 320

nm to 800 nm (which correspond to 3.8 and 1.5 eV, respectively). The absorption spectrum of GaPc dimer was almost the same as that of the monomer, but a new peak was observed around 450 nm.



**Fig.2** Optical absorption spectra of GaPc dimer/ $C_{60}$  solar cells

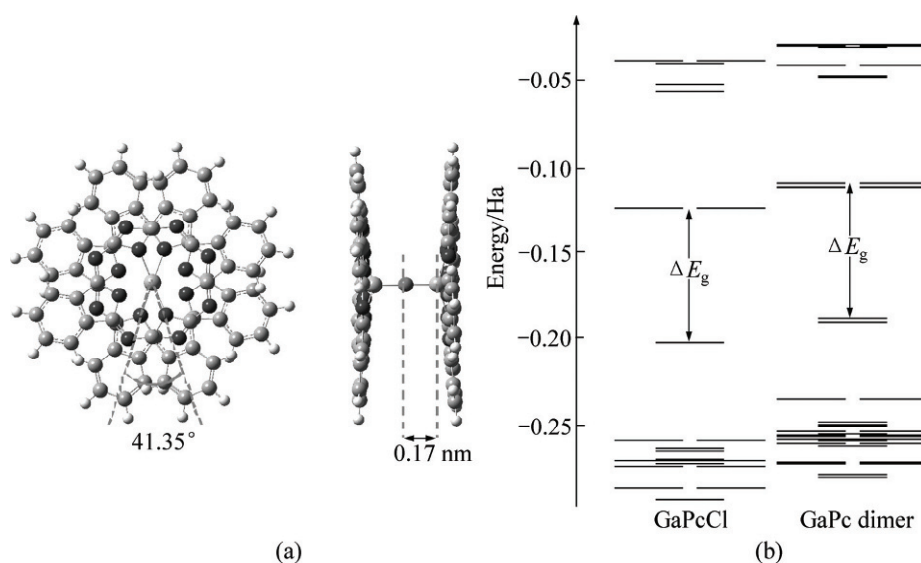
X-ray diffraction pattern of GaPc dimer layer is shown in Fig.3. The diffraction pattern shows a peak at  $2\theta=6.9^\circ$ , which corresponds to lattice spacing of 1.27 nm. A particle size of GaPc dimer was calculated from Scherrer's formula to be 16.6 nm.



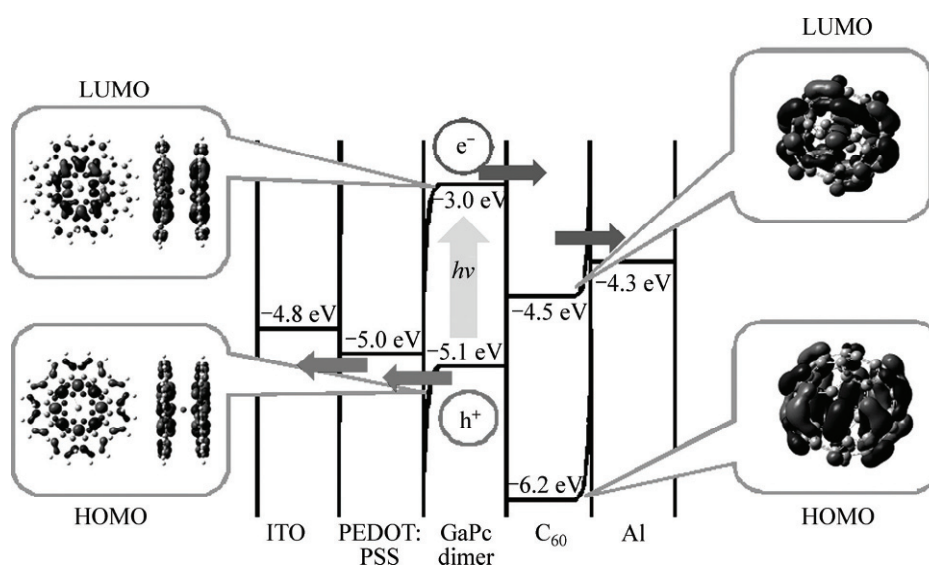
**Fig.3** XRD pattern of deposited GaPc dimer thin film

Figure 4(a) shows a molecular structure of GaPc dimer after structural optimization. Two planes are parallel, the rotational degree is  $41.35^\circ$ , and the distance between GaPc monomers is about 0.34 nm. Figure 4(b) shows the energy levels of GaPc monomer and GaPc dimer. The HOMO and LUMO levels increase a little compared to those of the monomer, but the energy gap of the GaPc dimer is 2.1 eV, which is not changed by dimerization.

The energy level diagram and electronic structures of the solar cell were calculated and summarized as shown in Fig.5. Previously reported values except GaPc dimer were used for the energy levels of the figures by



**Fig.4** Molecular structure of GaPc dimer after structural optimization (a) and energy levels of GaPc monomer and GaPc dimer (b)



**Fig.5** Energy level diagram of ITO/PEDOT:PSS/GaPc dimer/C<sub>60</sub>/Al solar cell

adjusting to the present work[4–6]. The HOMO and LUMO levels of GaPc in Fig.5, and HOMO and LUMO of two phthalocyanine monomers were stirred and piled up, respectively. The interaction between two phthalocyanine monomers is not able to be confirmed in Fig.5. When light is incident from the ITO side, excitation by the light absorption happens at the p-n interface, and electrons and holes are produced by charge separation. Electrons are transported to an Al electrode, and holes are transported to an ITO substrate. Energy barrier would exist near the semiconductor/metal interface. Carriers would transport from -4.5 eV to -4.3 eV by hopping conduction. Improvement of the present solar cells would be possible by the introduction of a buffer layer, change of annealing conditions, and the

improvement of the microstructure is also necessary to obtain high efficiency.

Although the energy gap and energy level of GaPc dimer were hardly changed by dimerization in the present work, the power conversion efficiency was significantly improved. It is known that the  $\pi$  electron system is enhanced by dimerization, and high carrier mobility can be expected[7]. Since enhancing the  $\pi$  electron system was not confirmed by dimerization in the present study, the improvement of efficiency is believed that molecular orientation and crystallinity were improved by ordered array due to dimerization, which led to the decrease of carrier recombination. As a result, open-circuit voltage was greatly improved, which led to the high conversion efficiency.

Various crystallizations of  $\mu$ -oxo-bridged gallium phthalocyanine dimer have been reported[8–9]. When the crystallographic structure is different, initial surface potential, photosensitivity and residual surface potential are also different. Further crystallographic structure should be investigated in the future.

#### 4 Conclusions

GaPc/fullerene solar cells were fabricated and characterized. The device based on the GaPc dimer provided  $\eta$  of  $4.2 \times 10^{-3}\%$ , FF of 0.27,  $V_{oc}$  of 0.14 V, which are better than those of the cells based on GaPc monomer. The present solar cells showed a wide optical absorption ranging from 320 nm to 800 nm. The energy gap of GaPc dimer was  $\sim 2.1$  eV. A carrier transfer mechanism was discussed based on energy level diagram.

#### Acknowledgments

This work was partly supported by Grant-in Aid for Scientific Research, JSPS.

#### References

- [1] YANG F, SHTEIN M, FORREST S R. Morphology control and material mixing by high-temperature organic vapor-phase deposition and its application to thin-film solar cells [J]. *J Appl Phys*, 2005, 98: 014906.
- [2] XUE J, UCHIDA S, RAND B P, et al. Asymmetric tandem organic photovoltaic cells with hybrid planar-mixed molecular heterojunctions [J]. *Appl Phys Lett*, 2004, 85: 5757.
- [3] RAND B P, XUE J, UCHIDA S, et al. Mixed donor-accepter molecular heterojunctions for photovoltaic applications [J]. *J Appl Phys*, 2005, 98: 124902.
- [4] OKU T, TAKEDA A, NAGATA A, et al. Fabrication and characterization of fullerene-based bulk heterojunction solar cells with porphyrin,  $\text{CuInS}_2$ , diamond and exciton-diffusion blocking layer [J]. *Energies*, 2010, 3: 671–685.
- [5] OKU T, NAGAOKA S, SUZUKI A, et al. Formation and characterization of polymer/fullerene bulk heterojunction solar cells [J]. *J Phys & Chem Sol*, 2008, 9: 549–552.
- [6] OKU T, KAKUTA N, KAWASHIMA A, et al. Formation and characterization of bulk hetero-junction solar cells using  $\text{C}_{60}$  and perylene [J]. *Mater Trans*, 2008, 69: 1276–1279.
- [7] IGLESIAS R S, CLAESSENS C G, TORRES T, et al. Subphthalocyanine-fused dimers and trimers: synthetic, electrochemical, and theoretical studies [J]. *J Org Chem*, 2007, 72: 2697–2977.
- [8] YAMASAKI Y, TAKAKI K. Synthesis of  $\mu$ -oxo-bridged hetero-metal phthalocyanine dimer analogues and application for charge generating material in photoreceptor [J]. *Dyes and Pigments*, 2006, 70: 105–109.
- [9] YAMASAKI Y, KURODA K, YAKAKI K. Synthesis of new polymorphs of  $\mu$ -oxo metal (III) phthalocyanine dimers and their photoconductive properties [J]. *J Chem Society of Japan, Chem and Industrial Chemistry*, 1997, 12: 887–898.