Demonstration of an electret generator for energy harvesting without any charging process: Utilization of spontaneous orientation of polar molecules

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1. Introduction

Electret generators (EGs) for energy harvesting have attracted much attention because of their potential applications [1, 2]. EGs usually include an air gap and electret which is a dielectric material with a quasi-permanent electrical charge or dipole polarization [3], between the electrodes. In EGs, an electrostatic field of the electret in a variable capacitor is used to convert mechanical energy into electricity [4]. Thus, an importance of the electret must be emphasized because the output current depends on the surface charge density ($\sigma$) of that. In order to obtain a high $\sigma$, various charging processes, such as corona charging and thermal poling, have been developed. In fact, in perfluorinated polymers (CYTOP), a high $\sigma$ of 2.0 mC/m$^2$ was achieved by using corona charging [5]. From view point of mass production, however, the charging processes are one of the factors contributing to decrease productivity. Thus a simplification of the fabrication process of the electret is highly required.

Our group found the formation of giant surface potential (GSP) in the vacuum deposited film of tris-(8-hydroxyquinolinato) aluminum (Alq$_3$) which is typical polar molecule for organic...
Figure 1. (a) Schematic illustration of electret generator (EG) for energy harvesting. (b) Chemical structures of Alq3 (top) and TPBi (bottom). (c) Schematic illustration of organic thin film composed of polar molecule with spontaneous orientation polarization. (d) Measurement setups for Kelvin probe and generated current measurements.

light-emitting diodes (top figure in Fig. 1(b)) [6]. The surface potential ($V_s$) linearly increased with the film thickness and reached 28 V at 560 nm. Second harmonic generation measurements revealed that this GSP of the Alq3 film originates from the spontaneous orientation of the molecule. This result means that the positive and negative polarization charges of $\pm 1.4 \text{ mC/m}^2$ exist on the surface and reverse side of the film as shown in Fig. 1(c). After that, we found that GSP appears in various organic polar materials [7, 8]. Further, Sugi et al. reported long stability of GSP in Alq3 film (10% loss in 10 years) [9], suggesting that Alq3 can be regarded as electret.

In this study, we propose a novel EG utilizing the molecules having GSP in the film as an electret. Because these molecules are spontaneously ordered, and thus the charged film are formed without the need for charging process, hereafter, these molecules are referred to as self-assembled electret (SAE). One of the problem of the application of SAE to EG is their photo sensitivity. In the case of Alq3, the $V_s$ disappeared by white light irradiation for 1 hour. This is because the photo-generated excitons are dissociated in the film, and the electrons and holes move to the surface and reverse side of the film, respectively, resulting in compensation of the polarization charges. Thus in this work, we applied 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) because its optical band gap (3.5 eV) is wider than that in Alq3 (2.8 eV) [10, 11], in order to reduce the light absorption (bottom figure of Fig. 1(b)). We found that the $V_s$ reached 46.5 V at 739 nm in TPBi vacuum evaporated film without any charging process. The $\sigma$ was estimated to be 1.8 mC/m$^2$ which is comparable to polymer-based electret after corona charging (for example, 2.0 mC/m$^2$ for CYTOP [5]). In addition, the $V_s$ was quite stable in vacuum and dark condition for 1 hour. Finally, we developed the model EG device including TPBi SAE and an AC current in nano-ampere order clearly appeared due to the vibration of the electrode. This result strongly suggests that the application of SAE to EGs enables the elimination of charging process for electret, leading to facilitating the fabrication process of the device.
2. Experiment
TPBi was purchased from Luminescence Technology Corp. (sublimed, > 99.5%). Film preparation and KP measurement were performed in evaporation and measurement chambers, respectively, that both chambers are directly connected each other. Film preparation was incrementally formed on indium-tin-oxide (ITO) by vacuum deposition at a typical deposition rate of 0.2 nm/s. \(V_s\) was evaluated by Kelvin probe (KP) measurement system (UHVKP020, KP Technology) in vacuum at each step of the deposition. A base pressure in the chambers was lower than \(4 \times 10^{-4}\) Pa. Because \(V_s\) is sensitive to light [6], all the above procedures were carried out in the dark or under red light illumination.

In KP, the \(V_s\) was obtained from the external voltage \((V_{\text{ext}})\) when a flowing AC current becomes zero during probe vibration (Fig. 1(d)). In other words, the probe of KP can be used as vibration electrode in EG in the case of \(V_{\text{ext}} = 0\) V. Thus a generated current in the model EG was evaluated KP measurement system with a vibration frequency of 55 Hz; I/V amplifier (SR570, SRS) was connected to the probe and the output voltage was detected by oscilloscope (TDS 2001C, Tektronix). \(V_{\text{ext}}\) was set to be zero during the measurements of generated current.

3. Results and discussion
An inset in Fig. 2(a) shows the thickness dependence of \(V_s\) in TPBi vacuum evaporated film. \(V_s\) linearly increased with the film thickness, and finally reached 46.5 V at 739 nm, indicating the spontaneous orientation of permanent dipole moment of TPBi molecule. This result clearly suggests that charged film was fabricated without any charging process. Using the relative permittivity of 2.87 in TPBi [7], the \(\sigma\) was estimated to be 1.8 mC/m² from the slope of the inset (72.7 mV/nm). Because this value is comparable to polymer-based electret after corona charging, it is expected that this film can be utilized as electret in EG.

![Figure 2](image)

**Figure 2.** (a) Variation of \(V_s\) as a function of time in dark and vacuum condition. Inset indicates the thickness dependence of the \(V_s\). (b) Property of output current in the model EG due to electrode vibration. The frequency of the vibration was set to be 55 Hz.

Before moving to the evaluation of output current in the model EG, the stability of the \(V_s\) was measured. Figure 2(a) shows the variation of \(V_s\) as a function of time in dark and vacuum condition. \(V_s\) was quite stable at least within the measurement range (1 hour). This result indicates that the TPBi film has required properties of electret in EGs, namely, high \(\sigma\) and its stability.

Let us turn to the evaluation of generated current characteristics in model EG device with TPBi. By substituting the probe in KP for vibration electrode of the model EG device, the
measurement was performed. Figure 2(b) shows the variation of output current as a function of time. This measurement was carried out in dark and vacuum condition without exposure to air. An AC current of nano-ampere order clearly appeared and the frequency was completely same as the probe frequency of 55 Hz (18.2 ms). This result obviously demonstrates that the current was generated by electrode vibration in model EG utilizing TPBi as SAE.

4. Conclusion
In summary, we developed a novel EG without the need for any charging processes by utilizing spontaneous orientation polarization of TPBi molecule. $V_{sp}$ of TPBi exceeded 46 V at 739 nm without any charging processes and the $\sigma$ was obtained to be 1.8 mC/m$^2$. This value is comparable to $V_{sp}$ of CYTOP after corona charging, clearly suggesting a high availability of TPBi film as electret for EGs. Finally, we demonstrated that the model EG utilizing TPBi as electret generated current in nano-ampere order. We believe that the application of SAEs will open up the novel ways for the realization of EGs for energy harvesting.

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References
[1] Beeby S P, Tudor M J and White N M 2006 Meas. Sci. Technol., 17 (2006) R175
[2] Suzuki Y 2011 IEEJ Trans 6 101
[3] Sessler G M 1998 Electrets Third Edition (California: Laplacian Press)
[4] Hinchet R, Ghaffarinejad A, Lu Y, Hasani J Y, Kim S-W, Basset P 2018 Nano Energy, 47 401
[5] Kashiwagi K, Okano K, Miyajima T, Sera Y, Tanabe N, Morizawa Y, Suzuki Y 2011 J. Micromech. Microeng. 21 125016
[6] Ito E, Washizu Y, Hayashi N, Ishii H, Matsuie N, Tsuboi K, Ouchi Y, Harima Y, Yamashita K, Seki K 2002 J. Appl. Phys. 92 7306
[7] Noguchi Y, Miyazaki Y, Tanaka Y, Sato N, Nakayama Y, Schmidt T D, Brüttig W, Ishii H 2012 J. Appl. Phys. 111 114508
[8] Noguchi Y, Lim H, Isoshima T, Ito E, Hara M, Chin W W, Han J W, Kinjo H, Ozawa Y, Nakayama Y, Ishii H 2013 Appl. Phys. Lett. 102 203306
[9] Sugi K, Ishii H, Kimura Y, Niwano M, Ito E, Washizy Y, Hayashi N, Ouchi Y, Seki K 2004 Thin Slid Films 464-465 412
[10] Dalasinski P, Lukasiak Z, Wodziyla M, Rębarz M, Bała W, 2006 Opt. Mater. 28 98
[11] Gao Z, Lee C S, Bello I, Lee S T, Chen R-M, Luh T-Y, Shi J, Tang C W 1999 Appl. Phys. Lett. 74 865