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HIGH-PERFORMANCE PERFLUORINATED POLYMER ELECTRET FILM FOR MICRO POWER GENERATION

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Abstract: The development of a new high-performance polymer electret material with high surface charge density, stability, and high thermal resistibility of electric charge was studied. Previously, we found that MEMS-friendly perfluorinated polymer CYTOP™ CTL-M (Asahi Glass Co., Ltd.) shows excellent electret properties. In the present study, it is reported that the electret property and the thermal stability of CYTOP™ electret are markedly improved by doping silane coupling reagent into polymer. The charge density of 1.5 mC/cm^2, which is 1.6 times larger than that of the undoped CYTOP™, has been obtained on 16 μm-thick film. In addition, the power generation of 0.585 mW, which is about twice of our previous data, has been achieved at a low seismic frequency of 20Hz.

Key words: Electret, Energy harvesting, Micro power generation, Perfluorinated polymer, CYTOP

1. INTRODUCTION

Recently, the micro power generation systems as the alternatives of conventional secondary batteries attracted much attentions. It is known that the devices applying to RFIDs and mobile sensor networks consume a low electrical power. The vibration-driven energy harvesting devices are proposed for these applications [1-3]. Since the frequency range of vibration existing in the environment is below a few tens of Hz, electret power generators should have higher performance than electromagnetic ones [4-8].

We recently reported that CYTOP™ CTL-M (Asahi Glass Co., Ltd.), MEMS-friendly amorphous perfluorinated polymer, can possess high surface charge density, which is stable enough for electret material [7,8]. We also found that up to 0.28 mW can be obtained with the CYTOP™ electret at an oscillation frequency as low as 20Hz. However, higher surface charge density is required for better performance, and charge stored in CTL-M becomes unstable at relatively low temperature. In the present study, a novel electret material based on CYTOP™ is proposed for higher surface charge density and thermal stability, and its electret properties are systematically investigated.

2. ELECTRET POWER GENERATOR

Figure 1 shows a schematic of the micro electret generator designed in our previous study [7]. When the in-plane vibration is generated, the seismic mass with the electret brings about a relative motion to the counter electrode on the bottom substrate. Thus, the amount of induced charge on the counter electrode is changed corresponding to the overlapping area. Consequently, electric current is generated in the external circuit. The seismic mass is supported by high-aspect-ratio soft springs made of Parylene [9], which enables large amplitude of vibration and low resonance frequency.

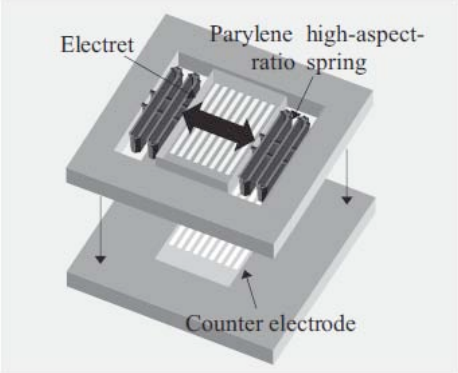


Fig. 1: Schematic of micro seismic electret power generator.

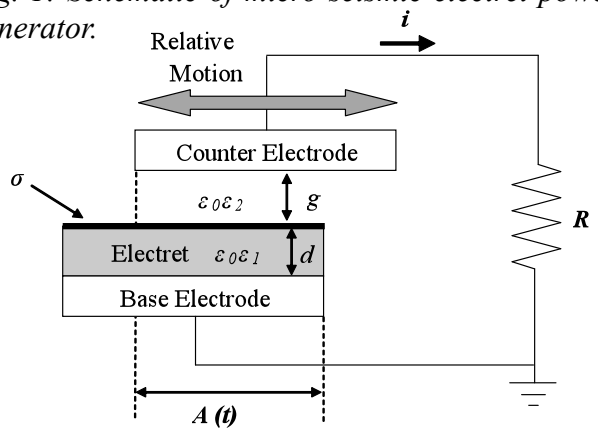


Fig. 2: Model of electret power generator.

Figure 2 shows a schematic of the simplified generator structure, where σ, *d*, *g*, and *A* are respectively the surface charge density, the thickness of electret, the gap between the electret and the counter electrode, and the overlapping area. Boland et al. [5] show that the maximum output power P_{MAX} is proportional to the squared surface charge density (σ^2), and is increased with the thickness of electret (*d*). On the other hand, the optimal external load R_{MAX} is independent of σ, but linearly dependent on *d* and *g*. P_{MAX} is also proportional to the time derivative of the overlapping area *dA(t)/dt*. Thus, the vibration frequency, the amplitude of vibration, and the number of poles should also have large impact on the generator performance.

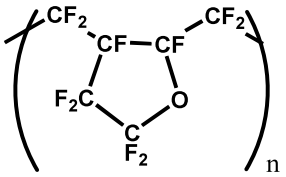
3. POLYMER ELECTRET MATERIAL

Various kinds of materials have been examined for electrets [10]. Among them, polymer dielectric materials, especially fluorinated polymers such as PTFE, are generally employed. Hsich et al. [11] use Teflon® AF (Du Pont) as the electret material for their MEMS microphone.

In our previous work [12], we found that CYTOP™ CTL-809M (Asahi Glass Co., Ltd.), which is amorphous perfluorinated polymer, can be also used for electrets. The candidates of dielectric for electret need to meet the following three requirements;

(a) Compatible with MEMS fabrication technique
(b) Easy to be formed into thick film
(c) Having high dielectric strength

CYTOP™ is compatible with MEMS fabrication process; it is soluble in perfluorinated solvents, and thus thick films can be obtained by multiple spin-coating. In addition, coated films can be patterned easily with photolithography process and O_2 plasma etching.



CTL-A : -COOH
CTX-S : -CF_3
CTL-M : -CONH-C_3H_6-Si(OC_2H_5)$_3$

Fig. 3: The molecular structure and the end groups of CYTOP™.

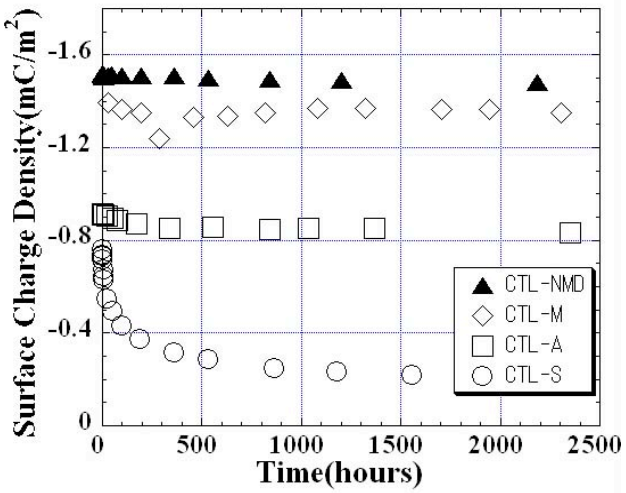
Tsutsumino et al. [7] found that the surface charge density of CYTOP™ is three times larger than that of Teflon® AF. Since power output of electret generator is proportional to the square of the surface charge density, electret generators with CYTOP™ can produce electricity nine times larger than generators with Teflon® AF.

The molecular structure of CYTOP™ is shown in Fig. 3. CYTOP™ is the perfluorinated polymer, so there are no hydrogen atom in the main chain, and that leads to unique properties as follows; (i) high chemical stability in any acids, alkalis, and organic solvents except for perfluorinated solvents, (ii) low surface energy (17 dyne/cm), (iii) high thermal stability (thermal decomposition temp is over 350 ˚C), (iv) low dielectric constant (2.1), (v) high volume resistivity (>10^{17}Ωcm). There are three different types of CYTOP™, which end groups are different respectively; the carboxylic acid type （CTL-A）, trifluoromethyl type (CTL-S), and aminosilane type (CTL-M) [13].

To evaluate the performance of the electret material, we have measured temporal change of the surface charge density σ by using a surface voltmeter (Model279, Monroe Electronics). 16 -μm-thick CYTOP™ was spin-coated on 0.3-mm-thick copper substrate with area of 30x30 cm^2. The sample was charged by corona charging with -8 kV needle voltage for 3 minutes at 120 ˚C.

Figure 4 shows the surface charge density data obtained for CTL-S, CTL-A, CTL-M, and CTL-NMD, which is a new material developed in

the present study. Samples were stored at 23 ˚C and 60 % humidity. This figure shows that 'pure' CYTOP^{TM} CTL-S is the least stable, and the surface charge density is reduced to about 30% of its initial value in 1500 hours. On the other hand,



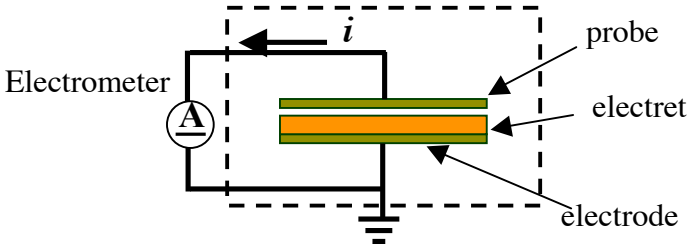
small amount of functional end groups like

Fig. 4: Time trace of the surface charge density of Perfluorinated polymer electret films,CYTOP^{TM} CTL-S, CTL-A, CTL-M and CTL-NMD.

carboxylic acid or aminosilane significantly enhance the electret performance; the surface charge density becomes higher, and the charge decay is suppressed. Especially, aminosilane end group (CTL-M) has the best performance to promote the surface charge density. To introduce more aminosilane into the CYTOP^{TM} electret, we doped silane coupling reagent to CTL-A, accomplished the highest surface charge density of 1.5 mC/cm^2 (CTL-NMD)

To examine the thermal stability of charged electret, the open circuit thermally-discharge (TSD) measurement [14] has also been performed. Different TSD spectra peaks correspond to different charge trap mechanisms in dielectric materials [10, 14]; the peak corresponding to the dipole appears at the lowest temperature near the glass transition temperature (T_g=*108* ˚C). Peaks at the higher temperatures correspond to the surface and bulk traps. Therefore, TSD spectra are very useful for optimizing charging conditions and materials for more stable electrets.

The electret sample (e.g. copper substrate) and a facing probe were connected as shown in Fig.5, and heated up at the rate of 1 ˚C/min. Since the temperature increased, thermal energy was applied to electret and the trapped charges were released. The discharged current was measured with an electrometer (Model 6517A, Keithley Instruments) set into the circuit. As shown in Fig.



6, TSD spectra of CTL-S has a peak at 135 ˚C,

Fig. 5: Experimental setup of Thermally-stimulated-discharge (TSD) measurement.

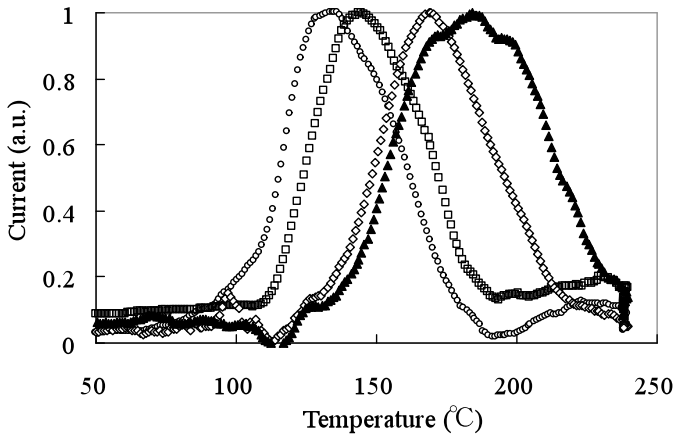


Fig. 6: Thermally-stimulated-discharge (TSD) spectra of CYTOP^{TM} electret films.

which is the lowest among four samples examined. The peak shifted to higher temperature, when the functional end group is introduced into the chemical structure of CYTOP^{TM}. Especially, aminosilane promotes the thermal stability of trapped charge effectively, and the peak temperature of CTL-NMD TSD spectra has been improved to 185 ˚C, which is even higher than that of CTL-M and CTL-A. Therefore, not only the surface charge density, but also the thermal stability of charges can be improved with the doping of silane coupling reagent.

4. POWER GENERATION EXPERIMENT

Figure 7 shows the experimental setup for power generation, which consists of a patterned electret, a counter electrode, an alignment XYZ stage, and an electromagnetic shaker [7,8]. The electret and the counter electrode were microfabricated with standard lithography process. By using multiple spin coating technique, 16 μm-thick electret film was obtained after curing, followed by O_2 plasma etching for patterning.

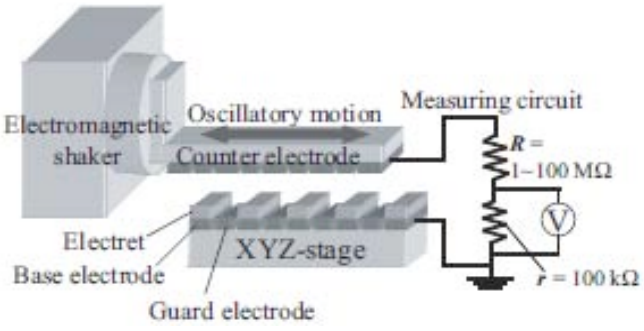


Fig. 7: Schematic of power generation experiment setup.

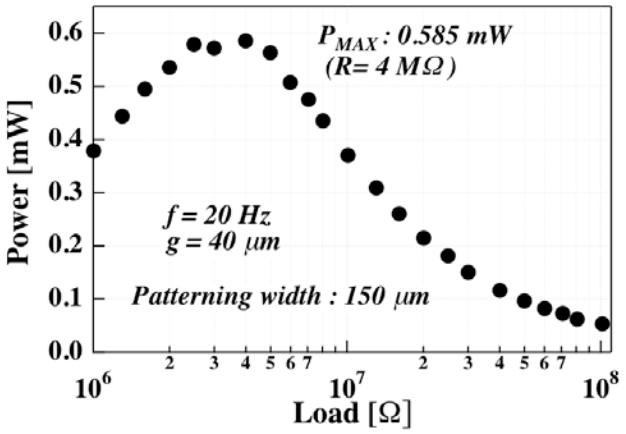


Fig. 8: Power output versus external load.

Finally, corona charging technique was applied to acquire surface potential of more than -550V. Total area of the electret was 20 x 20 mm^2 with an interdigital electrode configuration, where the line/space is 150 μm.

Figure 8 shows the output power with the CTL-M electret thus fabricated versus the external load for the oscillation amplitude of 1.2 mm_{p-p} at 20Hz. Peak power output of 0.595 mW, which is about twice of our previous data [8], has been obtained at the external load of 4 MΩ. Power generation experiment using the new electret material is now undertaken.

5. CONCLUSION

We examined MEMS-friendly perfluorinated polymer CYTOP™ with different functional end groups for electret generator applications through measurements of surface charge density and thermally-stimulated discharge. We have found that the aminosilane end group provides better surface charge density and thermal stability, and developed a novel electret material with the doping of silane coupling reagent. We also have obtained 0.59 mW at a low seismic frequency of 20Hz in our prototype power generator, which is about twice of our previous data.

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