The development of a high-performance perfluorinated polymer electret and its application to micro power generation

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Abstract
Recently, micro power generation using electrets has attracted much attention due to its large power output at a low frequency range. Since the theoretical power output is proportional to the square of the surface charge density of the electret, the development of a high-performance electret is required. In the present study, it is shown that the surface charge density of a CYTOP electret is significantly improved by the addition of terminal groups. Based on this fact, a novel high-performance polymer electret has been developed by doping a silane-coupling reagent into the polymer. A series of measurements of surface potential and TSD (thermally stimulated discharge) spectra was made for various CYTOP films prepared with different silane-coupling reagent concentrations. It is found that the surface charge density, charge stability and thermal resistibility of electric charges are markedly improved by the doping. A surface charge density of 1.5 mC cm^{-2}, which is three times larger than that of Teflon AF, has been obtained on a 15 μm thick film. In addition, the thermal stability of the CYTOP electret is superior to that of Teflon AF. Power generation experiment is also performed using the patterned CYTOP electret of 20 × 20 mm^2. At a low seismic frequency of 20 Hz, 0.7 mW power generation has been accomplished, which is about 2.5 times higher than our previous result.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

An electret is a dielectric material with a quasi-permanent charge. Eguchi [1] first developed a carnauba wax electret using a thermal polarization method. The charge in carnauba wax thus prepared has been stable after 36 years [2]. Since then, various applications of electrets, such as acoustic/mechanical transducers and air filter, have been proposed [3]. Power generation using electret-based electrostatic induction is also demonstrated [4, 5].

More recently, MEMS devices using electrets have been prototyped. Hsieh *et al* [6] developed a MEMS microphone with high sensitivity. Boland *et al* [7] microfabricated a rotational electret power generator and obtained 25 μW

power with a rotor 8 mm in diameter. Tsutsumino *et al* [8, 9] developed a seismic electret generator with 20 × 20 mm^2 grid electrets/electrodes and demonstrated 0.28 mW power generation at an oscillation frequency of 20 Hz. A radiation dosimeter for a batteryless wireless γ-ray sensor [10], a low-voltage droplet manipulation method using liquid dielectrophoresis on an electret (L-DEPOE) [11] and electrostatic levitation using a micro-patterned polymer electret [12] have also been proposed.

For conventional applications of electrets, fluorinated polymer materials, such as PTFE and FEP, are often used. However, they are not compatible with the MEMS processes, since they are insoluble in solvents. In addition, the surface charge density should be improved for higher performance of
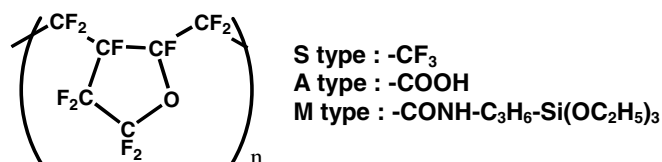
Figure 1. The molecular structure and the end groups of CYTOP.

Figure 2. Schematic of a corona charging setup.

Figure 3. Time trace of the surface charge density of CTL-S for various molecular weights (thickness: 15 μm).

the devices. Hsieh *et al* [6] and Boland *et al* [7] employed Teflon® AF (Du Pont) as their electret film, which is a perfluorinated amorphous polymer. Lo and Tai [13] found that fluorinated parylene (parylene HT®) provides very high surface charge density. We recently reported that CYTOP^{TM} CTL-M (Asahi Glass Co., Ltd), a MEMS friendly amorphous perfluorinated polymer, can provide three times higher surface charge density than that of Teflon AF [8, 9]. Since the theoretical power output of electret generators is proportional to the square of the surface charge density [7], electret generators with CYTOP CTL-M have potential to produce nine times larger power than similarly built generators with Teflon AF.

The objectives of the present study are to develop a new electret material for higher surface charge density and thermal stability based on CYTOP and to evaluate its performance in micro power generation.

2. Development of a high-performance perfluorinated polymer electret

Perfluorinated polymers such as PTFE and FEP are excellent electret material because of their electrostatic property, but it hardly applies to microdevices because of the difficulty of thin-film coating. CYTOP is also a kind of perfluorinated polymer, but it is compatible with a 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 conventional photolithography and O$_2$ plasma etching.

Figure 1 shows the molecular structure of CYTOP, which is characterized by its perfluorinated cyclic structure [14]. Because of its specific chemical structure, CYTOP has a unique combination of properties as follows:

(i) High chemical stability in any acids, alkalis and organic solvents except for perfluorinated solvents and some kinds of partially fluorinated solvents.
(ii) High volume resistivity ($>10^{17}$ Ω cm) and high breakdown strength (>110 kV mm^{-1}).
(iii) Low dielectric constant of 2.1.
(iv) Low water absorption ($<0.01\%$).
(v) Low surface energy (17 dyne cm^{-1}).
(vi) High thermal stability (the thermal decomposition temperature is over 350 °C).
(vii) Excellent optical properties.

Several MEMS applications, such as protective coating for the wet etching process, dielectric for interlayer insulation and hydrophobic coat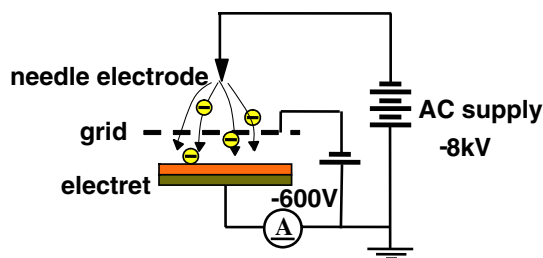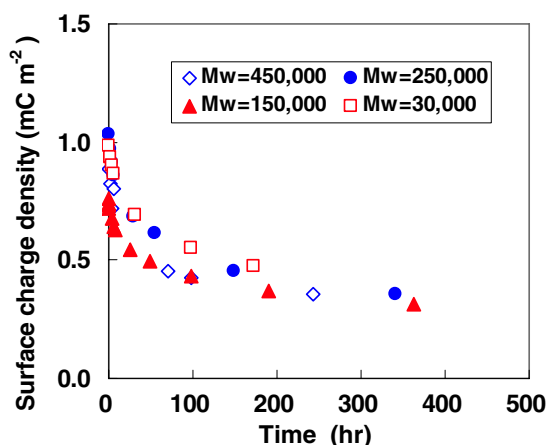ing, have been proposed for these special features. There are three different types of commercial grade CYTOP, with a different end group, i.e., trifluoromethyl (CTL-S), carboxyl (CTL-A) and amidosilyl (CTL-M) [15]. The modification of the end group is performed to increase the physical and chemical properties of CYTOP. CTL-S has excellent transparency and non-adhesion properties because of the absence of a functional end group. Carboxyl end groups of CTL-A form hydrogen bonding with the hydroxyl groups of organic and inorganic substrate, and amidosilyl end groups of CTL-M can form strong chemical bonding with an inorganic substrate to promote the adhesion property dramatically.

2.1. Evaluation of the surface charge density

In order to evaluate the performance of CYTOP as an electret material, the temporal change of the surface charge density σ was examined. A 15 μm thick CYTOP was spin-coated on a 0.3 mm thick copper substrate with an area of 30×30 cm^2. The samples were then charged by a corona charging technique for 3 min as shown in figure 2. The needle and grid voltages are -8 kV and -600 V, respectively. The samples were kept at 120 °C, which is slightly higher than the glass transition temperature ($T_g = 108$ °C) of CYTOP. The samples were stored at 23 °C and 60% humidity. The surface potential was measured with a surface voltmeter (Model 279, Monroe Electronics).

Figure 3 shows the surface charge density of CTL-S, the end group of which is CF$_3$. The molecular weight M_w was
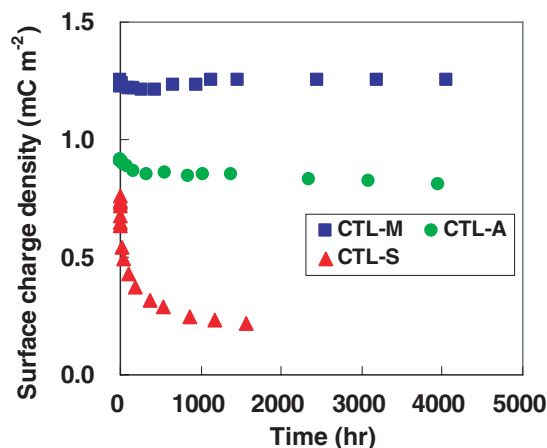
Figure 4. Time trace of the surface charge density of CYTOP with a different end group, i.e., CTL-S, CTL-A and CTL-M (thickness: 15 μm).
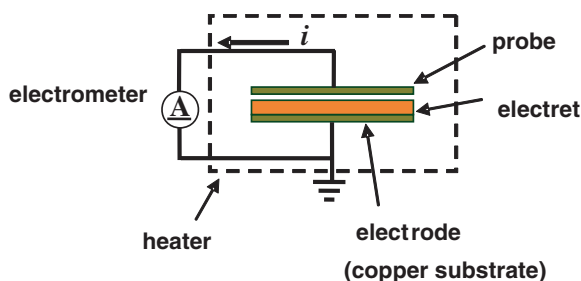

Figure 5. Experimental setup of thermally stimulated discharge (TSD) measurement.

systematically changed from 30 000 to 450 000. Whereas the initial surface charge density is about 1 mC m^{-2}, it is reduced to about 30% of its initial value within 400 h in all the cases. Thus, the molecular weight has a minor effect on the surface charge density. Figure 4 shows the surface charge density of CTL-S, CTL-A and CTL-M. The initial surface charge density of CTL-M is as high as 1.3 mC m^{-2} and it is kept for more than 4000 h. The charge in CTL-A is also stable, but the surface charge density is lower than that of CTL-M. Therefore, a small number of functional end groups such as carboxyl or amidosilyl significantly enhance the electret performance; the surface charge density becomes higher, and the charge decay is suppressed. Especially, among commercial grades of CYTOP, the amidosilyl end group (CTL-M) has the best performance to promote the surface charge density.

2.2. Thermal stability of an electret

In order to examine the thermal stability of charged electrets, the open-circuit thermally stimulated discharge (TSD) measurement [16] has also been performed. Different TSD spectrum peaks correspond to different charge trap mechanisms in dielectric materials [3, 16]; the peak corresponding to the dipole appears at the lowest temperature near the glass transition temperature. Peaks at the higher temperatures correspond to the surface and bulk traps. Therefore, the TSD spectra are very useful for

optimizing charging conditions and materials for more stable electrets.

Figure 5 shows the setup for the TSD measurement. The electret sample is placed against a facing probe and heated up at a rate of 1 °C min^{-1}. When the temperature increased, the trapped charges are released due to the thermal energy. The discharged current is measured with an electrometer (Model 6517A, Keithley Instruments) set into the circuit. In the present study, the TSD peak temperature where the current has a peak is used to compare the TSD data for different materials.

As shown in figure 6(*a*), CYTOP with lowest molecular weight of $M_w = 30\,000$, which has low T_g (see table 1), exhibits large TSD spectra at a relatively low temperature. The peak temperature T_{TSD} is 79 °C. The peak temperatures for CYTOP with higher molecular weights are all higher and around 135–153 °C. On the other hand, T_{TSD} for Teflon AF is higher than that of CTL-S as shown in figure 6(*b*). Thus, the TSD peak temperature T_{TSD} is increased with T_g among the polymer materials examined.

Figure 6(*c*) shows the TSD spectra of CTL-S, CTL-A and CTL-M. The TSD peak temperature T_{TSD} for CTL-S is the lowest. On the other hand, CYTOP samples with a functional end group (CTL-A/CTL-M) have higher T_{TSD} than that for CTL-S. Especially, the introduction of an amidosilyl end group (CTL-M) significantly increases the thermal stability, and T_{TSD} is increased to 170 °C.

2.3. Improvement of the electret property

It is now clear that the amidosilyl end group in CYTOP dramatically improves not only the surface charge density, but also the thermal stability of the charges. This fact encourages us to further increase the concentration of the amidosilyl end group in CYTOP, since the concentration of the amidosilyl in CTL-M is only on the order of few hundreds of ppm. However, the maximum concentration of amidosilyl in CTL-M is limited by the amounts of terminal groups of the polymer. Thus, we employ silane-coupling reagents and mix with CTL-A in order to introduce a large number of amidosilyl into the CYTOP structure. In our preliminary tests, we found that aminosilane (3-aminopropyl(diethoxyl)methylsilane) is the best material for this purpose. Aminosilane is not soluble in perfluorinated solvents for CYTOP, but can be dissolved in a CYTOP solution by adding a few per cent of fluorinated alcohol as a solubilizer.

Figure 7(*a*) shows the surface charge density of a 15 μm thick electret film for different concentrations of aminosilane. By doping only 0.6–3.0% of aminosilane into CTL-A, the surface charge density has been doubled; the surface charge density as high as 1.5 mC m^{-2} has been achieved, and it remains constant over 4000 h. This novel aminosilane-doped electret also possesses the excellent thermal stability of charges. Figure 7(*b*) shows the TSD spectra of aminosilane-doped CTL-A compared with that of CTL-A and CTL-M. The peak temperature is shifted to a much higher temperature of 184 °C.
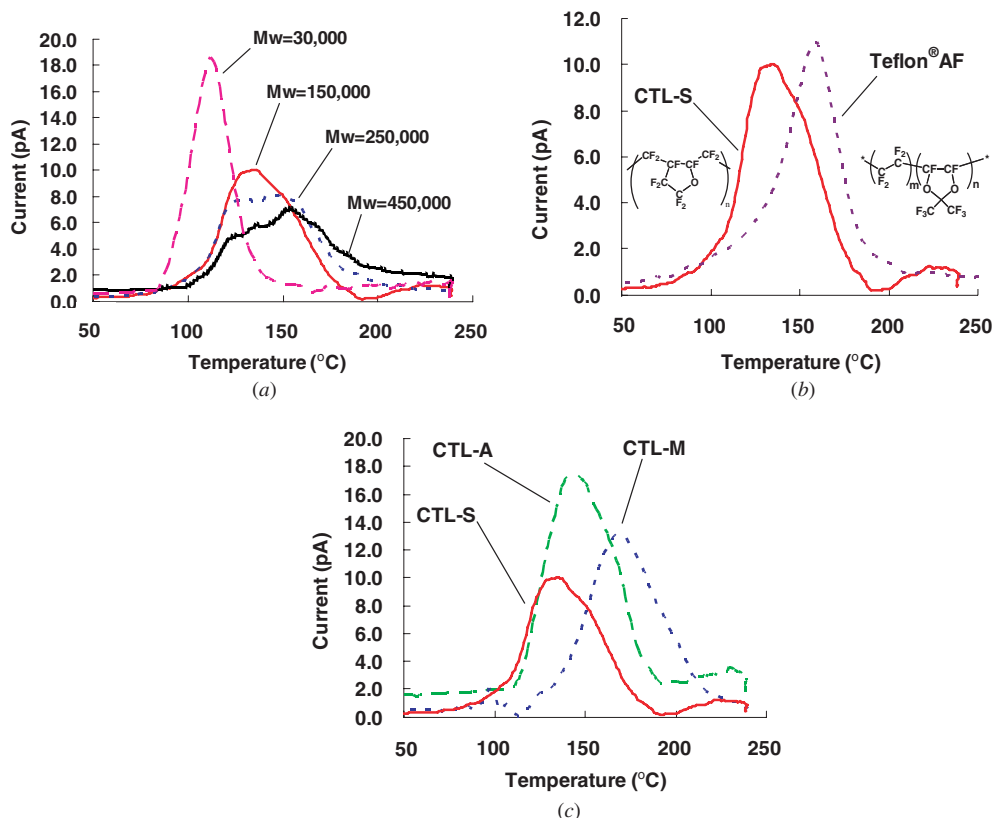
Figure 6. Thermally stimulated discharge (TSD) spectra of CYTOP electret films: (*a*) molecular weight dependence of CYTOP, (*b*) comparison of CYTOP and Teflon AF and (*c*) TSD spectra for different end groups of CYTOP.
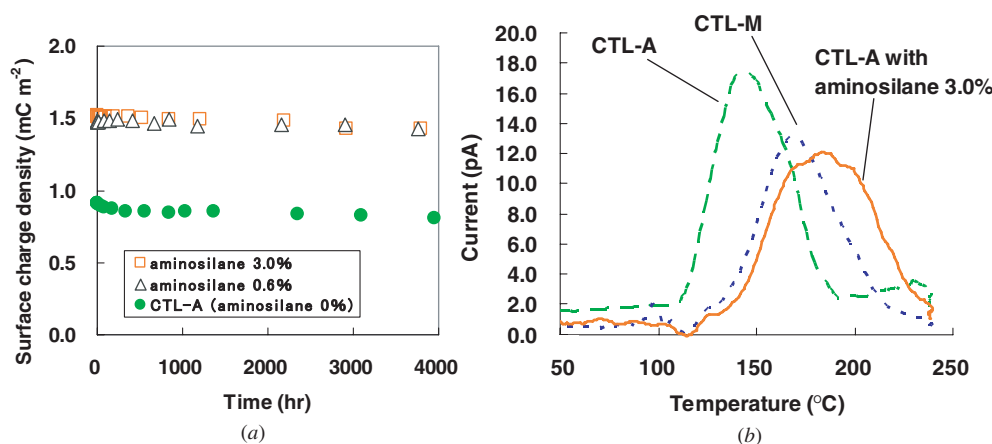

Figure 7. (*a*) Time trace of the surface charge density of aminosilane-doped CYTOP. The amount of doped aminosilane is 0.6% and 3.0% per weight of a CYTOP polymer. (*b*) TSD spectra of CTL-A, CTL-M and aminosilane-doped CYTOP.

3. Evaluation of the new electret material in micro power generation

Figure 8 schematically shows the experimental setup for power generation, which consists of a patterned electret plate, a counter electrode, an alignment XYZ stage and an electromagnetic shaker [8, 9]. The electret and the counter electrode were microfabricated with a standard lithography process. Figure 9 shows the fabrication process of the patterned electret plate. First, a Cr/Au/Cr electrode with a thickness of 20/200/20 nm was deposited on a 0.7 mm thick Pyrex wafer using an electron-beam evaporator, followed by
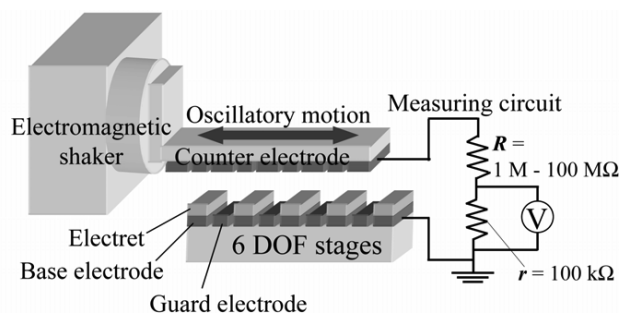

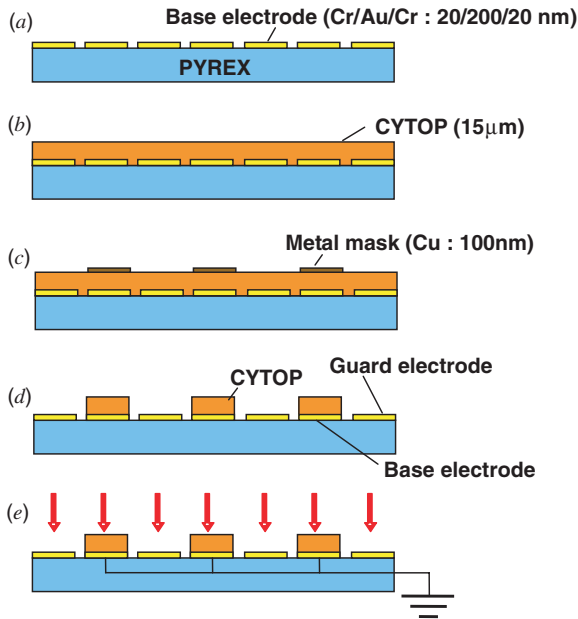**Figure 8.** Schematic of power generation experiment setup.

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Figure 9. The fabrication process of the patterned electret plate: (*a*) deposit and pattern base electrode (Cr/Au/Cr: 20/200/20 nm), (*b*) spin-on and cure electret film, (*c*) deposit and pattern metal mask, (*d*) O_2 plasma etch and remove metal mask and (*e*) corona charging.

Figure 10. A patterned electret plate. The width of both the electret and guard electrode is 150 μm and the total area of the electret is 20×20 mm^2.

Table 1. The molecular weight dependence of the glass transition temperature (T_g) of the perfluoropolymer electret and the peak temperature of its TSD spectra.

	T_g (°C)	TSD peak temperature (T_{TSD}) (°C)
CYTOP ($M_w = 30\,000$)	80	79
CYTOP ($M_w > 150\,000$)	108	135–153
Teflon AF	160	160

patterning with photolithography and wet etching. Then, an aminosilane-doped CTL-A solution (13 wt%) was spun-on at a rotational speed of 1000 rpm for 20 s and pre-baked at 100 °C for 10 min. This coating process was repeated three times to obtain a 15 μm thick film, and then the coated wafer was fully cured at 200 °C for 60 min. Next, a 200 nm thick copper layer was evaporated on the CYTOP layer and patterned as the metal mask. Finally, the electret layer was etched by O_2 plasma with a 100 W RF power for 60–70 min. Figure 10 shows the patterned electret plate fabricated by the procedure described above. The total area of the electret was 20×20 mm^2 with an interdigital electrode configuration, where the line/space is 150 μm. Corona charging was employed to obtain a surface potential of -640 V. The counter electrode was fabricated with the similar process.
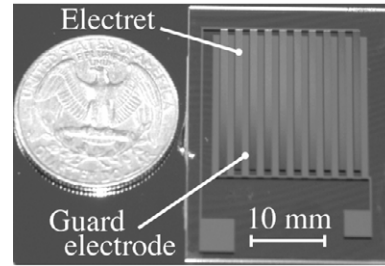
Both substrates are fixed on a six-axis stage in such a way that the surfaces are parallel to each other. The gap between the counter electrode and the top surface of the electret is set at 40 μm. Since the surface potential is higher than the minimum voltage of the Paschen curve in air, the whole setup is installed in a glove box in which SF_6 gas is filled in order to avoid discharge between the electret and the counter electrode. A more detailed experimental procedure can be found in [9].

Figure 11(*a*) shows the output power with the aminosilane-doped CTL-A electret thus fabricated versus the external load for the oscillation amplitude of 1.2 mm$_{p-p}$ at 20 Hz. A peak power output of 0.7 mW, which is about two and a half times higher than our previous result with CTL-M [9], has been obtained at an external load of 2.5 MΩ. The peak-to-peak voltage amplitude is as large as 168 V.
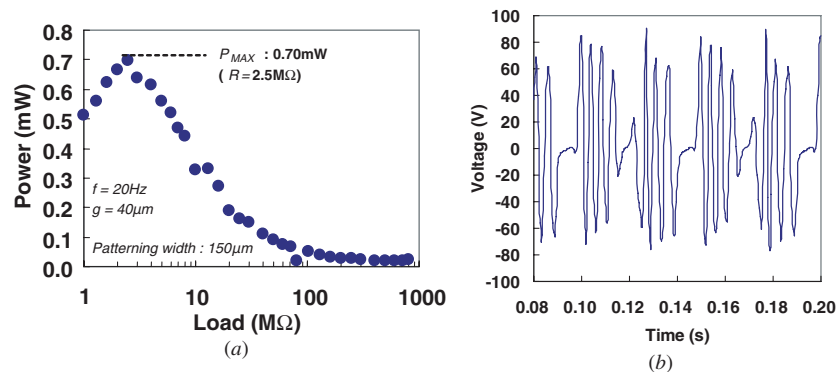

Figure 11. (*a*) Power output versus external load. (*b*) Output voltage signal.

4. Conclusion

We investigated a MEMS friendly perfluorinated polymer CYTOP with different functional end groups for a polymer electret. The surface charge density and thermally stimulated discharge spectra were systematically examined. We have found that the amidosilyl end group significantly improves the surface charge density and the thermal stability. Based on this fact, we have developed a novel electret material by introducing a silane-coupling reagent into the CYTOP polymer. A surface charge density as large as 1.5 mC m^{-2} has been obtained for a 15 μm thick film, and it remains constant over 4000 h. We also evaluated the performance of the present electret film in micro power generation. We have obtained as large as 0.7 mW at a low seismic frequency of 20 Hz, which is about two and a half times higher than our previous result.

Acknowledgments

References

[1] Eguchi M 1925 On the permanent electret *Philos. Mag.* **49** 178–80

[2] Takamatsu T 1991 Life time of thermal electrets of carnauba wax, esters, fatty acids and alcohols *7th Int. Symp. Electrets (Berlin)* pp 106–10

[3] Sessler G M 1998 *Electrets* 3rd edn (Morgan Hill, CA: Laplacian Press)

[4] Jefimenko O D 1978 Electrostatic current generator having a disk electret as an active element *IEEE Trans. Ind. Appl.* **IA-14** 537–40

[5] Tada Y 1992 Experimental characteristics of electret generator using polymer film electrets *Japan. J. Appl. Phys.* **31** 846–51

[6] Hsieh W H, Yao T J and Tai Y-C 1999 A high performance MEMS thin-film Teflon electret microphone *Int. Conf. Solid State Sensors Actuators (Transducers '99) (Sendai)* pp 1064–7

[7] Boland J, Chao C-H, Suzuki Y and Tai Y-C 2003 Micro electret power generator *16th IEEE Int. Conf. MEMS (Kyoto)* pp 538–41

[8] Tsutsumino T, Suzuki Y, Kasagi N and Sakane Y 2006 Seismic power generator using high-performance polymer electret *19th IEEE Int. Conf. MEMS '06 (Istanbul)* pp 98–101

[9] Tsutsumino T, Suzuki Y, Kasagi N, Kashiwagi K and Morizawa Y 2006 *Int. Workshop Micro and Nanotechnology for Power Generation and Energy Conversion Applications (PowerMEMS 2006) (Tokyo)* pp 279–82

[10] Son C and Ziaie B 2006 A micromachined electret-based transponder for *in situ* radiation measurement *IEEE Electron Dev. Lett.* **27** 884–6

[11] Wu T, Suzuki Y and Kasagi N 2008 Electrostatic droplet manipulation using electret as a voltage source *21st IEEE Int. Conf. MEMS 2008 (Tucson)* pp 591–4

[12] Tsurumi Y, Suzuki Y and Kasagi N 2008 Non-contact electrostatic micro-bearing using polymer electret *21st IEEE Int. Conf. MEMS 2008 (Tucson)* pp 511–4

[13] Lo H-W and Tai Y-C 2008 Parylene-HT-based electret rotor generator *21st IEEE Int. Conf. MEMS 2008 (Tucson)* pp 984–7

[14] Yamamoto K and Ogawa G 2005 Structure determination of the amorphous perfluorinated homopolymer: poly [perfluoro(4-vinyloxyl-1-butene)] *J. Fluorine Chem.* **126** 1403–8

[15] *CYTOP^{TM} Technical Bulletin* (Kanagawa, Japan: Asahi Glass Co., Ltd)

[16] Seggern H 1979 Identification of TSC peaks and surface-voltage stability in Teflon FEP *J. Appl. Phys.* **50** 2817–21