# High Voltage Sensitivity of Organic Pyroelectric Sensors with Polarization Treatment during Evaporation Process

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## Abstract

Control of molecular orientation and electric dipoles in a pyroelectric thin film is one of the most important factors to improve the performance of organic infrared ray (IR) sensors. In this study, we have controlled the molecular dipole in a vinylidene fluoride (VDF) oligomer thin film by applying electric field between micro-gapped comb-like electrodes during vacuum deposition. The dipoles in the normally oriented VDF oligomer were highly aligned to the applied electric field in in-plane direction. The pyroelectric IR sensors, fabricated by the oriented VDF oligomer thin film, exhibited the excellent performance even without the poling treatment after the film deposition. A voltage sensitivity of the sensor showed 1473 V/W at 1 Hz, which was much higher value than that of typical sensors applied with the post-poling (~ 200 V/W). The improvement of the sensitivity is considered to be caused by the reduction of injected charges on the poling treatment, which usually causes the suppression of the dipole fluctuations for temperature change.

### 1. Introduction

Ferroelectricity provides a potential ability to develop IR sensors due to their intrinsic pyroelectric nature. The continuous efforts to establish these sensors have been studied on inorganic ferroelectrics. Although these materials based IR sensors have set a performance standard, the use of metal-free nontoxic materials is preferred for future eco-friendly operations. The organic pyroelectric materials are one of promising candidates as lead-free IR sensors.

Among the study of ferroelectric organic materials, poly vinylidene fluoride (PVDF) is one of the potential molecules applied to the sensors, because it has a relatively large pyroelectric coefficient and an applicability to wet processes. Since the pyroelectricity of PVDF originated from a crystalline I phase, it is extremely important to obtain highly crystallized and molecular oriented films for achieving high sensitive sensors. However, PVDF thin films fabricated by spin-coating is a mixture of crystalline and amorphous phases.

To obtain highly the oriented thin films, we previously performed vacuum deposition of VDF oligomer; we found that VDF oligomer could form crystalline I phase with parallel molecular orientation to the substrate at substrate temperature  $(T_s)$  of 123 K. The thin films with parallel molecular orientation exhibited good ferroelectric and pyroelectric performance [1], however, these electric properties disappeared during the device heating due to the changes of molecular ordering from parallel to perpendicular. For realizing the sensors with good thermal stability, we fabricated perpendicularly oriented VDF oligomer thin films by depositing at the  $T_s$ above 243 K [2]. We achieved polarization switching by applying an electric field using micro-gapped comb-like electrodes to exhibit a remnant polarization ( $P_r$ ) of 130 mC/m<sup>2</sup> and pyroelectric coefficient of  $-70 \ \mu C/m^2 K$ , large values among organic ferroelectrics [3]. However, coercive field  $(E_c)$  ranging from 100 to 150 MV/m was required in order for the dipoles to be switched; the VDF oligomer dipoles with the high crystallinity hardly rotated in a response to applied field, causing a possibility of device dielectric breakdown.

In this study, we demonstrate applying electric field to gaseous state VDF oligomer molecules during deposition as effecting way to obtain highly oriented dipoles without the post-poling treatment to provide pyroelectric voltage outputs with good responsivity.

# 2. Experiments

The comb-like gold electrodes were deposited on Si/SiO<sub>2</sub> substrates with the gap of 1.3 µm. The VDF oligomer [CF<sub>3</sub>(CH<sub>2</sub>CF<sub>2</sub>)<sub>17</sub>CF<sub>3</sub>] was deposited in vacuum (10<sup>-4</sup> Pa) while at the T<sub>s</sub> of 323 K. During the deposition, DC voltage of 10 V, which corresponded to electric field of 7.7 MV/m, was applied between the electrodes. The applied electric field in this work is much smaller than the  $E_c$  of typical VDF oligomers (~130 MV/m). The molecular orientation and crystalline phases in the films were evaluated by a Fourier transform infrared (FT-IR) spectroscopy. The pyroelectric responses of the fabricated sensor was measured by the following setup. Incident IR was irradiated to the sensors from the blackbody, and modulated the frequency with a mechanical chopper. The pyroelectric currents were amplified using an IV convertor, and the output voltages were measured with a lock-in amplifier. To evaluate the degree of polarization, especially induced by applying voltage during the deposition, the polarization switching current were measured through a current densities (J) - the electric field (E) characteristics.

# 3. Results and Discussion

Figure 1 shows the FT-IR reflection spectrum of the VDF oligomer thin film obtained by deposition under the electric field. The distinctive absorption peaks at 1415 cm<sup>-1</sup> (CH<sub>2</sub> wagging) and 1076 cm<sup>-1</sup> (CC asymmetric stretching) indicate the ferroelectric I phase formation and perpendicular orientation of VDF oligomers to the substrate.



Fig. 1 FT-IR reflection spectrum of the VDF oligomer thin film fabricated by vacuum deposition under the electric field of 7.7 MV/m.



Fig. 2 Voltage sensitivities of sensors versus the frequency of IR.

Figure 2 shows the voltage sensitivities of the pyroelectric sensors versus the frequency of the modulated IR. The VDF oligomer deposited with applying the small electric field during the depositions exhibited extremely large value taking 1473 V/W at 1Hz, while the conventional sandwich sensor of the VDF oligomer fabricated on Si showed only 70 V/W even after the poling treatment. It should be noted that the value is much large, because the Si/SiO<sub>2</sub> with a large heat capacity will cause the less temperature changes under IR. Since the origin of the pyroelectricity is the releasing of compensated charges due to the dipole fluctuation to the temperature changes, the injected charges introduced in the films disturb the fluctuation and pyroelectric response. These charge injections are usually caused during the poling by the large electric field (> $E_c$ ). Therefore, we attribute the difference in the voltage sensitivity between them to the injection of these charges. For the normally poling-treated devices, the injected charges disturbed the dipole fluctuation. On the other hand, applying electric field during the deposition suppress the injected of charges even though the electric field was enough for the dipoles to orient between the electrodes.

To verify that the electric field applied during the deposition affect the dipole orientation, we carried out ferroelectric hysteresis observation on the VDF oligomer thin film as graphically shown in Fig. 3. The current density peak at around +100 MV/m (position (II)) is caused by the switching of the dipoles which did not orient during the deposition. The peak at around -80 MV/m (position (III)) is attributed to the switching of almost all the dipoles polarized by the application of positive bias. The polarizations calculated from the area of these peaks are about 50 and 150 mC/m<sup>2</sup>, providing the polarization of as-deposited VDF oligomer thin film (position (I)) as  $100 \text{ mC/m}^2$ ; this is the matching value to the one of typical VDF oligomer film poling treated after deposition. The applied electric field during deposition was 7.7 MV/m, an extremely lower value than  $E_c$  of VDF thin film. Large electric field during the deposition is not required for orientation of VDF oligomer dipoles in high-mobility gaseous state.



Fig. 3 *J*–*E* curve of the VDF oligomer thin film fabricated with applying electric field during the deposition.

#### 4. Conclusions

VDF oligomer dipoles highly oriented between the comblike electrodes in in-plane direction with perpendicular molecular ordering and good crystallinity. Large electric field was not required for the dipole orientation, as the electric field efficiently affected the molecular dipoles in high-mobility gaseous state. The pyroelectric sensors consisting of VDF oligomer thin film showed significant increase in the output voltages owing to the dipole orientation and the suppression of the charge injections. Our findings enable the easy, effective fabrication of high performance pyroelectric sensors, permitting the exploitation of organic ferroelectrics as a new pyroelectric sensing device components in the future.

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#### References

- [1] K. Noda et al., J. Appl. Phys. 93 (2003) 2866.
- [2] Y. Yoshida et al., J. Appl. Phys. 36 (1997) 7389.
- [3] T. Inoue et al., Appl. Phys. Express 8 (2015) 111601.