

Heat Resistance Improvement of Deposited Vinylidene Fluoride Oligomer Based-Infrared Sensors by Parylene C Coating

Yohei Sutani¹, Tatsuya Fukushima¹, Akimitsu Mori¹, Yasuko Koshiba¹,
Tetsuhiro Kodani², Takashi Kanemura², and Kenji Ishida¹

¹ Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University

1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan

Phone: +81-78-803-6188 E-mail: kishida@crystal.kobe-u.ac.jp

² DAIKIN INDUSTRIES, LTD.

Umeda Center Building

2-4-12, Nakazaki-Nishi-cho, Kita-ku, Osaka 530-8323, Japan

Abstract

For vinylidene fluoride (VDF)-based pyroelectric sensors, a voltage sensitivity decreases under high-temperature condition because of molecular orientation change and/or re-sublimation of VDF molecules in the films. In this study, we have successfully reduced the performance degradation of the pyroelectric sensors under the condition by poly(chloro-para-xylylene) (Parylene C) deposition on the sensors. The sensors without Parylene C degraded markedly and its voltage sensitivity at 0.2 Hz decreased from 551 to 0.86 V/W after a heat resistance test at 125 °C for 500 hours. Whereas, that with Parylene C reduced the decrease of the sensitivity (from 551 to 430 V/W at the same frequency) owing to preventing the destruction of electrodes with molecular orientation change and sublimation of VDF oligomer thin films.

1. Introduction

The environmentally friendly sensors are needed for realizing the Internet of Things (IoT) society because it is expected that more than 1 trillion sensors will be manufactured each year and up to 45 trillion sensors will be needed in 2040 to manage the society [1-2].

Ferroelectrics are typically used for pyroelectric sensors in order to detect gas, human body, or heat source abnormality. Before now, extensive and intensive researches on inorganic ferroelectrics have been performed energetically [3-5]. However, the inorganic ferroelectrics as typified by lead zirconate titanate (PZT) have a high-environmental load. Thus, it is necessary to study eco-friendly alternative materials to PZT toward the coming age of IoT society that consumes sensors in quantities.

Among the study of organic ferroelectrics, vinylidene fluoride (VDF) materials are one of the potential molecules applied to the infrared-ray (IR) sensors because it has pyroelectricity and applicability to wet processes. Since the pyroelectricity of VDF materials originated from a molecular chain structure (*all-trans*) and a crystalline, it is extremely important to obtain highly crystallized and molecular chain oriented thin films for achieving high-sensitivity sensors. However, VDF polymer thin films fabricated by spin-coating is a mixture of crystalline and amorphous phases.

To obtain highly oriented VDF thin films, we previously

carried out vacuum evaporation of VDF oligomer; we found that VDF oligomer could form a crystalline phase with a parallel molecular orientation to the substrate at a substrate temperature (T_s) of 123 K during evaporation. The parallel oriented thin films exhibited good ferroelectric and pyroelectric performance [6-9]. However, the performance degrades during high-temperature driving, because VDF molecular orientation in the film, like alkane, changes from parallel to perpendicular on a substrate and/or re-sublimation occurs [10].

In this study, we deposited Parylene C layer on the VDF oligomer-based pyroelectric sensor to improve the heat resistance. Parylene C is thermally and chemically stable itself as well as can uniformly covers and adheres the surface of the device without interspaces between Parylene C on the sensor, the molecular orientation change and re-sublimation of VDF oligomers are expected to suppress in the high-temperature.

2. Experiments

A metal-insulator-metal capacitor structure of Al (60 nm) / VDF oligomer (1 μ m) / NiCr (25 nm) was fabricated on a polyethylene terephthalate substrate. Al and NiCr were deposited at T_s of room temperature, and the VDF oligomer was deposited at T_s of 123 K by vacuum evaporation. Poly(chloro-para-xylylene) (Parylene C) was polymerized and film-formed by a chemical vapor deposition method using a vacuum evaporation apparatus. A triangular wave voltage was applied for a polarization treatment. The molecular orientation and crystalline phase in the films were evaluated by a fourier transform infrared (FT-IR) spectroscopy. The pyroelectric responses of the fabricated IR sensors were 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 converted using a resistance and a voltage follower, and the output voltages were measured with a lock-in amplifier. The chopping frequency was varied from 0.2 Hz to 80 Hz, and the frequency dependence of the voltage sensitivity was calculated. The pyroelectric sensor properties before and after heat resistance test based on an Automotive Electronics Council AEC-Q101 Grade 1 (125 °C, 500 hours) were evaluated.

3. Results and Discussion

Figure 1 shows the FT-IR spectra of the VDF oligomer thin films measured by reflection absorption spectroscopy (RAS) and transmission (Trans.) methods. The peaks were reasonably assigned to the VDF oligomer: CF_2 symmetric stretching ($\nu_s(\text{CF}_2)$, 846 cm^{-1}) and CC antisymmetric stretching ($\nu_a(\text{CC})$, 1072 cm^{-1}) modes are observed in Fig. 1. It was confirmed that the VDF oligomer was parallel oriented to the substrate, as $\nu_s(\text{CF}_2)$ was strongly observed in RAS method and $\nu_a(\text{CC})$ was strongly observed in Trans. method.

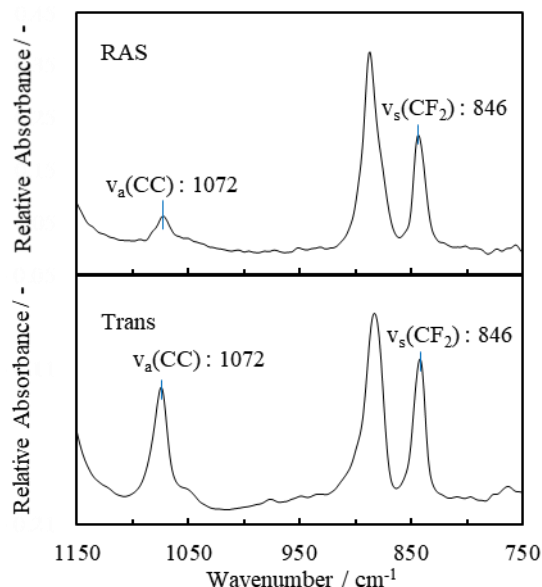


Fig. 1 FT-IR RAS and Trans. spectra of the VDF oligomer thin film fabricated by vacuum evaporation.

Figure 2 (a) shows output voltage waveform of the sensor at a chopping frequency of 0.2 Hz before and after the heat resistance test. For the sensor with Parylene C, breakage of the upper electrode did not observe after heat resistance test, and the output voltage was almost the same before the test. Whereas, the waveform of the sensor without Parylene C drastically changed with a decrease of output voltage and the electrode was partially destroyed after the test. Figure 2 (b) shows the voltage sensitivity versus chopping frequency. The sensitivity of the sensor at 1 Hz with Parylene C layer decreased from 551 to 430 V/W after the test. Although the heating temperature of $125\text{ }^{\circ}\text{C}$ was higher than phase transition temperature [11], the decrease in sensor performance was suppressed to 20% by Parylene C. For the sensor without Parylene C, the sensitivity decreased from 551 to 0.86 V/W at the same frequency. From the results, we considered that Parylene C prevented morphology change owing to the Parylene C layer.

4. Conclusions

In this work, we have investigated the Parylene C coating on VDF oligomer based pyroelectric sensor to improve heat resistance. The decrease in voltage sensitivity was reduced by 20% irrespective of high temperature driving condition. Parylene C layer would prevent molecular orientation change

with the breakdown of upper electrode in the pyroelectric infrared sensor. Our research results will advance in the field of organic pyroelectric sensors and is one of the important knowledge to produce worldwide in the future.

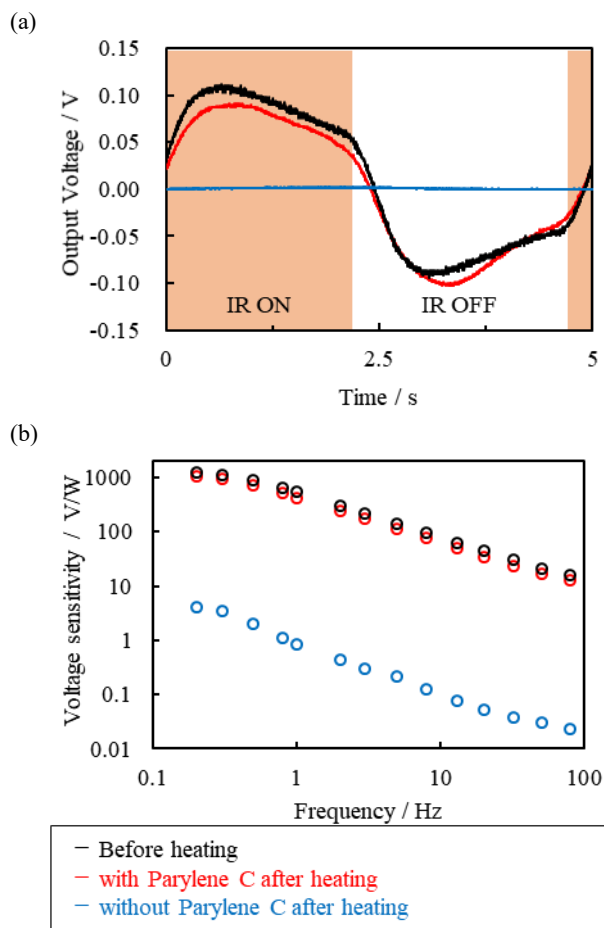


Fig.2 Pyroelectric properties of the fabricated sensors before and after heat resistance test; (a) output voltage waveforms under irradiation of IR at chopping rate of 0.2 Hz, (b) voltage sensitivity versus the chopping frequency of IR irradiation.

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