The Fabrication and Characteristics of the Pyroelectric IR Sensor using P(VDF/TrFE) Thin Films Fabricated by the **Spin Coating Technique**

Sung-yeol Kwon

Abstract - The pyroelectric sensor of P(VDF/TrFE) film as sensing materials has been fabricated and evaluated with another commercial pyroelectric sensor using ceramic materials for sensing. The device was mounted in TO-5 housing to detect infrared light of a $5.5 \sim 14 \mu \text{m}$ wavelength. The NEP(noise equivalent power) and specific detectivity D* of the device were $2.13 \times 10^{-8} \text{ W}$ and 9.37×10^6 cm/W under emission energy of 13 μ W/cm², respectively.

Keywords - pyroelectric, IR, P(VDF/TrFE), thin film, sensors

1. Introduction

Nowadays thermal pyroelectric infrared sensor materials are TGS single crystal, LiTaO3, PbTiO3, PZT, PLT, PVDF (polyvinylidene fluoride) and its copolymer.[1] Ferroelectrics polymers offer several advantages over ceramic and single crystal materials. They are easily fabricated into large sheets and can be cut or bent into a complex shape without damage to the film. Since Kawai^[3] in 1969 made the first observation of pyroelectricity in a uniaxially drawn and poled PVDF, ferroelectric polymers have been intensively investigated.

PVDF film can be used as a sensing element but a mechanical stretching technique is necessary for obtaining the pyroelectric effect.^[1-3] On the other hand, a poled VDF/ TrFE (vinylidene fluoride trifluoroethylene) copolymer film is reported to be pyroelectric without stretching, making it a suitable candidate for pyroelectric sensors. [2-6]

For the realization, a pyroelectric infrared sensor using P(VDF/TrFE) films is fabricated by the spin coating technique. Aluminum electrode formed at both sides of the copolymer film to a capacity type infrared sensor. But if copolymer film thickness is less than a few ten of micrometers, both electrodes shorted. It is a major problem to make a pyroelectric infrared sensor using P(VDF/TrFE) thin films. Moreover, it is necessary to develop a high quality pyroelectric sensor as the industry demand is increasing.

2. Experiments & measurements

The substrate, silicon, has a high thermal expansion coefficient, and FET of the pre amplification part can be in-

tegrated in it. SiO₂ layer of 3000 Å thickness was depos-

ited on the silicon substrate as an insulating layer. An Al bottom electrode was deposited on the SiO₂ layer by a thermal evaporator. The copolymer sample was formed by 67 mol% vinylidene fluoride(VDF) and 33 mol% trifluoroethylene (TrFE), as supplied in powder form by Piezotech S. A. France. A 9.0 ml 2-butanone (Methyl Ethyl Ketone) at 80 °C is used as a solvent. The VDF/TrFE copolymer $(1.0\pm0.1 \text{ g})$ is dissolved in the hot 2-butanone solvent, resulting in a 10 wt%. to concentrate the VDF/TrFE copolymer. During the mixing process, the solution sample is heated up to 80 °C. After the copolymer is completely dissolved, the solution cooled down to room temperature. And then the solution is spun on the Al bottom electrode. The spin coating is performed with two different combinations of the spinning rate and time in succession: (500 rpm, 2 sec.) and (5000 rpm, 30 sec.). The first combination is slow and short allowing the solution to be spread over the whole substrate. The second combination is quicker and takes longer to obtain the desired thickness. An advantage of this two-step spinning is the uniformity of the copolymer thickness. The resulting thickness is $1.6~\mu m$. The thickness of the copolymer is measured by an alpha stepper. (Tencor Co.)

During cooling of the deposited copolymer layer, local shrinking will take place and causes local stresses. [2] To evaporate the remaining 2-butanone solution, recover the local stresses, enhance its crystallization and improve the adhesion between the copolymer and the aluminum electrode. The annealing treatment has been conducted in two steps. First, a sample is annealed at 25 °C for 24 hours. Second, a sample is annealed at 120 °C for two hours. The crystallization of the copolymer will increase. [2,5] The local stresses are recovered. All the 2 - butanone is now evaporated from the copolymer. This annealing temperature is quite lower than the other ceramic material processing. There are more many advantages to fabricate devices. [1-6] A

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Sung-Yeol Kwon is with Division of Electrical Control & Instrumentation Engineering, Pukyong National University, Korea.

3000 Å top aluminum electrode is deposited on the copolymer layer. Because the VDF/TrFE film has a low melting point, a very careful aluminum electrode deposition technique is essential. This aluminum electrode is also used as a mask for etching the copolymer film.

All 2-butanone is now evaporated from the copolymer. But for the adhesion between the copolymer and the aluminum electrode, another annealing treatment is needed. After the top electrode deposition, a sample is annealed at around 160 °C for 10 minutes. The adhesion between the copolymer and the aluminum electrode will also be enhanced. The lamellar becomes thicker, and the improvement of copolymer structure results in a high crystallinity. Then, the temperature is slowly decreased to 25 °C. This process is illustrated in Fig. 2 and 3.

To have an infrared sensor array, pyroelectric copolymer must be patterned.[1,2,4,6] Furthermore, by allowing aluminum wire bonding and IC housing, and the bonding pad have to be freed. Therefore, some areas of the copolymer have to be etched. Wet etching is used to etch the copolymer. Methyl ethyl ketone (2-butanone) is used as an etching solvent with wet etching. Experiments have been carried out to evaluate the etch results. The etch-rate of the copolymer film is around 2 μm/min at 30 °C and increases as the temperature increases. The higher etch rate and etch temperature result in remnant copolymer film on the bottom electrode and the influenced to adhesion between the copolymer film and top electrode is not good. After wet etching process, a sample is annealed at 160 °C for 20 minutes again to enhance the adhesion between the copolymer and the aluminum electrode. Then a sample is annealed at 120 °C for 1 hour to evaporate humidity absorbed in a sample during the wet etching process. Fig. 1 shows a SEM photograph after wet etching using a top electrode as a mask.

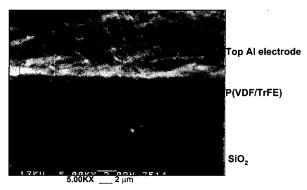


Fig. 1 SEM photograph of P(VDF/TrFE) film after etching.

3. Results and discussion

Table 1. Shows a condition to measure the sensors signal and noise output. The sensor was evaluated with other commercial pyroelectric sensors using PLT thick film and ceramic materials for sensing. The NEP(noise equivalent power) of the sensors using the PLT thick film and ceramics as sensing materials was 6.40×10^{-7} W and 8.08×10^{-7} W. Specific detectivity D* was 2.21×10^{5} cm/W and 2.47×10^{5} cm/W, respectively.

The P(VDF/TrFE) thin film of 1.6 μ m as sensing materials, was fabricated by the spin coating technique, and the NEP and specific detectivity D* of the device was 2.13 \times 10⁻⁸ W and 9.37 \times 10⁶ cm/W. Fig. 7 and 8 are a significant output data (NEP, D*) compared with other pyroelectric infrared sensor using ceramic materials. The pyroelectric sensor of 1.6 μ m of the P(VDF/TrFE) thin film is used sensing materials, the NEP value was one order lower than the other commercial infrared sensor using ceramic materials, and the D* value was one order higher than the other commercial infrared sensor.

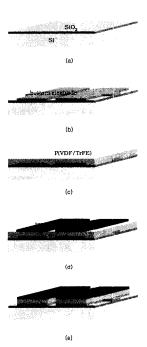
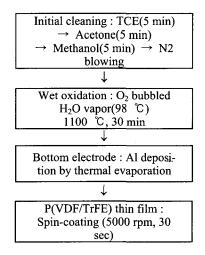


Fig. 2 Schematic diagrams of the fabrication procedure for a pyroelectric sensor.



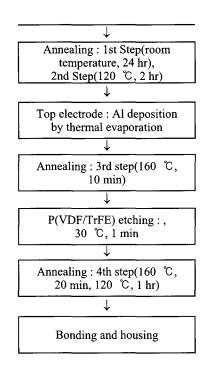


Fig. 3 Flow chart for a pyroelectric sensor.

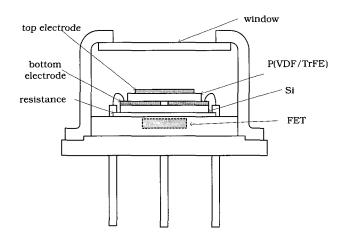


Fig. 4 Schematic diagram of housing sensor.

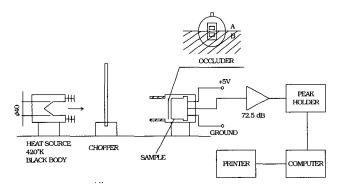


Fig. 5 Schematic diagram of the output signal measurement system.

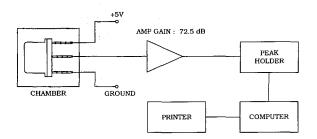


Fig. 6 Schematic diagram of the noise measurement system.

Table 1 Conditions to measure signal and noise output.

Ambient temperature		25 °C
Black body temperature		420 K
Aperture of black body		40 mm
Emission of infrared energy		13 μW/cm²
Chopping frequency		1.0 Hz
Amp. Gain	Signal	72.5 dB(1Hz)
	Noise	72.5 dB
3 dB bandwidth		0.4~4.5 Hz
Stabilization time (noise)		3 min
Measuring time (noise)		20 sec

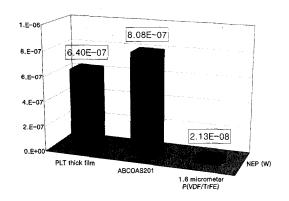


Fig. 7 Data compared with other pyroelectric infrared sensors using ceramic materials. (NEP)

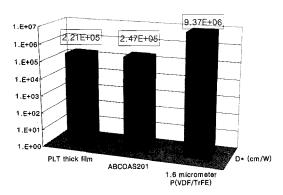


Fig. 8 Data compared with other pyroelectric infrared sensors using ceramic materials. (D*)

4. Conclusion

A pyroelectric sensor of 1.6 μm P(VDF/TrFE) thin film as sensing materials has been fabricated and evaluated with other commercial pyroelectric sensor using ceramic materials for sensing. Also the sensor device was mounted in TO-5 housing to detect infrared light of 5.5 \sim 14 μm wavelength. The NEP(noise equivalent power) and specific detectivity D* of the device were 2.13 \times 10⁻⁸ W and 9.37 \times 10⁶ cm/W under the emission energy of 13 μ W/cm², respectively.

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Sung-Yeol Kwon received the B.S degree in electronic materials engineering from Suwon University in 1990. The M.S degree received from Graduate School of Industry major in electronic materials Kyungpook National University in 1993. And received Ph.D degree in sensor engineering from Graduate

School Kyungpook National University in 2000. From august 2000 to march 2002 he has been with School of Electronic & Electrical Engineering Kyungpook National University as an assistant professor. Since March 2002 he has been with Division of Electrical Control & Instrumentation Engineering at Pukyong National University as a full time instructor. His research interests are sensor & actuator technology using MEMS. He is a member of the Korean sensor society, KIEE, and IEEE.