

Fabrication and Characteristics of Pyroelectric Infrared Sensor Using PbTiO₃/P(VDF/TrFE) Nanocomposites Thin Film (ICCAS 2004)

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Abstract: A pyroelectric sensor using PbTiO₃/P(VDF/TrFE) nanocomposites thin film for sensing materials has been fabricated and evaluated with other commercial pyroelectric sensors that use ceramic materials for sensing. The device was mounted in a TO-5 housing to detect infrared light of 5.5 ~ 14 μm wavelength. The NEP (noise equivalent power) and specific detectivity D* of the device were 1.30 × 10⁻⁸ W and 1.53 × 10⁷ cm/W respectively under emission energy of 13 μW/cm² respectively. This result shows a better characteristic than the other commercial pyroelectric infrared sensors.

Keywords: pyroelectric, nanocomposites, sensor, thin film

1. INTRODUCTION

Thermal pyroelectric infrared sensor materials include TGS single crystal, LiTaO₃, PbTiO₃, PZT, PLT and PVDF (polyvinylidene fluoride) as well as its copolymer.^[1] Ferroelectric polymers offer several advantages over ceramic and single crystal materials. They are easily fabricated into large sheets and can be cut or bent into complex shapes without damage to the film. Therefore, since Kawai^[3], in 1969, made the first observation of pyroelectricity in 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 obtain a pyroelectric effect.^[1-3] On the other hand, a poled VDF/TrFE (vinylidene fluoride trifluoroethylene) copolymer film is reported to be pyroelectric without stretching, thus making it a suitable candidate for pyroelectric sensors.^[2-6] But pyroelectric is low than the other ceramic materials and also it has a piezoelectricity as well. So we using a PbTiO₃/P(VDF/TrFE) nanocomposites thin film for pyroelectric infrared sensor.

For the realization pyroelectric infrared sensors use PbTiO₃/P(VDF/TrFE) films fabricated by the spin coating technique.^[7] Aluminum electrodes are formed at both sides of the copolymer film to capacity type infrared sensor.^[7] However the copolymer film thickness is less than ten micrometers, that the both top and bottom electrode easily shorted. This difficulty is a major problem to make a pyroelectric infrared sensor using PbTiO₃/P(VDF/TrFE) thin film.^[8] in this research the problem is overcome. Moreover it is necessary to develop high quality pyroelectric sensors as industry demand is increasing.

2. EXPERIMENTS & MEASUREMENTS

The substrate, silicon, has a high thermal expansion coefficient, and an FET of the preamplification portion can be integrated into it. A 3000 Å thickness SiO₂ layer was deposited on a silicon substrate as a insulating layer. Al bottom electrode was deposited on an SiO₂ layer by a thermal evaporator. The copolymer sample was formed by using 67 mol% Vinylidene Fluoride(VDF) and 33 mol%

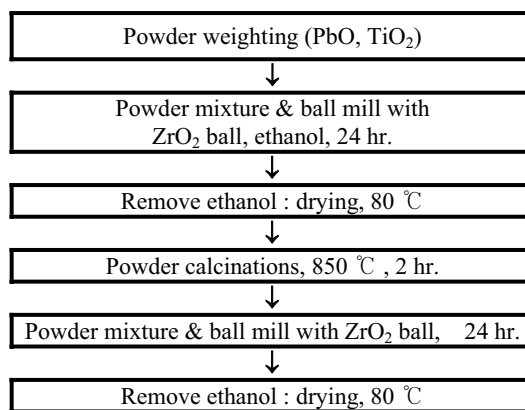


Fig. 1. A process flow chart for manufacture PbTiO₃ powder

trifluoroethylene (TrFE), as supplied by Piezotech S. A. France, in powder form. For a making ceramic-polymer composites thin film, PbTiO₃ ceramic powder used. Figure 1. shows a process for making a PbTiO₃ ceramic powder. . A 9.0 ml 2-butanone (Methyl Ethyl Ketone) at 80 °C was used as a solvent. The VDF/TrFE copolymer (1.0±0.1 g) is dissolved in the hot 2-butanone solvent, resulting in a 10 %wt. concentrating VDF/TrFE copolymer. During the process, the solution sample is heated up to 80 °C. After the copolymer was completely dissolved, the solution cooled down to room temperature. Then PbTiO₃ powder mixed with P(VDF/TrFE) solution. The powder in the mixture was dispersed in an ultrasonic bath for a hour to produce a composite suspension. The agglomerations that were not broken up by ultrasonic agitation settled on the bottom and were discard. The amount of PbTiO₃ powder is adjusted by 0.13 ceramic volume fraction factor. Then the solution was spun on the Al bottom electrode. The spin coating was performed with two different combinations of spinning rates and times in succession: {(500 rpm, 2 sec.) and (5000 rpm, 30 sec.)}. The first combination was slow and short, thus allowing the solution to be spread over the whole substrate. The second combination is quicker and longer, thus allowing us to obtain the desired thickness. An advantage of this two-step

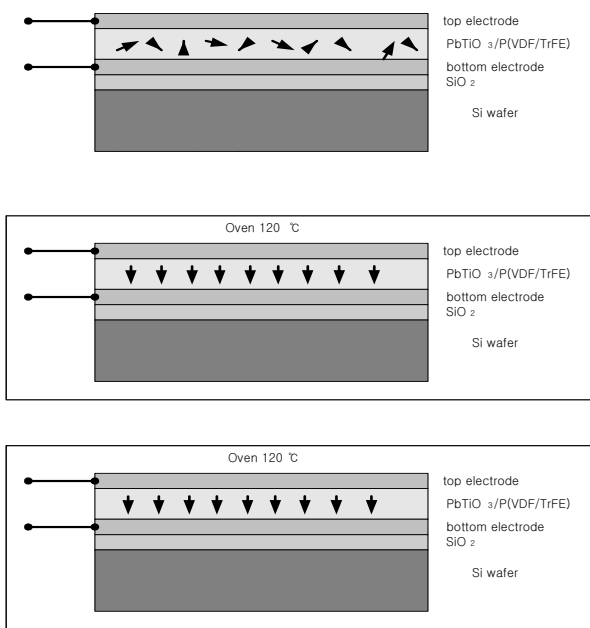


Fig. 2. Poling conditions for PbTiO₃

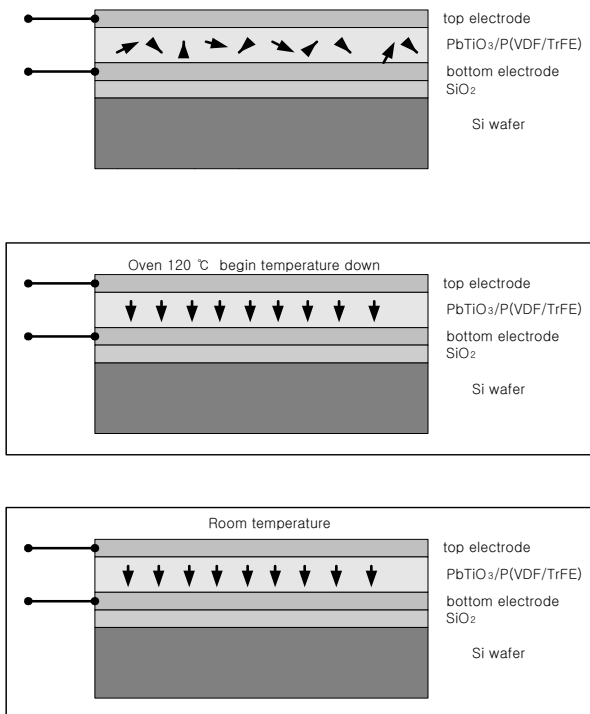


Fig. 3. Poling conditions for P(VDF/TrFE)

spinning is the uniformity of the film thickness. The resulting thickness is a 2.6 μm . The thickness of the film is measured by an alpha stepper. (Tencor Co.)

During the cooling of the deposited composite film layer, local shrinking takes place and causes local stresses.^[2] To evaporate the remaining 2-butanone solution and improve the adhesion between the composite film and the aluminum electrode annealing treatment conducted. This annealing

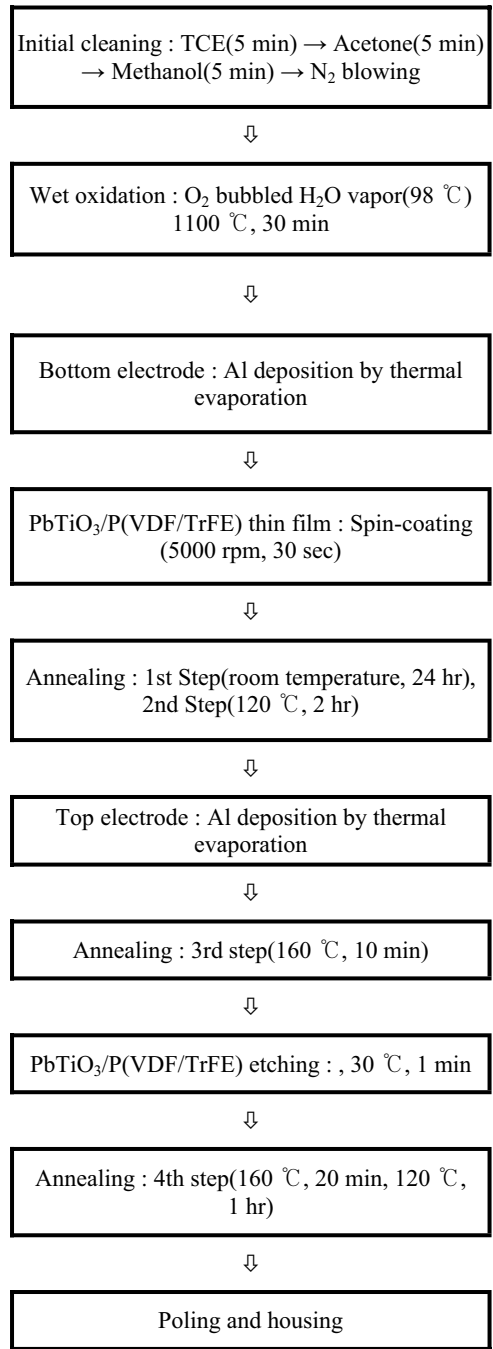


Fig. 4. A flow chart for a pyroelectric sensor.

treatment is 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. The local stresses are also recovered. All 2-butanone is now evaporated from the copolymer. This annealing temperature is quite low than the other ceramic material processing. There are many advantages to fabricating devices as well.^[1-6] A 3000 Å top aluminum electrode is deposited on the composite film layer.

In order to impart polarization to the composite film, it must be poled by applying a high electric field to align the dipoles. A stepwise DC thermal poling in the air used^[11]. To pole the PbTiO₃ in the composite film, the sample was heated

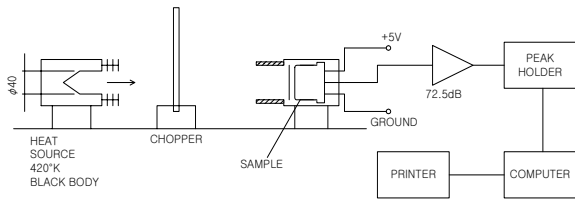


Fig. 5. A schematic diagram of output signal measurement system.

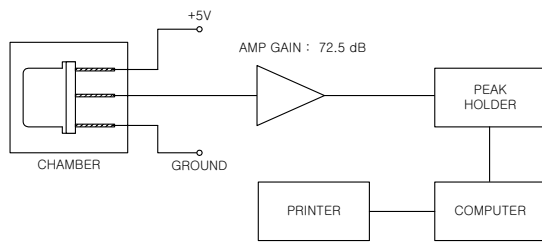


Fig. 6. A schematic diagram of noise measurement system.

Table 1. Signal and noise output measuring conditions.

Ambient temperature	25 °C	
Black body temperature	420 K	
Aperture of black body	40 mm	
Emission of infrared energy	13 $\mu\text{W}/\text{cm}^2$	
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 s	

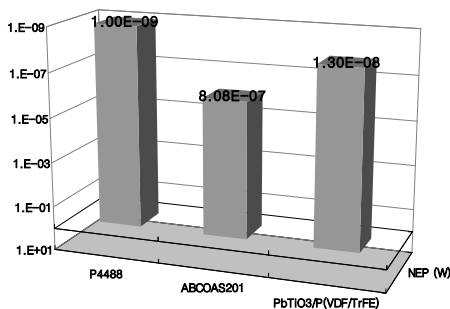


Fig. 7. Data compared with other pyroelectric infrared sensor using ceramic materials. (NEP)

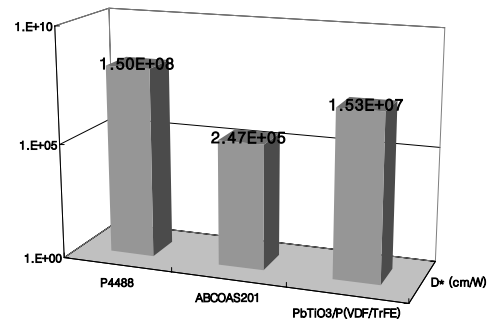


Fig. 8. Data compared with other pyroelectric infrared sensor using ceramic materials. (D^*)

in an oven to a temperature of 110 °C which was above the Curie temperature of P(VDF/TrFE). A DC voltage of 70 KV/mm applied between the top and bottom electrode for 30 min, then the voltage was decreased to zero and the two electrodes was short circuited for 10 min. The short-circuit process would help to relax the internal stress induced during poling, therefore reducing the danger of electrical breakdown. After repeating the above process of applying voltage and short-circuiting, the sample was cooled slowly to room temperature with the field kept on so as to pole P(VDF/TrFE). Then the sample shorted-circuited and annealed for 17 hours at 60 °C to eliminate the contribution of thermally stimulated current in subsequent pyroelectric measurements. Next the temperature is slowly decreased to 25 °C. This poling process is illustrated at Figures 2 and 3.

The device was mounted in a TO-5 housing to shield it from surrounding noises and other interferences. Because there are FET and sheet resistance in a TO-5 package between the sensing area and FET detachment, the length is minimized. Figure 5 shows a schematic diagram of the output signal measurement system. It is also measured on the condition in Table 1. Figure 6 shows a schematic diagram of a noise measurement system. Table 1 shows the signal and noise output measuring conditions. All these measurement system and condition is the same condition for the other commercial pyroelectric infrared sensor.

3. RESULTS AND DISCUSSION

Table 1 shows fabricated sensors signal and noise output measuring conditions. Under this condition, all measurement done. The sensors' signal voltage output was 1.5 V and their noise voltage output was 150.0 mV. And then NEP (noise equivalent power) and detectivity D^* calculated. The NEP and specific detectivity D^* of the PbTiO₃/P(VDF/TrFE) nanocomposites thin film sensor device were 1.30×10^{-8} W and 1.53×10^7 cm/W under emission energy of 13 $\mu\text{W}/\text{cm}^2$ respectively. Figures 7 and 8 shows a compare data with other pyroelectric infrared sensors using ceramic materials. (NEP, D^*).

4. CONCLUSION

A pyroelectric sensor using 2.6 μm PbTiO₃/P(VDF/TrFE) nanocomposites thin film for sensing materials has been

fabricated and evaluated with other commercial pyroelectric sensors that use ceramic materials for sensing. The device was mounted in a TO-5 housing to detect infrared light of $5.5 \sim 14 \mu\text{m}$ wavelength as same as commercial pyroelectric infrared sensor. The NEP (noise equivalent power) and specific detectivity D^* of the device were $1.30 \times 10^{-8} \text{ W}$ and $1.53 \times 10^7 \text{ cm}^2/\text{W}$ respectively under emission energy of $13 \mu\text{W}/\text{cm}^2$. And it is high performance than the other commercial pyroelectric infrared sensor.

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