# The Fabrication and Characteristics of 0-3 $PbTiO_3$/P(VDF/TrFE) Nanocomposite Thin Films for Passive Pyroelectric Infrared Sensors

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**Abstract** - 0-3 $PbTiO_3$/P(VDF/TrFE) nanocomposite thin films for passive pyroelectric infrared sensors were fabricated by a two-step spin coating technique. 65 wt% VDF and 35 wt% TrFE was formed into a P(VDF/TrFE) powder. Nano size $PbTiO_3$ powder was used. 0-3 connectivity of $PbTiO_3$/P(VDF/TrFE) composite film was successfully achieved and observed using SEM photography. The dielectric constant and pyroelectric coefficient were measured and compared with P(VDF/TrFE). A very low dielectric constant (13.48 at 1 kHz) and sufficiently high pyroelectric coefficient (3.101 nC/cm$^2$•k at 50 ℃) were measured. This nanocomposite can be used for a new pyroelectric infrared sensor to achieve better performance.

**Keywords:** $PbTiO_3$/P(VDF/TrFE), Pyroelectric, Sensors, Thin film

## 1. Introduction

Pyroelectricity is the electrical response of a material to a change in temperature. It is found in any dielectric materials containing spontaneous or frozen polarization resulting from oriented dipoles. [1, 15] Nowadays, thermal pyroelectric infrared sensor materials include TGS single crystal, $LiTaO_3$, $PbTiO_3$, PZT, PLT and PVDF (polyvinylidene fluoride) as well as their copolymers. [1, 8] Ferroelectric polymers offer many 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, 15] made the first observation of pyroelectricity in uniaxially-drawn and poled PVDF in 1969, ferroelectric polymers have been intensively investigated. [2, 9-14]

Since the copolymer and composite film thickness is less than ten micrometers, the top and bottom electrodes are easily shorted in the process. As such, they cannot be used for other applications. [7] In this research, this difficulty was overcome by using composite thin films for pyroelectric infrared sensors. The delicate poling process induced to a composite film was also explored. The dielectric and pyroelectric properties of a composite film were investigated for use with a pyroelectric infrared sensor.

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## 2. Fabrication & Measurements

The copolymer was formed by using 67 mol% Vinylidene Fluoride (VDF) and 33 mol% trifluoroethylene (TrFE), as supplied by Piezotech S. A. France, in powder form. In creating a ceramic-polymer composite thin film, newly developed nano size $PbTiO_3$ ceramic powder was used. [14-16] A 9.0 ml 2 -butanone (Methyl Ethyl Ketone) at 80℃ was used as a solvent. The VDF/TrFE copolymer (1.0±0.1 g) was dissolved in the hot 2-butanone solvent, resulting in a 10%wt. concentrating VDF/TrFE copolymer. During the process, the sample solution was heated up to 80℃. Once the P(VDF/TrFE) was completely dissolved, the solution was allowed to cool down to room temperature, at which point $PbTiO_3$ powder was mixed with the P(VDF/TrFE) solution. The powder in the mixture was dispersed in an ultrasonic bath for an hour to produce a composite suspension. The agglomerations that were not broken up by ultrasonic agitation settled on the bottom and were discarded. Only $PbTiO_3$ powder mixed with P(VDF/TrFE) solution was used to make a thin film.

The amount of $PbTiO_3$ powder was adjusted for making a 0.13 and 0.10 ceramic volume fraction factor. To increase the ceramic volume fraction factor of a ceramic-polymer composite film, a greater amount of $PbTiO_3$ powder was added to the solution. However, even though more $PbTiO_3$ powder was added to the solution, it did not increase the ceramic volume fraction factor. The maximum amount of $PbTiO_3$ powder resulted in a 0.13 ceramic volume fraction factor.

The solution was then spun on an 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 entire substrate. The second combination was quicker and longer, thus allowing us to obtain the desired thickness. A 3000 Å top aluminum electrode was deposited on the composite film layer.

During the cooling process of the composite film deposited on the bottom layer of the aluminum, local shrinking took place and caused local stress. [2] To evaporate the remaining 2-butanone solution in the composite film and to improve the adhesion between the composite film and the bottom aluminum electrode, an annealing treatment was conducted. This annealing treatment was conducted in two steps. First, a sample was annealed at 25 ℃ for 24 hours. Second, a sample was annealed at 120 ℃, which is up to the melting temperature of a P(VDE/TrFE) copolymer for two hours. By these annealing treatments the crystallization of the copolymer increased. [2] The local stress in the composite film caused by electrode deposition was also recovered. All 2–butanone (methyl Ethyl Ketone) was by now evaporated from the copolymer in the composite film. Next, a 3000 Å top aluminum electrode was deposited on the composite film layer. This annealing process and electrode deposition were performed at quite low temperatures compared to other commercial ceramic sensor material processing systems [1-6], one of just several advantages to fabricating these devices. [1-6]

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 was used. [11] To pole the $PbTiO_3$ in the composite film, the sample was heated in an oven to a temperature of 110 ℃, which was above the Curie temperature of P(VDF/TrFE). A DC voltage of 70 KV/mm was applied between the top and bottom electrode for 30 min, then the voltage was decreased to zero and the two electrodes were short circuited for 10 min. The short-circuiting process relaxed the internal stress induced during the poling process, therefore reducing the risk of electrical breakdown. After repeating the above process of applying voltage and short-circuiting, the sample was cooled slowly for more than 2 hours until it reached room temperature with the field kept on so as to pole P(VDF/TrFE). Then the sample shorted-circuited and annealed for 24 hours at 60 ℃ to eliminate the contribution of thermally stimulated current in subsequent pyroelectric measurements.

Using the XRD analyses method, $PbTiO_3$ confirmed peroveskite structure. The thickness of the composite film was measured by an alpha stepper. (Tencor Co.) The resulting thickness was 2.6 μ m. Usually when taking a SEM picture of P(VDF/TrFE) film, the film burns out by a high energy electron beam from the SEM. Therefore, it was very difficult to see the surface of the polymer film. [2, 11 & 15] However, in this research, the particle size of the $PbTiO_3$ powder was measured by SEM photography successfully. The composite film dielectric constant measured by impedance analyzer (HP4192A) and pyroelectric coefficient was measured by a semiconductor parameter analyzer (HP4145B).

## 3. Results & Discussion

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.)}. An advantage of this two-step spinning is the resulting uniformity of the film thickness, which is 2.6 μm. That is a very thin film as compared to other ceramic-polymer composite films. [15]

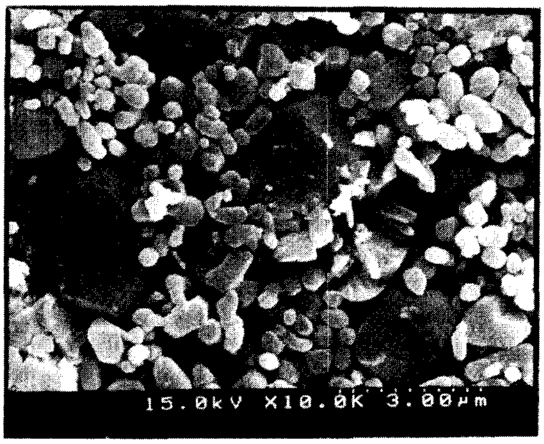


**Fig. 1** SEM microphotography of $PbTiO_3$ powder

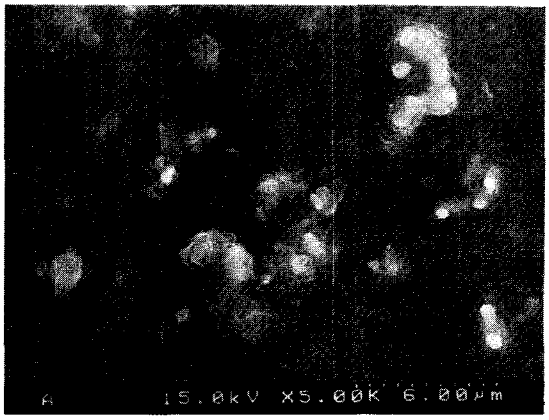


**Fig. 2** Scanning electron micrograph for $PbTiO_3$/P(VDF/TrFE) composite thin film after annealing. ($\psi$ = 0.13)

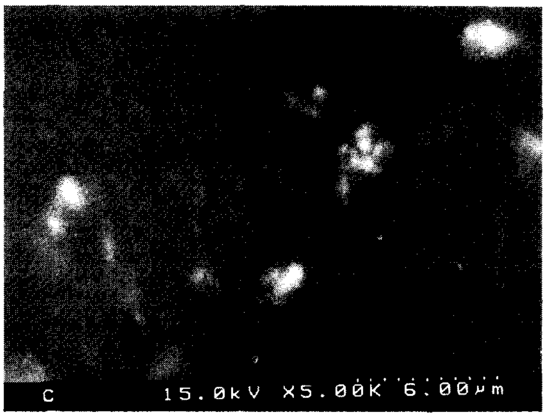


**Fig. 3** Scanning electron micrograph for $PbTiO_3$/P(VDF/TrFE) composite thin film after annealing. ($\psi$ = 0.10)

Fig. 1 shows a SEM microphotograph of $PbTiO_3$ powder that was used to form a composite film. From the picture we can see the majority of particle size is 300 nm with a few 3 μm larger size particles having been formed. Because the film thickness of the composite is less than 3 μm, it can form a 0-3 connectivity with the polymer layer. [15] Fig.s 2 and 3 show the composite surface SEM photography. SEM photography shows a $PbTiO_3$ ceramic and P(VDF/TrFE) creating a 0-3 connectivity that is clearly difficult to see so far. [15] It can be seen that the films are quite homogeneous and there are no large agglomerations of $PbTiO_3$ particles. [18] Furthermore from Fig.s 2 and 3 by the ceramic volume fraction factor, the $PbTiO_3$ powder differential quantities in the composite film is verified. All three SEM photographs confirm uniform ceramic dispersion within a film so that it is a 0-3 connectivity rather than a 1-3 connectivity. [15]

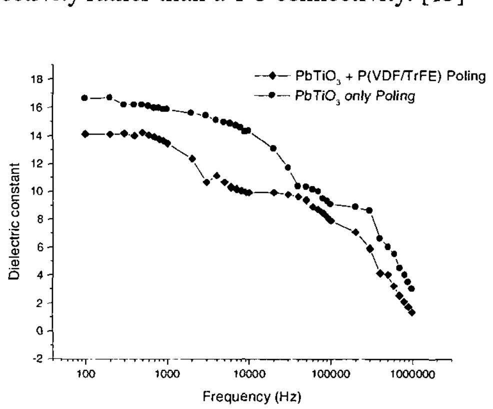


**Fig. 4** Dielectric constant of $PbTiO_3$/P(VDF/TrFE) composite thin film as a function of frequency.($\psi$ = 0.13)

Fig. 4 shows only $PbTiO_3$ poled within a composite film to be a higher dielectric constant than $PbTiO_3$ and P(VDF/TrFE), which are both poled in composite films. This double kind of poling technique is done very carefully. [14, 15 & 17]

These results mean that when poling is performed above the Curie temperature of P(VDF/TrFE), P(VDF/TrFE) was not effected during the $PbTiO_3$ poling process. As well $PbTiO_3$ and P(VDF/TrFE) both poled in the same direction of net dipoles showed that the dielectric constant was lower than when only $PbTiO_3$ was poled. As expected, the only dielectric constant that $PbTiO_3$ poled within a composite was 15.87 at 1 kHz.

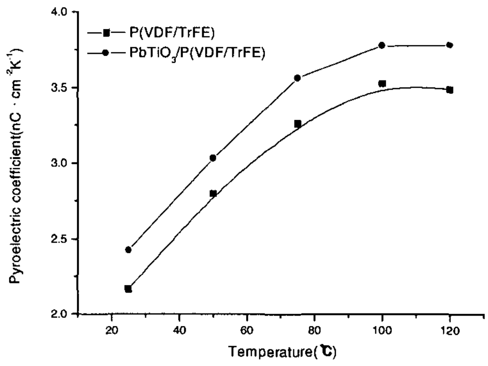


**Fig. 5** Pyroelectric coefficient of the P(VDF/TrFE) films and PbTiO3/P(VDF/TrFE) composite thin film($\psi$ = 0.13) as a function of temperature.

The pyroelectric coefficient of 0-3 connectivity $PbTiO_3$ /P(VDF/TrFE) nanocomposite film is more enhanced than P(VDF/TrFE).

Fig. 5 shows a pyroelectric coefficient of poled P(VDF/TrFE) film and $PbTiO_3$ /P(VDF/TrFE) nanocomposite film. The pyroelectric coefficient of $PbTiO_3$/P(VDF/TrFE) composite film is 3.101 nC/cm$^2$•k at 50℃. That is a higher pyroelectric coefficient than ordinary P(VDF/TrFE) that is 2.798 nC/cm$^2$•k at 50℃.

## 4. Conclusions

A $PbTiO_3$/P(VDF/TrFE) 0-3 nanocomposite thin film with a 0.10 and 0.13 of ceramic volume fraction factor were fabricated by a two-step spin coating technique and characterized. 0-3 connectivity of $PbTiO_3$/P(VDF/TrFE) composite film was observed by SEM photography successfully. Using these SEM pictures, the composite film connectivity was confirmed to be 0-3. As well, from the measurement of various dielectric constant and pyroelectric coefficient films, all merits of 0-3 $PbTiO_3$/P(VDF/TrFE) nanocomposite film were greater than P(VDF/TrFE). [16] Therefore, both the low dielectric constant and the high pyroelectric coefficient of composite thin film can be used for a new pyroelectric infrared sensor in order to achieve superior performance.

## Acknowledgement

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