[논 문] 한국재료학회지
Kor. J. Mater. Res.
Vol. 17, No. 4 (2007)

Pyroelectric Characteristics of 0-3 $PbTiO_3$/P(VDF/TrFE) Nanocomposites Thin Films for Infrared Sensing

Sung-Yeol Kwon†

Department of Electrical Control and Instrumentation Engineering, Pukyong National University, San 100 Young-Dong, Nam-Gu, Pusan, 608-739, Korea

(2006년 9월 11일 받음, 2006년 12월 12일 최종수정본 받음)

Abstract 0-3$PbTiO_3$/P (VDF/TrFE) nanocomposites thin films for passive pyroelectric infrared sensor have been fabricated by two-step spin coating technique. 65 wt% VDF and 35 wt% TrFE was formed to a P(VDF/TrFE) powder Nano size $pbTiO_3$ powder was used. 0-3 connectivity of $PbTiO_3$/P(VDF/TrFE) composites film is achieved and also observed by SEM photography successfully. The dielectric constant, and pyroelectric coefficient measured and compared with P (VDF/TrFE). A very low dielectric constant (13.48 at 1 kHz) and high enough pyroelectric coefficient (3.101 $nC/cm^2 \cdot k$ at 50°C) neasured. This nanocomposites can be used for a new pyroelectric infrared sensor for better performance.

Key words $PbTiO_3$/P(VDF/TrFE), Nanacomposites, Pyroelectric.

1. Introduction

This study made a composite showing higher pyroelectric characteristic than P(VDF/TrFE) by putting nono-size $PbTiO_3$, which is ceramic, into P(VDF/TrFE) poloyer that is used as the material of pyroelectric infrared sensors. Pyroelectricity is the electrical response of a material to change in temperature. It is found in dielectric materials containing spontaneous or frozen polarization resulting from oriented dipoles.[1,2,5] Nowadays, thermal pyroelectric infrared sensor materials include TGS (Triglycine Sulphate) single crystal, $LiTaO_3$, $PbTiO_3$, PZT, PLT and PVDF (polyvinylidene fluoride) as well as its copolymer. 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 in 1969 Kawai made the first observation of pyroelectricity in uniaxially-drawn and poled PVDF, ferroelectric polymers have been intensively investigated.[1-4,6-14]

The copolymer was formed using 67 mol% vinylidene fluoride (VDF) and 33 mol% trifluoroethylene (TrFE) supplied by Piezotech S. A., France in powder. To make a composite film, newly developed nano-size $PbTiO_3$ ceramic powder was used. A 9.0 ml 2-butanone (Methyl-Ethyl Ketone) at 80°C was used as a solvent. During the process, the sample solution is heated up to 80°C. After P(VDF/TrFE) was completely dissolved, the solution was cooled down to room temperature. Then $PbTiO_3$ 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.[6] Agglomerations that were not broken up by ultrasonic agitation settled on the bottom and were discarded.

The amount of $PbTiO_3$ powder was adjusted for making 0.13 and 0.10 ceramic volume fraction factor. Then the solution was 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 spread over the whole substrate. The second combination is faster and longer, thus allowing us to obtain the desired thickness. An advantage of this two-step spinning is the uniformity of the film thickness. The thickness of the film is measured by an alpha stepper (Tencor Co.). The resulting thickness was a 2.6 μm. The dielectric and pyroelectric properties of the composite film were investigated for a pyroelectric infrared sensor.

2. Results and Discussion

Fig. 1 shows a SEM microphotograph of $PbTiO_3$ powder

†Corresponding author
E-Mail : sungyeol@pknu.ac.kr (S. - Y. Kwon)

used to form a composite film. In the picture we can see that the majority of particles are 300 nm large.

So it can be a form of 0-3 connectivity with polymer layer.[15] Fig. 2 and 3 show SEM photographs of the composite surface. The SEM photographs show that a $PbTiO_3$ ceramic and P(VDF/TrFE) make 0-3 connectivity clearly, which has been difficult to observe so far.[15] We can see that the films are quite homogeneous and there are no large agglomerations of $PbTiO_3$ particles. In addition, according to ceramic volume fraction factor, $PbTiO_3$ powder had different quantities in the composites film. The SEM photographs confirm that the film makes uniform ceramic dispersion within in a film, so it is 0-3 connectivity, not 1-3 connectivity.[15]

Fig. 4 shows that the dielectric constant is higher when only $PbTiO_3$ was poled in the composite than when both $PbTiO_3$ and P(VDF/TrFE) were poled. This result indicates that poling was performed above the Curie.

The graph shows that P(VDF/TrFE) is not affected by $PbTiO_3$ poling when the $PbTiO_3$ poling is performed at temperature higher than the Curie temperature of P(VDF/TrFE). And, as expected, the dielectric constant

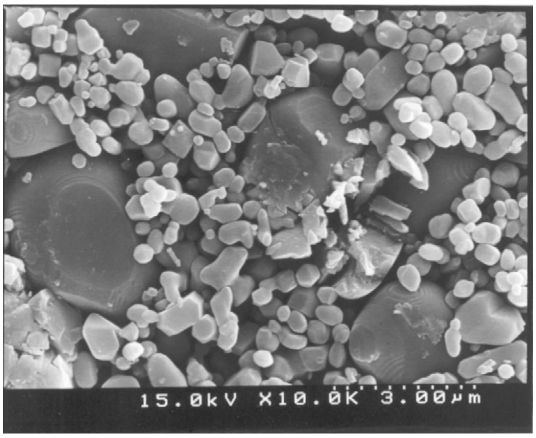

Fig. 1. SEM microphotograph for $PbTiO_3$ powder.

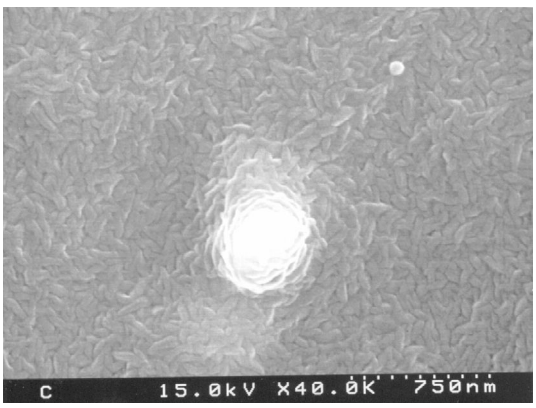

Fig. 2. SEM micrograph for $PbTiO_3$/P(VDF/TrFE) composite thin film after annealing. ($\psi = 0.13$)

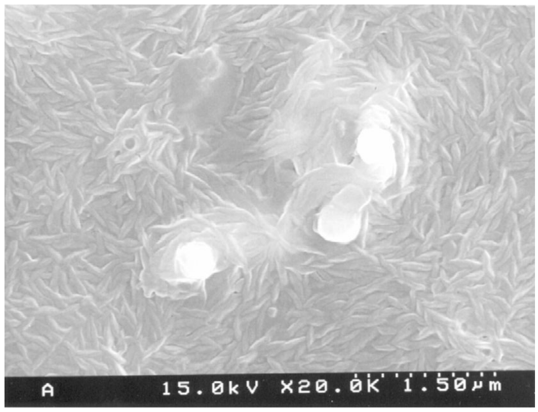

Fig. 3. SEM micrograph for $PbTiO_3$/P(VDF/TrFE) composite thin film after annealing. ($\psi = 0.10$)

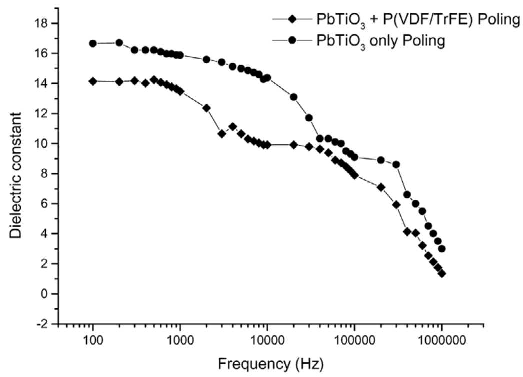

Fig. 4. Dielectric constant of $PbTiO_3$/P(VDF/TrFE) composite thin film as function of frequency. ($\psi = 0.13$)

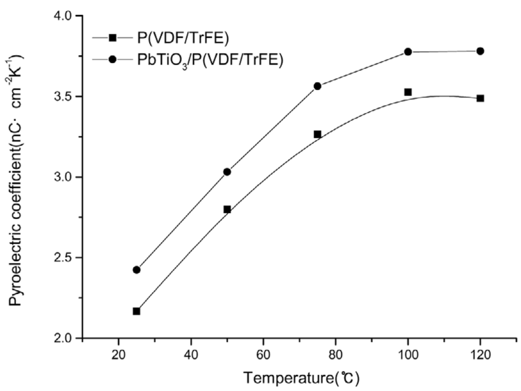

Fig. 5. Pyroelectric coefficient of P(VDF/TrFE) film and $PbTiO_3$/P(VDF/TrFE) composite thin film ($\psi = 0.13$) as a function of temperature.

was lower when both $PbTiO_3$ and P(VDF/TrFE) were poled in the same direction at net dipoles than when only $PbTiO_3$ was poled. The dielectric constant was 15.87 at 1 kHz when only $PbTiO_3$ was poled within the composite, and 13.38 when both $PbTiO_3$ and P(VDF/TrFE) were poled. The pyroelectric coefficient of 0-3 connectivity $PbTiO_3$/P(VDF/TrFE) nano-composite film was enhanced more than that of P(VDF/TrFE). Fig. 5 shows the pyroelectric coefficient of poled P(VDF/TrFE) film and $PbTiO_3$/P(VDF/TrFE) nano-composite film. The pyroelectric coefficient of $PbTiO_3$/P(VDF/TrFE) composite film was 3.101 $nC/cm^2 \cdot K$ at 50^oC. This is higher than that of ordinary P(VDF/TrFE), which is 2.798 $nC/cm^2 \cdot K$ at 50^oC.

$PbTiO_3$/P(VDF/TrFE) 0-3 nano-composite thin films with 0.10 and 0.13 of ceramic volume fraction factor have been fabricated by the two-step spin coating technique and analyzed. 0-3 connectivity of $PbTiO_3$/P(VDF/TrFE) composite film was observed successfully by SEM photography. The SEM picture confirmed 0-3 connectivity. And, in all properties, 0-3 $PbTiO_3$/P(VDF/TrFE) nano-composite film was superior to P(VDF/TrFE) copolymer. Therefore, with the good low-dielectric constant and high pyroelectric coefficient, the composite thin film can be used for a new pyroelectric infrared sensor for higher performance.

Acknowledgments.

This wok was supported by Korea Research Foundation Grant funded by the Korean Government (MOEHRD). (KRF-2005-214-D00299)

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