

속보

적외선 감지를 위한 0~3 PbTiO₃/P(VDF/TrFE) 복합체 필름의 향상된 초전 특성

권성열[†]

부경대학교 전기공학과

(2011년 3월 28일 접수, 2011년 5월 27일 수정, 2011년 6월 8일 채택)

Improved Pyroelectric Characteristics of 0~3 PbTiO₃/P(VDF/TrFE) Composites Films for Infrared Sensing

Sung-Yeol Kwon[†]

Department of Electrical Engineering, Pukyong National University,
599-1, Daeyeon 3-dong, Nam-gu, Busan 608-737, Korea

(Received March 28, 2011; Revised May 27, 2011;

Accepted June 8, 2011)

초록: 두 단계 스핀 코팅 방법을 사용하여 세라믹 체적 분율 0.10과 0.13의 PbTiO₃/P(VDF/TrFE) 0~3형 복합체료를 제작하고 분석하였다. 0~3형 PbTiO₃/P(VDF/TrFE) 복합체료를 SEM 전자현미경 사진으로 성공적으로 확인할 수 있었다. 이러한 전자현미경 사진을 통하여 복합체료의 0~3형 구조를 재확인하였다. 0~3형 PbTiO₃/P(VDF/TrFE) 복합체료는 P(VDF/TrFE) 공중합체보다 센서용 전기적 특성이 우수함을 나타내었다. 그러므로 이러한 낮은 유전상수와 높은 초전계수를 나타내는 0~3형 PbTiO₃/P(VDF/TrFE) 복합체료는 더 높은 성능을 나타낼 수 있는 새로운 초전형 센서 재료로 사용될 수 있다.

Abstract: PbTiO₃/P(VDF/TrFE) 0~3 composites thin films with 0.10 and 0.13 of ceramic volume fraction factor have been fabricated by two-step spin coating technique and analyzed. 0~3 connectivity of PbTiO₃/P(VDF/TrFE) composites film was observed successfully by SEM micrography. The SEM picture confirmed 0~3 connectivity. And, in all the properties, 0~3 PbTiO₃/P(VDF/TrFE) composites film was superior to P(VDF/TrFE) copolymer. Therefore, with a good low-dielectric constant and a high pyroelectric coefficient, the composite thin films can be used for a new pyroelectric infrared sensor of higher performance.

Keywords: PbTiO₃, P(VDF), P(VDF/TrFE), composites, infrared.

Introduction

This study made a composites showing a higher pyroelectric characteristic than P(VDF/TrFE) by putting PbTiO₃, which is ceramic, into P(VDF/TrFE) polymer 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 triglycine sulphate(TGS) single crystal, LiTaO₃, PbTiO₃, PZT, PLT, poly(vinylidene fluoride) (PVDF) and their copolymers. 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 damaging 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 PbTiO₃ 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 PbTiO₃ 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 Agglomerates that were not broken up by ultrasonic agitation were settled on the bottom and discarded.

The amount of PbTiO₃ powder was adjusted for making 0.13 and 0.10 ceramic volume fraction factors. 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 2.6 μm. The dielectric and pyroelectric properties of the composite film were investigated by an impedance analyzer (HP4192A) and a semiconductor parameter analyzer (HP4145B) for a pyroelectric infrared sensing.

Results and Discussion

Figure 1 shows a SEM microphotograph of PbTiO₃ powder used to form a composite film. We can see that the majority of particles are 300 nm large. So it can be a form of 0~3

[†]To whom correspondence should be addressed.
E-mail: sungyeol@pknu.ac.kr

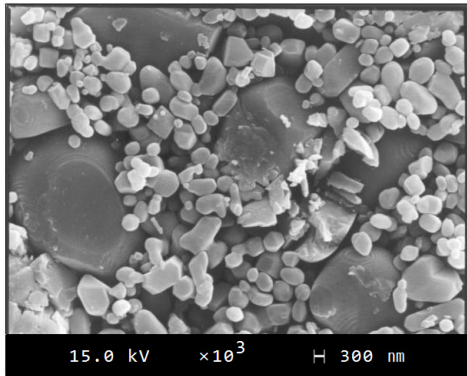


Figure 1. SEM micrograph for PbTiO_3 powder.

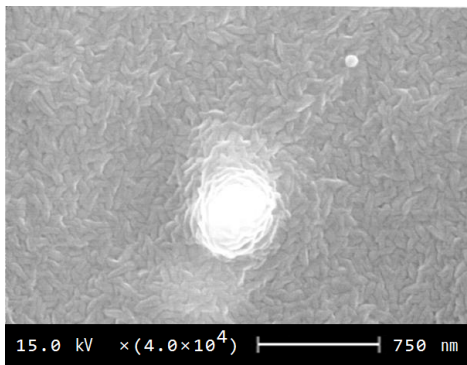


Figure 2. SEM micrograph for $\text{PbTiO}_3/\text{P(VDF/TrFE)}$ composite thin film after annealing ($\psi=0.13$).

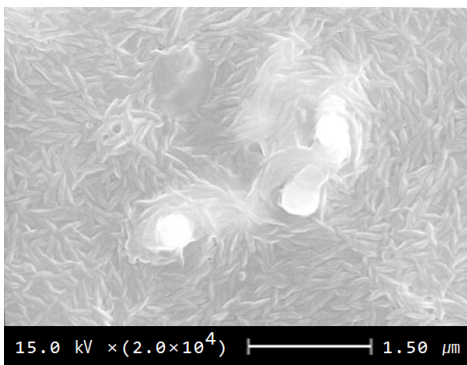


Figure 3. SEM micrograph for $\text{PbTiO}_3/\text{P(VDF/TrFE)}$ composite thin film after annealing ($\psi=0.10$).

connectivity with polymer layer.^{15–18} Figures 2 and 3 show SEM photographs of the composite surface. The SEM photographs show that a PbTiO_3 ceramic and P(VDF/TrFE) lamellar crystals make 0~3 connectivity clearly, which has been difficult to observe so far.^{15–18} 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 factors, PbTiO_3 powder had different quantities in the composites film. The SEM photographs confirm that

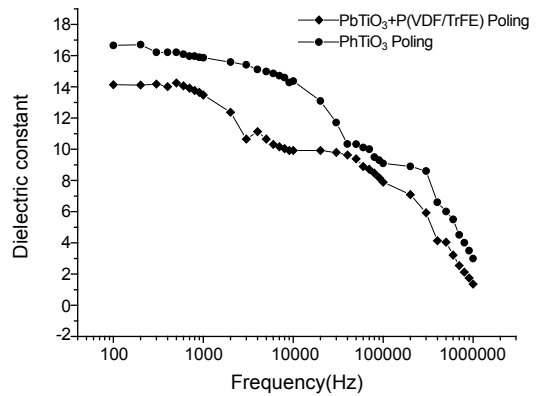


Figure 4. Dielectric constant of $\text{PbTiO}_3/\text{P(VDF/TrFE)}$ composite thin film as function of frequency ($\psi=0.13$).

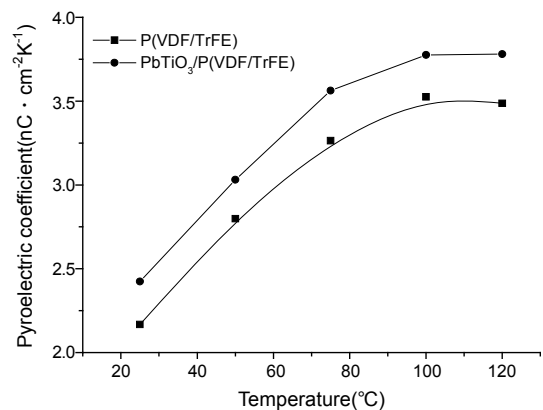


Figure 5. Pyroelectric coefficient of P(VDF/TrFE) film and $\text{PbTiO}_3/\text{P(VDF/TrFE)}$ composite thin film ($\psi=0.13$) as a function of temperature.

the film makes uniform ceramic dispersion within in a film, so it is 0~3 connectivity, not 1~3 connectivity.^{15–18}

Figure 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 temperature of P(VDF/TrFE).

Figure 5 shows that P(VDF/TrFE) in the composites thin film is not affected by PbTiO_3 poling process because the PbTiO_3 poling is performed at temperature higher than the Curie temperature of P(VDF/TrFE). As expected, the dielectric constant 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 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 $\text{PbTiO}_3/\text{P(VDF/TrFE)}$ nano-composite film was enhanced more than that of P(VDF/TrFE). Figure 5 shows the pyroelectric

coefficient of poled P(VDF/TrFE) film and PbTiO₃/P(VDF/TrFE) nano-composite film. The pyroelectric coefficient of PbTiO₃/P(VDF/TrFE) composite film was 3.101 nC/cm² · K at 50 °C. It is higher than that of ordinary P(VDF/TrFE), which is 2.798 nC/cm² · K at 50 °C.

A PbTiO₃/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 PbTiO₃/P(VDF/TrFE) composite film was successfully observed by SEM photography. The SEM picture confirmed 0~3 connectivity. And, in all properties, 0~3 PbTiO₃/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.

References

1. S. B. Lang, *Source Book of Pyroelectricity*, Gordon & Breach, London, 1974.
2. J. H. Kim, T. K. Park, H. Lee, and D. J. Lee, *Polymer (Korea)*, **3**, 101 (1995).
3. W. S. Kim, H. S. Song, B. O. Lee, K. H. Kwon, Y. S. Lim, and M. S. Kim, *Macromol. Res.*, **10**, 253 (2002).
4. H. Kawai, *Jpn. J. Appl. Phys.*, **8**, 975 (1969).
5. G. H. Kim, *Macromol. Res.*, **12**, 564 (2004).
6. J. G. Ryu, J. W. Lee, and H. Kim, *Macromol. Res.*, **10**, 187 (2002).
7. W. Ruppel, *Sens. Actuators A*, **31**, 225 (1992).
8. A. Lozinski, F. Wang, A. Uusimaki, and S. Leppavuori, *Meas. Sci. Technol.*, **8**, 33 (1997).
9. H. Kawai, *Jpn. J. Appl. Phys.*, **8**, 975 (1969).
10. R. J. Phelan, Jr., R. J. Mahler, and A. R. Cook, *Appl. Phys. Lett.*, **19**, 337 (1971).
11. D. Setiadi, P. P. L. Regtien, and P. M. Sarro, *Sens. Actuators A*, **52**, 103 (1996).
12. S. Y. Kwon and K.-W. Kim, *J. Korean Sensors Society*, **3**, 226 (1999).
13. R. E. Newnham, D. P. Skinner, and L. E. Cross, *Mater. Res. Bull.*, **13**, 525 (1978).
14. Y. Xu, *Ferroelectric Materials and Their Application*, Elsevier Science Publishers B. V., Amsterdam, 1991.
15. D. K. Das-Gupta, *Ferroelectric Polymers and Ceramic-Polymer Composites*, Trans Tech Publications, Switzerland, 1994.
16. T.-W. Son, J.-H. Kim, W.-M. Choi, F.-F. Han, and O.-K. Kwon, *Polymer(Korea)*, **35**, 130 (2011).
17. S.-K. Kim, J.-H. Ryu, H.-D. Kwon, C. H. Chang, and S.-H. Cho, *Polymer(Korea)*, **34**, 126 (2010).
18. S. Y. Kwon, *Journal of the Institute of Signal Processing and Systems(Korea)*, **3**, 74 (2002).