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속보

적외선 감지를 위한 0~3 $PbTiO_3$/P(VDF/TrFE) 복합체 필름의 향상된 초전 특성

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Improved Pyroelectric Characteristics of 0~3 $PbTiO_3$/P(VDF/TrFE) Composites Films for Infrared Sensing

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초록: 두 단계 스핀 코팅 방법을 사용하여 세라믹 체적 분율 0.10과 0.13의 $PbTiO_3$/P(VDF/TrFE) 0~3형 복합재료를 제작하고 분석하였다. 0~3형 $PbTiO_3$/P(VDF/TrFE) 복합재료를 SEM 전자현미경 사진으로 성공적으로 확인할 수 있었다. 이러한 전자현미경 사진을 통하여 복합재료의 0~3형 구조를 재확인하였다. 0~3형 $PbTiO_3$/P(VDF/TrFE) 복합재료는 P(VDF/TrFE) 공중합체보다 센서용 전기적 특성이 우수함을 나타내었다. 그러므로 이러한 낮은 유전상수와 높은 초전계수를 나타내는 0~3형 $PbTiO_3$/P(VDF/TrFE) 복합재료는 더 높은 성능을 나타낼 수 있는 새로운 초전형 센서 재료로 사용될 수 있다.

Abstract: $PbTiO_3$/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 $PbTiO_3$/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 $PbTiO_3$/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: $PbTiO_3$, P(VDF), P(VDF/TrFE), composites, infrared.

Introduction

This study made a composites showing a higher pyroelectric characteristic than P(VDF/TrFE) by putting $PbTiO_3$, 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, $LiTaO_3$, $PbTiO_3$, 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 $PbTiO_3$ ceramic powder was used. A 9.0 mL 2-butanone (methyl ethyl ketone) at 80 ℃ was used as a solvent. During the process, the sample solution is heated up to 80 ℃. 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] Agglomerates that were not broken up by ultrasonic agitation were settled on the bottom and discarded.

The amount of $PbTiO_3$ 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 $PbTiO_3$ 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

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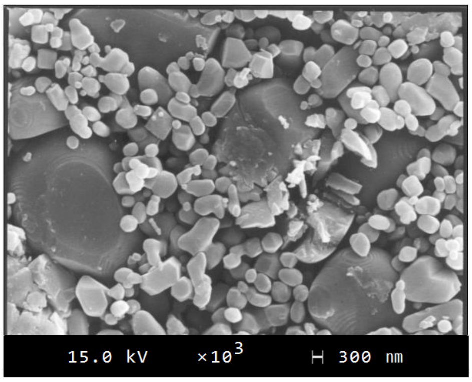

Figure 1. SEM micrograph for $PbTiO_3$ powder.

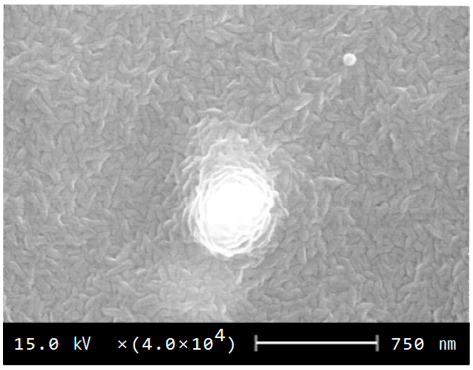

Figure 2. SEM micrograph for $PbTiO_3$/P(VDF/TrFE) composites thin film after annealing(ψ=0.13).

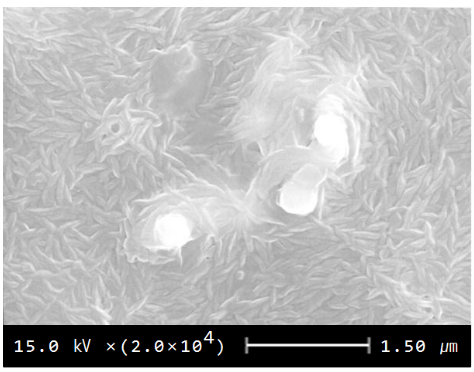

Figure 3. SEM micrograph for $PbTiO_3$/P(VDF/TrFE) composites thin film after annealing(ψ=0.10).

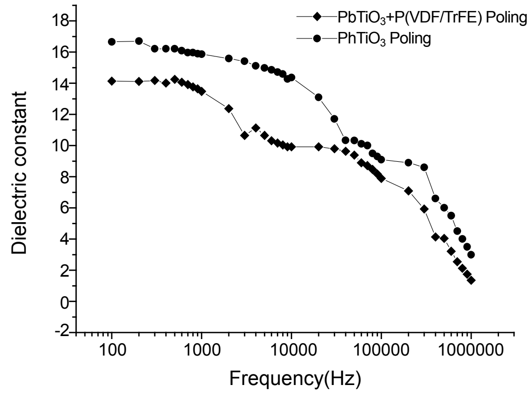

Figure 4. Dielectric constant of $PbTiO_3$/P(VDF/TrFE) composites thin film as function of frequency(ψ=0.13).

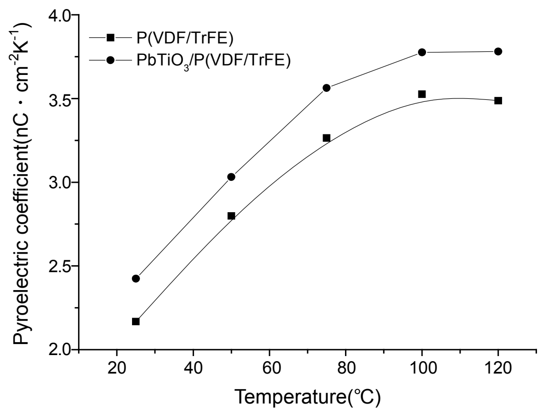

Figure 5. Pyroelectric coefficient of P(VDF/TrFE) film and $PbTiO_3$/P(VDF/TrFE) composites thin film (ψ=0.13) as a function of temperature.

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 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 $PbTiO_3$/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 $PbTiO_3$/P(VDF/TrFE) nano−composite film. The pyroelectric coefficient of $PbTiO_3$/P(VDF/TrFE) composite film was 3.101 nC/cm^2·K at 50 ℃. It is higher than that of ordinary P(VDF/TrFE), which is 2.798 nC/cm^2·K at 50 ℃.

A $PbTiO_3$/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 successfully observed 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.

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