Structure and Dielectric Properties of Plasma Polymerized P(VDF-TrFE) Film for Piezoelectric Nanogenerator

Eun Young Jung[1,2], Choon-Sang Park[3], and Heung-Sik Tae[2,4*]

[1]*The Institute of Electronic Technology, College of IT Engineering, Kyungpook National University, Daegu 41566, Korea*
[2]*School of Electronic and Electrical Engineering, College of IT Engineering, Kyungpook National University, Daegu 41566, Korea*
[3]*Electrical Engineering, Milligan University, TN 37682, USA*
[4]*School of Electronics Engineering, College of IT Engineering, Kyungpook National University, Daegu 41566, Korea*

Abstract: This work investigates the structrure and dielectric properties of P(VDF–TrFE) thin films that is grown by atmospheric pressure plasma (APP) process. The deposited P(VDF–TrFE) thin film shows an thickness of 4 µm. The deposited films were subjected to heat treatment on hotplate in air at 140°C. As a results, after heat treatment, the post-heated thin film has a smooth surface with P(VDF-TrFE) nanoparticles and crystalline phases (α and β phases). The detailed experimental results are under study and will be discussed in detail.

Keywords: Atmospheric pressure plasmas; plasma deposition; PVDF-TrFE thin film

1. Introduction

Currently, the developments tendency of piezoelectric nanogenerator, will be portable and stretchable electronic devices with light weight [1]. From this point of view, the polyvinylidene fluoride (PVDF) and its copolymers have good attractive attention in field of piezoelectric nanogenerator device due to their advantages such as mechanical flexibility, lightweight, piezoelectricity, dielectric property, thermal stability, and high chemical resistance, and good biocompatibility [1,2]. However, for these polymers, the dielectric coefficient and piezoelectricity are relatively low, compared to ceramic substances, such as barium titanate and lead zirconate titanate [2]. To further industrialize the application of piezoelectric polymers, it is necessary to exploit piezoelectric polymer with a high dielectric. Much research has been mostly performed on the point view of piezoelectric polymer materials [1-3]. Accordingly, we investigated the structure and dielectric properties of the deposited P(VDF-TrFE) thin film by APP process according to the heat treatment temperatures by using field emission-scanning electron spectroscopy (FE-SEM), X-ray diffractometer (XRD), Fourier transforms-infrared spectroscopy (FT-IR), and impedance analyzer.

2. Experimental setup

P(VDF-TrFE) powder was used as purchased. To prepare a P(VDF-TrFE) polymer solution with a content of 5%, a weigh of 1.95 g of P(VDF-TrFE) solid powder was diluted in a mixture with 40 mL DMF liquid solvent. This polymer solution was uniformly mixed on hotplate with a magnetic stirring bar for 24 h at 40°C to assure complete dissolution. The mixed polymer solution with DMF was coated on silicone substrates by our proposed APP technique [4,5]. After that, the deposited P(VDF-TrFE) film was subjected to heat treatment on hotplate in air for 3 h. The detailed conditions for P(VDF-TrFE) thin film fabricated by APP process are indicated in Table 1.

Table 1. Detailed conditions of P(VDF-TrFE) thin film fabricated by using atmospheric pressure plasma (APP) process used in this study.

Precursor liquid solution	5% P(VDF-TrFE) + 95% DMF
Driving voltage waveform	AC sinusoidal
Voltage (V_{p-p})	25 kV
Frequency	26 kHz
Argon pressure for vapor	500 sccm
Ar main gas pressure	2500 sccm
Bluff-body height	15 mm
Deposition time	1 h
Deposition temperature	Room temperature
Post-heating temperature	140°C
Post-heating time	3 h

The P(VDF-TrFE) thin film was evaluated on the surface structure and piezoelectric phase by using a FE-SEM imaging with 3 kV and 10 µA, respectively. The structural properties of P(VDF-TrFE) thin film were characterized by an X-ray diffractometer and Fourier transformation infrared spectroscopy. XRD diffraction signals were obtained with 2θ angle in the range of 10° to 50° and CuKα emission (λ= 1.54Å) was employed as the X-ray beam source. The ATR-FTIR spectra were acquired at a wavenumber resolution interval of 0.6 cm^{-1} in the region from 650 to 4000 cm^{-1} by using attenuated total reflection (ATR) conditions. To measure the capacitance and dielectric coefficient, a unit capacitor structure with a metal-insulator-metal capacitor films was used in the form of a sandwich type for measurement. The capacitance of P(VDF-TrFE) thin film was estimated in ranging frequency of 100 Hz and100 kHz by using an impedance analyzer at room temperature in air. And then, the dielectric coefficient was calculated from the measured capacitance values as following equation.

$$C = \varepsilon_o \varepsilon_r A/d$$

, where C is the measured capacitance, ε_r is the dielectric coefficient, A is the area of metal electrode, d is the film thickness and ε_o is the permittivity of vacuum. The thickness of P(VDF-TrFE) thin film was obtained using a profilometer.

3. Results

Figure 1 shows FT-IR results of P(VDF-TrFE) thin films deposited by APP process before and after heat treatment at 140ºC. As shown in Figure 1, all P(VDF-TrFE) thin films show mostly two crystalline phases (α and β phases), which represents the peaks at 1288 and 1400 cm^{-1} for β-phase and the peak at 765 and 975 cm^{-1} for α-phase, respectively [3,6]. The characteristic peaks caused by the DMF solvent primarily had two peaks at 1032 and 1664 cm^{-1}, which was identified to -C-N and -C=O bonds, respectively [5]. In Figure 1, it was confirmed that two peaks caused by the DMF component largely reduced after heat treatment at 140ºC. Thus, the formation of two phases can be contributed to the increment in the dielectric coefficient of P(VDF-TrFE) thin film.

Figure 2 represents the FE-SEM results of P(VDF-TrFE) thin films after heat treatment at 140ºC. The film thickness of post-heated P(VDF-TrFE) thin film was confirmed to be about 4 μm with a stylus profiler. After heat treatment at 140ºC, the deposited film has a smooth surface with P(VDF-TrFE) nanoparticles, as shown in Figure 2. Moreover, it was confirmed from SEM measurement that small amount of bubble particles due to the DMF solvent was attached to the P(VDF-TrFE) thin film.

4. Conclusions

In summary, we examined the structural and dielectric characteristics of P(VDF-TrFE) films by APP process, after heat treatment at 140ºC. After heat treatment at 140ºC, it can be observed that the post-heated thin film has a smooth surface with P(VDF-TrFE) nanoparticles. In FT-IR result, the post-heated films show mostly two crystalline phases (α and β phases), which represents the peaks at 1288 and 1400 cm^{-1} for β-phase and the peaks at 765 and 975 cm^{-1} for α-phase, respectively. Based on the experimental results, these two peaks contributed to the enhancement in the dielectric coefficient of P(VDF-TrFE) thin film after heat treatment at 140ºC. The additional experiment results of P(VDF–TrFE) thin film using FE-SEM, FT-IR, XRD, and impedance analyser are under study in terms of various heating temperatures and will be discussed in detail.

5. References

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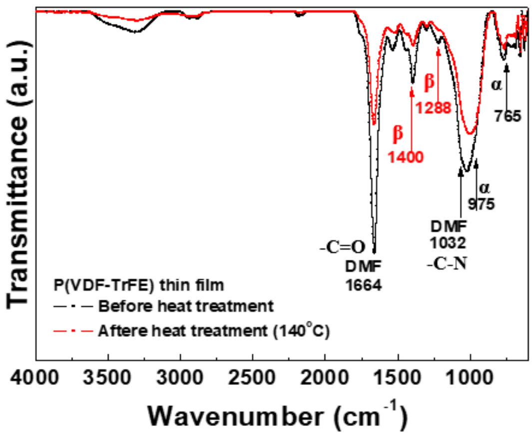

Fig. 1. ATR-FTIR results of P(VDF-TrFE) thin films on silicone substates before and after heat treatment at 140ºC.

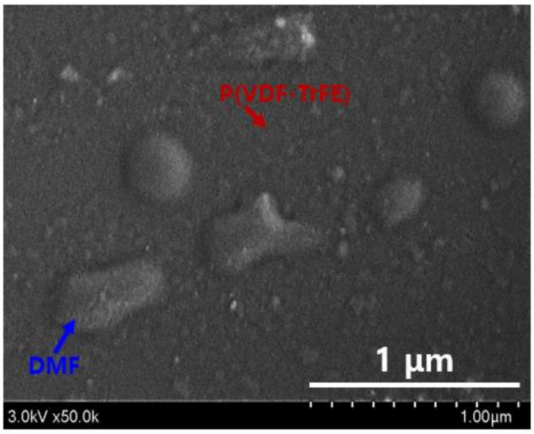

Fig. 2. FE-SEM results of P(VDF-TrFE) thin films after heat treatment at 140ºC.