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ABSTRACT

This paper systematically investigates the effects of the post-heating treatment on the structural characteristics of the polyvinylidene fluoride (PVDF) thin film that is deposited as the high-density thin films with nanoparticles by improving the sufficient nucleation of PVDF solution by atmospheric pressure plasma (APP) deposition system. The surface morphology of PVDF thin film was measured by using scanning electron microscopy (SEM), and structural characteristic of PVDF thin film was systematically investigated by X-ray diffraction (XRD) and Fourier transforms-infrared spectroscopy (FT-IR) with respect to different post-heating conditions in order to reduce the N,N-dimethylformamide (DMF) element and enhancing the crystalline phase of PVDF thin film. As the post-heating temperature was increased, the amount of bubble and bubble size were decreased. This means that the DMF solution is almost removed from the post-heated PVDF thin film, and the PVDF nanoparticles are clearly observed on the surface of PVDF thin film synthesized by APP deposition method. In FT-IR spectra, the peak intensity at $1669\,cm^{-1}$ for $-C=O$ by DMF solution highly decreases after post-heating treatment, and the crystalline phases of the PVDF thin film have mainly two phases (α and β phases), which indicates the peaks at 975 and $1402\,cm^{-1}$ for α-phase and the peak at $1072\,cm^{-1}$ for β-phase, respectively.

1. Introduction

In order to realize the flexible device, it is necessary to develop a new material for flexible applications. Numerous researches have been investigated in the field of inorganic materials such as graphene, zinc oxide (ZnO), and carbon nanotubes (CNTs) for flexible display and energy storage materials [1]. However, these inorganic materials have some limitation for stretchability and bendability of the flexible display and energy storage devices. Compared with those inorganic materials, the polymer materials seem to be

promising alternatives for flexible display and energy storage devices. In particular, polyvinylidene fluoride (PVDF) has been widely investigated during the last three decades fundamentally because of its unique properties such as mechanical properties, high chemical resistance, and good thermal stability. In addition, the PVDF polymer materials with piezoelectric properties have been recently employed for loudspeakers for flexible displays and force sensing in touch panel [2–5]. The PVDF has a semi-crystalline polymer comprised of polymorphic crystalline forms such as α, β, γ, and δ phases. Among them, the α-phase is the most general constitution because it is easily created from melt recrystallization at temperatures below 160 °C, while the β-phase is the mainly attractive, especially in view of better electrical performances for pyro and piezoelectric characteristics compared with those of the other phase structures [6]. Thus, PVDF in β-phase has been widely used in various electronic devices. The different phases of PVDF depend on the fabrication conditions such as solution, technique of coating, and annealing conditions. Many previous researches on the preparation and application of PVDF thin film by conventional method, such as spin coating, and solution casting [7–10], have been reported. In case of the conventional method, it is necessary to remove the residual N,N-dimethylformamide (DMF) solution on the PVDF thin film using PVDF/DMF solution, because a small amount of residual DMF can affect a formation of crystalline phase and electrical properties of PVDF thin film. The removal of DMF solution is generally performed through a heating process in a vacuum oven under 100 °C for tens of hours [10]. However, there are no reports on the characteristics of the PVDF thin film prepared by atmospheric pressure plasma (APP) deposition method. The plasma-polymerized polymer thin films have recently attracted many attentions because of their unique properties such as pinhole-free and structurally crosslinking. The low-pressure plasma assisted processes are well established and as such become popular method for the deposition of polymer-like films [11–15]. However, the necessity of expensive vacuum systems is pointed out to be the biggest disadvantage in industrial applications [11, 12]. Therefore, in order to overcome these disadvantages, the APP appears to be one of the most promising alternatives to deposit the polymer thin film especially on the point of view a less expensive and thermal heating-free process.

Accodingly, this study systematically investigates the effects of post-heating treatment on the crystalline phase of PVDF thin film that is deposited with PVDF/DMF solution by APP polymerization method. In particular, the surface morphology and structural phase are mainly examined with respect to different post-heating conditions in order to remove the DMF solution and enhance the crystalline phase using scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transforms-infrared spectroscopy (FT-IR) analyses.

2. Experiment

To form a PVDF solution with a concentration of 5%, a total of 1.95 g of PVDF powder (Sigma-Aldrich) with the α-phase was dissolved in a mixture with 40 mL DMF (DaeJung Chemicals Ltd.) solution. To efficiently dissolve the PVDF powder into a mixture and simultaneously suppress its agglomeration in the process of forming a PVDF
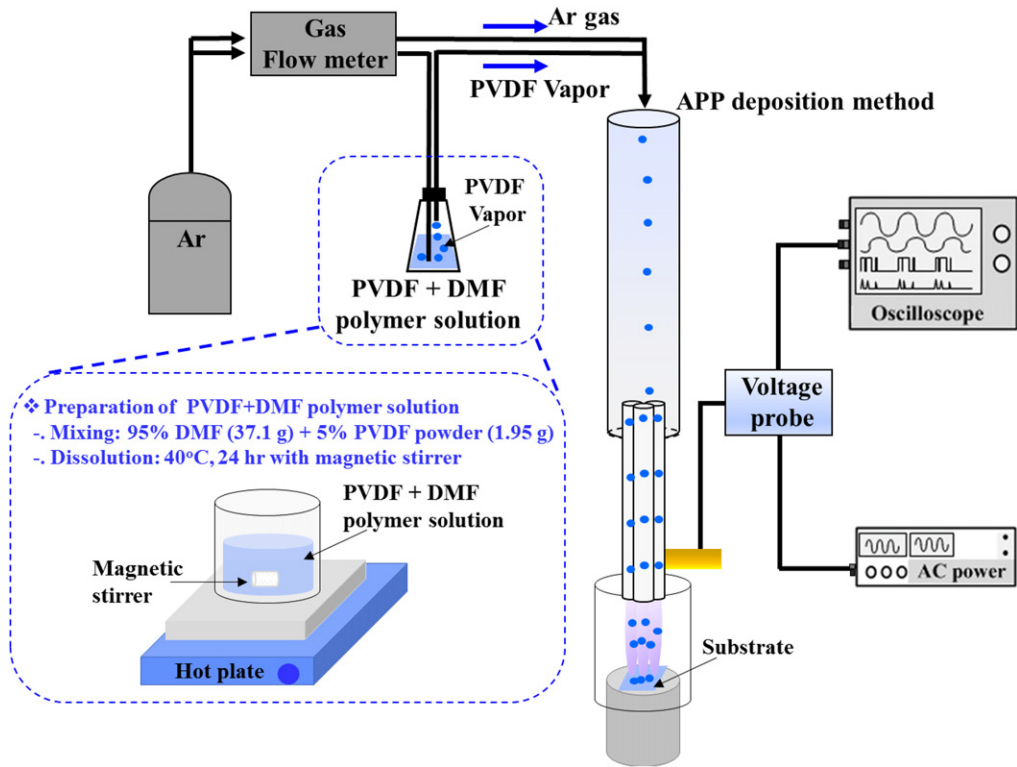
Figure 1. Schematic diagram of atmospheric pressure plasma (APP) deposition method.

Table 1. Deposition conditions of polyvinylidene fluoride (PVDF) thin film prepared by atmospheric pressure plasma (APP) deposition method.

PVDF polymer solution	5% PVDF powder (1.95 g) + 95% DMF (37.1 g)
PVDF vapor pressure	500 sccm
Ar gas pressure	2500 sccm
Voltage	12.5 kV
Frequency	26 kHz
Deposition time	1-, 3-hour
Deposition temperature	R. T.

solution, a magnetic stirrer with angular velocity 500 rpm was used and the PVDF/DMF solution was heated up to 40 °C for 24 hr, as shown in Figure 1. The cleaning of substrate was performed by using an ultrasonic bath in an acetone, ethanol, and de-ionized water for 20 min for each one after drying. Then, the PVDF solution was coated on glass substrate (1 cm x 1 cm) by the APP deposition method. The equipment for a novel APP polymerization system has been already explained by C-S Park et.al. [16, 17]. Argon gas was used as the plasma discharge gas at a flow rate of 2500 standard cubic centimeters per minute (sccm). PVDF/DMF solution was vaporized using a glass bubbler, which was supplied by argon gas with a flow rate of 500 sccm. The sinusoidal power with a peak value of 12.5 kV at a frequency of 26 kHz was applied to produce a plasma for depositing the PVDF thin film for 1-hour. The detailed deposition conditions of PVDF thin film were shown in Table 1.

Table 2. Post-heating conditions of PVDF thin film prepared by APP deposition method.

|	
Pre-heating temperature	60°C
Pre-heating time	10 min
Post-heating temperature	140°C, 160°C, 180°C
Post-heating time	1-, 3-hour
Heating rate	5°C/min
Cooling rate	5°C/min

In order to compose the crystalline phase of PVDF thin film after plasma deposition and simultaneously to remove the DMF within the deposited PVDF thin film, the PVDF thin film was heated on a hot-plate for 1- and 3-hour. through the 2-step heating process with respect to post-heating temperature at 140, 160, and 180 °C. The first-step is a pre-heating process for removing the solvent of DMF in PVDF thin film. Then, the second-step is a post-heating process for forming the crystalline phase of PVDF thin film and removing the solvent of DMF additionally. The as-deposited PVDF thin film was pre-heated at 60 °C for 10 min for removing the DMF solution and was subsequently post-heated at 140, 160, and 180 °C for 1- and 3-hour. The detailed post-heating conditions of PVDF thin film were shown in Table 2.

The surface morphology images of PVDF thin films were examined by scanning electron microscope (SEM; Hitachi SU8220). The thickness of PVDF thin film was measured using stylus profiler (KLA Tencor, P-7). The crystalline phases of the PVDF powder and thin film were determined by X-ray diffraction (XRD; D8 Discover Bruker) and Fourier transformation infrared spectroscopy (FT-IR; Vertex 70, Bruker) at the Korea Basic Science Institute (KBSI; Daegu). In XRD data, each scan was measured with 2θ angle ranging from 10° to 50°, the step scanning was performed at 0.08° intervals, and CuKα radiation ($\lambda = 1.54$Đ) was used as the X-ray source. The FT-IR spectra were measured by averaging 128 scans at a wavenumber resolution of 0.6 cm^{-1} in the range from 600 to 4000 cm^{-1} using attenuated total reflection (ATR) mode.

3. Results and discussion

Figure 2 shows the SEM images of as-deposited and post-heated PVDF thin films with respect to the various post-heating temperatures at 140, 160, and 180 °C for 1-hour. The thickness of PVDF thin film prepared by APP deposition method was about 2 μm for 1-hour by using stylus profiler. As shown in Figure 2 (a), the rough surface with bubbles of as-deposited PVDF thin film was observed, which was originated from DMF solution. As shown in Figures 2 (b), (c), and (d), as the post-heating temperature was increased, the amounts of bubble and corresponding bubble sizes were decreased. Also, the PVDF nanoparticles prepared by APP deposition method were apparently observed on the surface of PVDF thin film after post-heating at 180 °C for 1-hour.

In order to effectively reduce the DMF solution and improve the crystalline phase of PVDF thin film, the PVDF thin films were post-heated after APP deposition. Figure 3 shows the SEM images of the posted-heated PVDF thin films after APP deposition with respect to various post-heating temperatures at (a) 140, (b) 160, and (c) 180 °C for 3-hour. The SEM images of Figure 3 illustrated that with an increases in the post-heating temperatures, both the amount of bubble and the size of bubble were decreased.
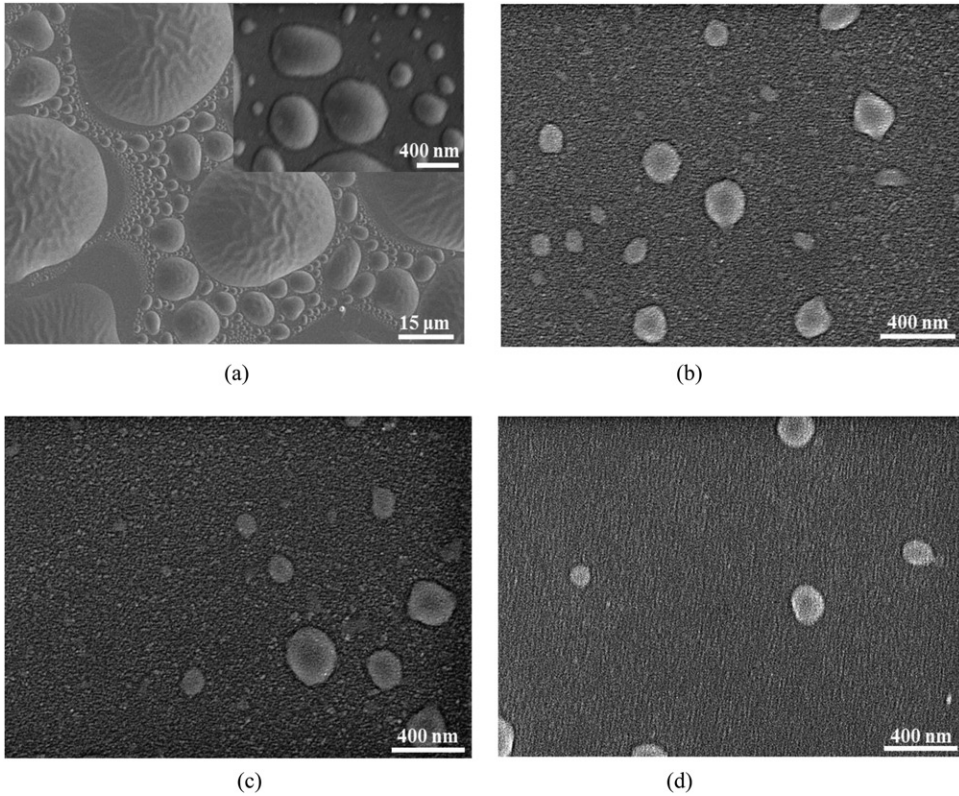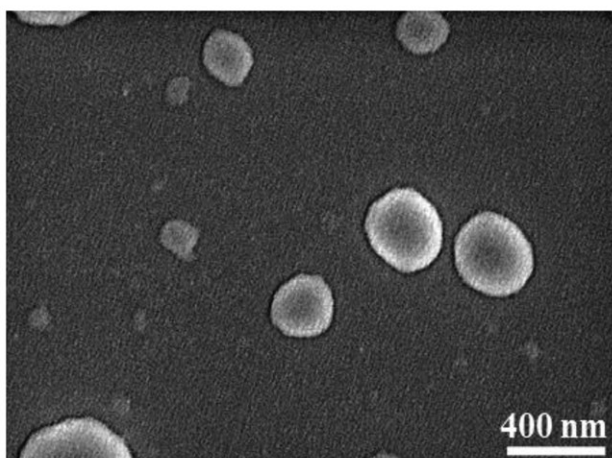
Figure 2. Scanning electron microscopy (SEM) image of (a) as-deposited and post-heated PVDF thin films prepared by APP deposition method with respect to various post-heating temperatures at (b) 140, (c) 160, and (d) 180 °C for 1-hour.

Consequently, the nanoparticles of the post-heated PVDF thin film were clearly observed after the 3-hour post-heating process.

Figure 4 shows the XRD pattern of PVDF powder and post-heated PVDF thin films with respect to the various post-heating temperatures at 140, 160, and 180 °C for 1- and 3-hour, respectively. As shown in Figure 4 (a), three prominent peaks were observed at $2\theta = 18.4°$ (020), $19.8°$ (110), and $26.4°$ (021), confirming that the original phase of PVDF used in this experiment was α-phase [9]. However, after deposition of post-heated PVDF thin films prepared by APP deposition method, α- and β-phases were observed in Figure 4 (b). The XRD patterns of PVDF thin films show an amorphous nature and no tendency such as the changes in the peak intensity depending on the different post-heating temperatures, especially for 1 hour-heating time condition. This result implies that the thermal energy provided during the 1-hour post-heating cycle would not feed enough an activation energy necessary for the PVDF thin film to have crystalline structure [6]. Thus, the post-heating time was increased from 1- to 3-hour for providing sufficient energy. As a result, the peak intensities of $2\theta = 22.6°$ for α-phase and $2\theta = 20.6°$ for β-phase for the 3-hour post-heating case were observed to be increased, compared with those for the 1-hour post-heating case.
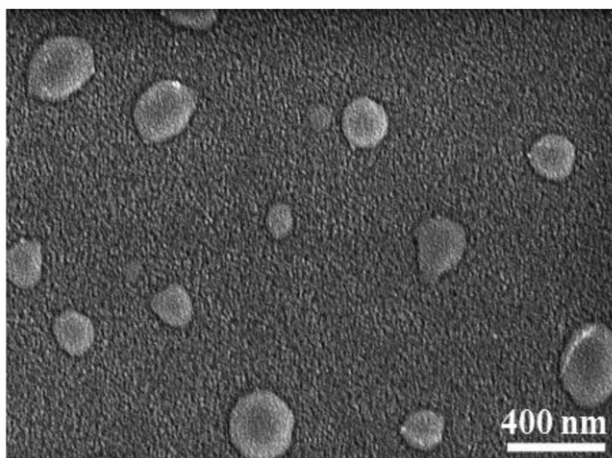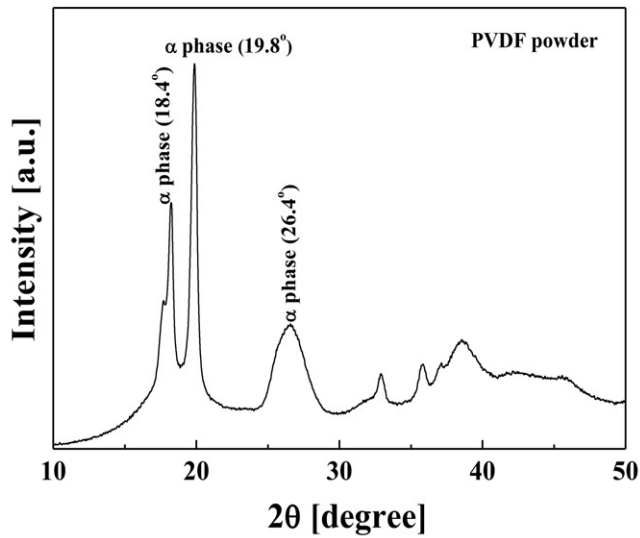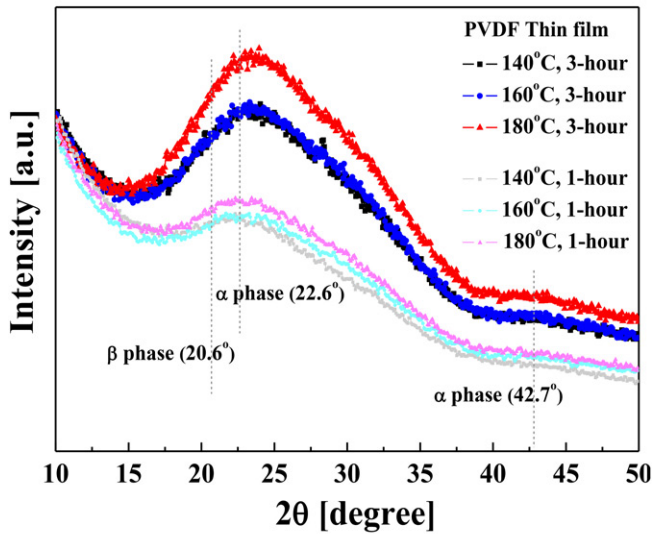
(a)

(b)
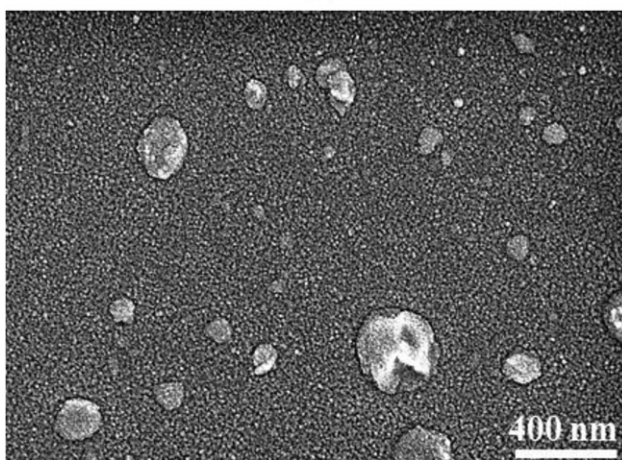
(c)

Figure 3. SEM image of PVDF thin films prepared by APP deposition method with respect to various post-heating temperatures at (a) 140, (b) 160, and (c) 180 °C for 3-hour.
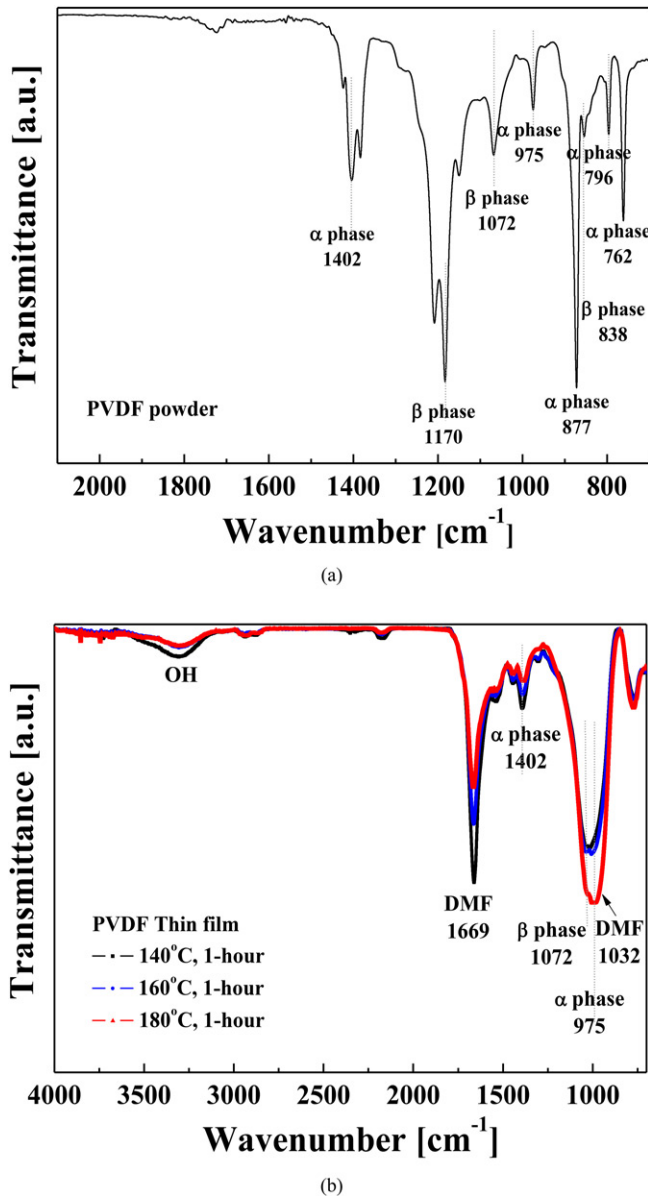
(a)

(b)

Figure 4. X-Ray diffraction (XRD) patterns of (a) polyvinylidene fluoride (PVDF) powder and (b) PVDF thin films prepared by APP deposition method with respect to various post-heating temperatures at 140, 160, and 180 °C for 1- and 3-hour.

Figure 5 shows Fourier transformation infrared spectroscopy (FT-IR) spectra ranging from 700 to 4000 cm^{-1} of (a) PVDF powder and (b) PVDF thin film prepared by APP deposition method with respect to various post-heating temperatures at 140, 160, and 180 °C for 1-hour. In case of PVDF powder in Figure 5 (a), the band vibration of 762 cm^{-1} was assigned to the CF$_2$ bending mode. The bands at 796 and 975 cm^{-1} were assigned to the CH$_2$ twisting mode. The bands at 1402 cm^{-1} was assigned to CF$_2$ wagging mode, and peak at 838 cm^{-1} was assigned to the CH$_2$ rocking mode. The peaks at

Figure 5. Fourier transformation infrared spectroscopy (FTIR) spectra of (a) PVDF powder and (b) PVDF thin films prepared by APP deposition method with respect to various post-heating temperatures at 140, 160, and 180 °C for 1-hour.

877 and 1072 cm^{-1} were assigned to the CC skeletal stretching vibration, and 1170 cm^{-1} was assigned to the CF$_2$ out-of-plane deformation [9]. In Figure 5 (a), the peaks at 762, 796, 975, and 1402 cm^{-1} represent the α-phase, whereas the peaks at 838, 877, 1072, and 1170 cm^{-1} represent the β-phase. Meanwhile, in case of PVDF thin film prepared by APP deposition method in Figure 5 (b), the FTIR peaks of α-phase at 975 and 1402 cm^{-1}, β-phase at 1072 cm^{-1}, and DMF element at 1669 cm^{-1} were observed after post-heating for 1-hour, respectively. After the 1-hour post-heating, the crystalline

Table 3. Absorption peaks of Fourier transformation infrared spectroscopy (FTIR) for crystalline phases of PVDF thin films prepared by APP deposition method and N,N-dimethylformamide (DMF) solution.

α-phase PVDF (cm^{-1})	762, 796, 975, 1402 cm^{-1}
β-phase PVDF (cm^{-1})	838, 877, 877, 1072, 1170 cm^{-1}
DMF (cm^{-1})	1032, 1669 cm^{-1}
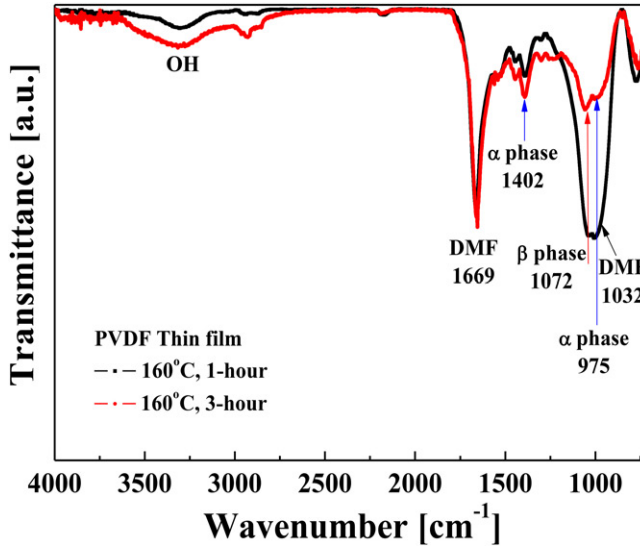
Figure 6. FTIR spectra of PVDF thin films prepared by APP deposition method with post-heating temperature at 160 °C for 1- and 3-hour.

phase of PVDF thin film mainly had two phases such as α- and β-phases in FTIR spectra. As shown in Figure 5 (b), the peaks at 975 and 1402 cm^{-1} were assigned to α-phase, and peak at 1072 cm^{-1} was assigned to β-phase. The absorption peaks of DMF solution originally had two characteristics bands at 1032 and 1669 cm^{-1}, which was assigned to -C-N and -C=O bonds, respectively. As shown in Figure 5 (b), as the post-heating temperatures were increased in the range from 140 to 180 °C for 1-hour, the peak intensities of 1032 and 1669 cm^{-1} for DMF solution were decreased, meaning that the amount of remaining DMF element was effectively decreased. The FTIR peaks of DMF solution and PVDF thin film are represented in Table 3.

In order to effectively reduce the DMF solution and improve the crystalline phase of the PVDF thin film, the post-heated time for the PVDF thin films prepared by APP deposition method was increased from 1- to 3-hour at the same temperature of 160 °C. Figure 6 shows FTIR spectra of the PVDF thin films that were post-heated under different post-heating conditions (1- and 3- hour heating time at 160 °C) after APP deposition. As shown in Figure 6, for the 3-hour post-heating condition, the peak intensity at 1032 cm^{-1} due to both the -C-N by DMF solution was significantly decreased, compared with that for the 1-hour post-heating condition. Whereas, after post-heating at 160 °C for 3-hour, the crystalline phases such as α and β of the PVDF thin film were observed to be increased, meaning that the crystalline phase could be enhanced effectively during the APP deposition with the post-heating for 3-hour.

5. Conclusions

This paper work investigated the characteristics of the post-heating treatment on the crystalline phase of the PVDF thin films prepared by APP deposition method. As the post-heating temperature was increased, the amounts of bubble and bubble sizes were decreased. Consequently, the nanoparticles of the post-heated PVDF thin film were clearly observed after the 3-hour post-heating. The XRD pattern of the post-heated PVDF thin film had amorphous nature, and the peak intensities of $2\theta = 22.6^{\circ}$ for α-phase and $2\theta = 20.6^{\circ}$ for β-phase were increased with an increase in the post-heating time from 1- to 3-hour. The FTIR spectra showed that as the post-heating temperatures were increased from 140 to 180 °C for 1-hour, the peak intensities of 1032 and 1669 cm^{-1} for DMF solution was decreased, meaning that the amount of remaining DMF element was effectively decreased. In particular, in the post-heating condition such as 3-hour heating time and heating temperature of 160 °C, the peak intensity at 1032 cm^{-1} due to the -C-N by DMF solution was significantly decreased, compared with that in the 1-hour and 160 °C post-heating condition. Whereas, after post-heating for 3-hour at 160 °C, the crystalline phases such as α and β of the PVDF thin films were observed to be increased, meaning that the crystalline phase could be enhanced effectively during the APP deposition with the post-heating for 3-hour. As a result, these results are expected to contribute to understanding the growth mechanism of PVDF thin films prepared using PVDF/DMF solution by APP deposition method.

Acknowledgement

References

[1]　M. Zou, Y. Ma, X. Yuan, Y. Hu, J. Liu, & Z. Jin, (2018). *Journal of Semiconductors*, 39(1), 011010.

[2]　T. Sugimoto, K. Ono, A. Ando, K. Kurozumi, A. Hara, Y. Morita, & A. Miura, (2009). *Acoust. Sci. & Tech.* 30, 2, 151–153.

[3]　K.-Y. Shin, J.-Y. Hong, & J. S. Jang, (2011). *Chem. Commun.*, 47, 8527–8529.

[4]　Y.-T. Wang, Y.-C. Hu, & K.-R. Chen, (2015). *Journal of the Chinese Society of Mechanical Engineers*, 36(1), 59–66.

[5]　S. Gao, X. Wu, H. Ma, J. Robertson, & A. Nathan, (2017). *ACS Applied Materials & Interfaces*, 9, 18410–18416.

[6]　I. Y. Abdullah, M. Yahaya, M. H. H. Jumali, & H. M. Shanshool, (2014). *AIP Conf. Proc.*, 1614, 147–151.

[7]　J. H. Park, N. Kurra, M. N. AlMadhoun, I. N. Odeh, & H. N. Alshareef, (2015). *J. Mater. Chem. C*, 3, 2366–2370.

[8]　Y. Zhu, H. Ye, L. Yang, L. Jiang, L. Zhen, J. Huang, Z. Jiao, & J. Sun, (2016). *Polymers & Polymer Composites*, 24(2), 167–172.

[9]　I. Y. Abdullah, M. H. H. Jumali, M. Yahaya, & H. M. Shanshool, *Advances in Environmental Biology*, (2015). 9(20), 20–27.

[10]　K. Ke, X. F. Wei, R. Y. Bao, W. Yang, Y. Luo, B. H. Xie, & M. B. Yang, (2014). *Polymer Testing*, 34, 78–84.

[11] W. Xiaomin, Y. Qianghua, Z. Yongjie, Y. Guiqin, & D. Chenzhong, *Plasma Science and Technology*, (2014). 16(1), 68–72.
[12] T. P. Kasih, S. I. Kuroda, & H. Kubota, *Plasma Process. Polym*., (2007). 4, 648–653.
[13] J. Phillips, C.C. Luhrs, & M. Richard, *IEEE TRANSACTIONS ON PLASMA SCIENCE*, (2009). 37(6), 726–739.
[14] J. Phillips, C.C. Luhrs, C. Peng, P. Fanson, & H. Zea, *J. Mater. Res.,*(2008). 23(7), 1870–1876.
[15] J. C. Weigle, C.C. Luhrs, C. K. Chen, W. L. Perry, J. T. Mang, M. B. Nemer, G. P. Lopez, & J. Phillips, *J. Phys. Chem. B*, (2004). 108(48), 18601–18607.
[16] C. S. Park, D. H. Kim, B. J. Shin & H. S. Tae, (2016). *Materials*, 9, 39, 1–12.
[17] C. S. Park, D. H. Kim, B. J. Shin, D. Y. Kim, H. K. Lee, & H. S. Tae, (2016). *Materials*, 9, 812.