International Journal of Scientific Research and Engineering Development-– Volume 6 Issue 6, Nov- Dec 2023

Available at www.ijsred.com

RESEARCH ARTICLE OPEN ACCESS

Preparation of Transparent Polyvinylidene Fluoride Layers for Optoelectronic Devices

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Abstract:

Erbium nitrate-doped polyvinylidene fluoride (PVDF) layers were prepared by adding 0.2g-Erbium into a PVDF sol under ultrasonification. The mixture was spin-coated onto glass substrates. The crystalline structure, surface morphology and transmittance in the visible range of the films were evaluated by X–ray diffraction analysis, atomic force microscopy and ultraviolet-visible spectroscopy. The dielectric properties of the films as a variation of the frequency were confirmed by an LCR meter. Ferroelectricity combined with the optical transmittance of PVDF confirms that the film is an attractive option for optoelectronic applications.

Keywords **—Erbium nitrate, PVDF, Transmittance**

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I. INTRODUCTION

PVDF is an electroactive material that exhibits a strong ferroelectric effect, as observed by Kawai in 1969. It is a semi-crystalline polymer, exhibiting an arrangement with carbon-fluorine dipole moments, and has been extensively studied because of its excellent chemical stability and piezoelectricity. Materials exhibiting piezoelectric properties have been widely used in electronic products, such as sensors and actuators [1], [2].

Four different crystal phases were observed for PVDF: α (monoclinic symmetry, a = 0.496 nm, b = 0.964 nm, c = 0.462 nm, and β = 90°), β (orthorhombic symmetry, a = 0.858 nm, b = 0.491 nm, and c = 0.256 nm), γ (monoclinic symmetry, a = 0.496 nm, b = 0.958 nm, c = 0.423 nm, and β = 92.9°); and δ (monoclinic symmetry, a = 0.496 nm, b = 0.964 nm, c = 0.462 nm, and β =90°). The β phase shows an all-trans (TTT) planar twist arrangement, wherein the dipole moments of the two carbon-fluorine (C-F) and two carbon-hydrogen (C-H) bonds combine such that the monomer exhibits a suitable dipole moment perpendicular to the carbon backbone. Consequently, the β phase possesses significant spontaneous polarity for each unit cell and displays an outstanding piezoelectricity [3].

Among the various techniques [4]–[6]used to prepare PVDF with polar β phase, mechanical spreading is generally applied. By extending the PVDF films to 90 °C, a maximum β phase content of 80% was achieved [7]. However, this technique is unsuitable for thin films on a substrate.

Authors in previous work [4] employed a hydrated calcium nitrate as a nucleating mediator to prepare electroactive PVDF layers. Our previous study revealed that the hydrate salt played a role as nucleation locations for the crystallization of PVDF molecules, and the intermolecular hydrogen bonding and dipolar relations accelerated a TTT arrangement and β-phase structure [5].

Transparent and homogeneous PVDF layers have recently been investigated for their adaptability to optoelectronic fields, such as through mixing with soluble polymers, synthesizing non-crystalline structures, and drawing at high temperatures [6], [7]. However, a high atmospheric pressure or processing temperature is required to fabricate transparent PVDF layers.

In this study, we present the preparation of transparent β phase dominant PVDF films for optoelectronic applications. Hydrated salt such as an erbium nitrate, was introduced during the process without mechanical stretching. The crystalline structure, optical transmittance, and electrical properties of PVDF layers containing erbium nitrate were evaluated for use in optoelectronic devices.

II. EXPERIMENTAL

PVDF (Mw = 180,000) and dimethylformamide (DMF) were obtained from Sigma Aldrich. The 10 wt%-PVDF pellets were melted in DMF sol and mixed for 3 h at 60 °C in order to prepare pure PVDF sol. To obtain an Er-doped PVDF mixture, 0.2 g erbium (III) nitrate [$Er(NO_3)_3 \cdot 5H_2O$] was added. This mixture was then agitated for 10 h at 60 °C to completely dissolve the dopant. Soda–lime-silica glass (SLSG) was used as the substrate. Previous to spin-coating, SLSG plates were washed in deionized water, dipped in H_2O_2, and lastly cleaned in acetone. Coating solution was spin-coated on the glass plates at 1500 rpm for 20 s. The as-deposited layer was heated at 100 °C for 60 min.

Thickness of the finally heated layers was about 0.5 µm, not shown here, as confirmed by examination of the cross-sectional appearance via a field-emission scanning electron microscope (FE-SEM; S-4700, Hitachi, Japan). The crystallinity of the layer was identified by high-resolution X-ray diffraction (HR-XRD, X'pert-PRO, Philips, Netherlands). A scanning probe microscope (SPM, PSIA, Republic of Korea) by employing a tapping method in air was used to investigate the surface micro-structure of the layer. An ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy (CARY 500 Scan, Varian, Australia) was used to obtain optical transmittance. The transmittance was standardized to that of a SLSG glass as a reference. Permittivity and loss tangent as a function of frequency variation was evaluated by using an LCR meter (PM 6306, Fluke, U. S. A.) in the frequency range from 100 Hz to 1 MHz.Piezoelectric characterization of the layers was performed to determine the electrical reply of the samples when a single weight was affected by the impact of a load [8].

III. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction patterns of the pure PVDF and Er-doped-PVDF films. The difference in crystalline phase as a function of Er-doping were confirmed through XRD with a θ-2θ scan operated at 30 kV and 40 mA with CuK_α radiation at a wavelength of 0.154 nm. As shown in Fig. 1, the major peak at approximately 2θ = 20.6 - 20.7°, which is related to the super-positioning of the (110) and (200) reflections of the polar β phase of PVDF [4], can be recognized for all the films. Peaks related to the non-polar α phase (17° to 18.6°, and 26° to 32°), were not identified in any of the PVDF films after heat treatment. No other secondary phase corresponding to erbium nitrate was identified. However, as shown in Fig. 1, the PVDF layer after Er-doping, the peak intensity corresponding to β (110) / (200) reflections considerably increase.

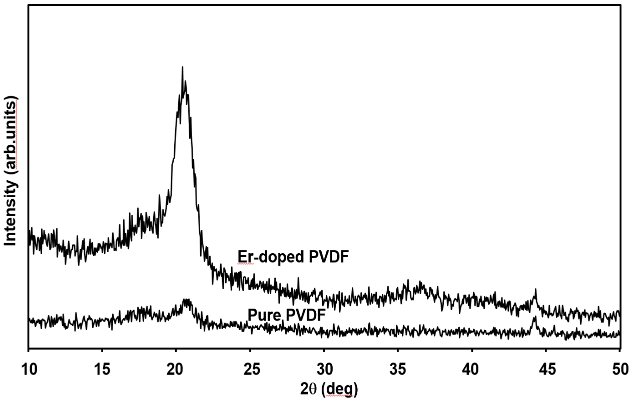

Fig. 1XRD spectra of pure PVDF and Er-doped PVDF films on an SLSG substrates.

From our previous reports on the preparation of Mg-doped-PVDF thin films, the polar β phase appeared as the main phase with the addition of hydrated-metal salt influenced the formation of the β phase, leading to a partial arrangement of the PVDF backbone with the silicon wafer surface as a substrate [9]. Similarly, in this study, the strong hydrogen bonding (O-H···F-C) fabricated at the boundaries in the middle of $Er(NO_3)_2 \cdot 5H_2O$ and PVDF molecules, along with the dipolar interactions between PVDF and DMF, tend to produce a locally oriented packing of CH_2-CF_2 dipoles, which is related to the β phase.

Among various hydrated metal salts, the capability of $Er(NO_3)_3 \cdot 5H_2O$ to promote β phase formation has been studied since it possesses sufficient pyroelectric properties over the infrared spectra region and is able to easily combine to PVDF [10].

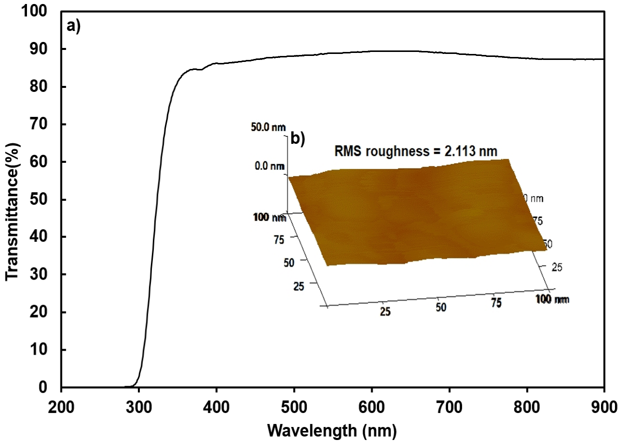

Fig. 2Transmittance spectrum (a) within visible spectral region and SPM photograph (b) of Er-doped PVDF films.

SPM investigation was done to confirm the surface micro-structure and surface smoothness of the Er-doped PVDF. The SPM image and root mean square (RMS) roughness are shown in Fig. 2 (b). Homogeneous PVDF layers were prepared after Er-doping. A three-dimensional grain out-growth was not observed in the PVDF layer, and finally a regular compact homogeneous layer without holes and crackswas obtained.

Variations in the surface morphology and RMS roughness also influence the optical transmittance within the visible spectral region of the PVDF layers, which is a valuable parameter in several applications, in combination with the use of transparent conductive oxides (TCOs) as electrodes for signal display. The optical transmittance within the visible spectral region from 900 to 200 nm was measured using a UV-vis spectrophotometer for the Er-doped PVDF layer on the SLSG substrate. As shown in Fig. 2 (a), a relatively high transmittance of nearly 90% was achieved within the visible spectrum region of the PVDF films. Optical transmittance is expected to depend on several factors, such as oxygen deficiency, surface morphology, surface smoothness, and impurity centre [11]. We can assume that the high transmittance of the PVDF films is attributed to the homogeneous surface structure with low surface roughness, as confirmed through SPM, Fig. 2(b), which reduces the light scattering. Homogeneous transparent PVDF films containing a polar β phase were fabricated through Er-doping.

The variation in the dielectric constants of the Er-doped PVDF films as a function of frequency is shown in Fig. 3 (a). To achieve a parallel-plate capacitor structure, aluminium layers were thermally evaporated on the top and bottom of the layers as the electrodes. The bottom electrode was deposited onto the SLSG substrate prior to coating. The dielectric constant was calculated using the relationship, $\varepsilon = \frac{Cd}{\varepsilon_0 A}$, where C denotes the capacitance of the layer (F). The factor ε_0 denotes the dielectric permittivity in a free space (8.854×10^{-12} F/m), and A indicates the connecting area of the electrode (m^2). The parameter d indicates the thickness of the layer (m). The relative dielectric constant could be calculated after the capacitance was obtained. To obtain an accurate capacitance, four PVDF layers per heating temperatures were examined using an LCR meter at different frequency levels varying from 100 Hz to 1 MHz.

As shown in Fig. 3 (a), the dielectric permittivity of the Er-doped PVDF layer exhibits a decrease in the low-frequency range from 100 Hz to 1 MHz owing to the characteristics of the ferroelectric materials, that is, the crystal structure and lattice configuration. At high frequencies, the electric response of the film delays the applied field anddirects the loss [12]. The polarizationcharacteristic of a dielectric material changes with the frequency variance of the applied electric field, providing changes in capacitance and permittivity. The dipole alignment of the Er-doped PVDF layers at low frequencies does not vary the same as it does at a high frequency. This is because the dipoles are unable to replace their alignment with the applied field at a higher frequency, resulting in a lower relative dielectric permittivity [12].

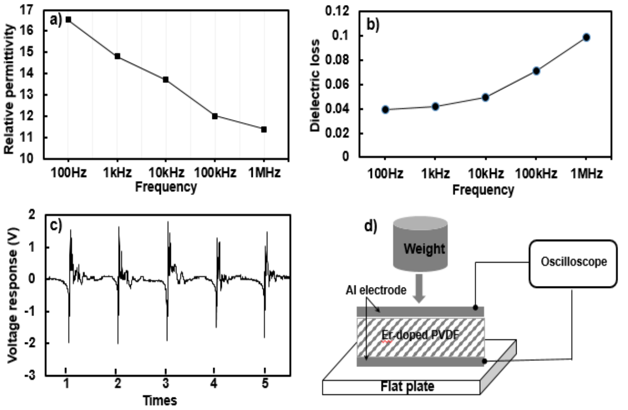

Fig. 3Dielectric permittivity (a), tangent loss (b), piezoelectric reply (c), and trial apparatus to evaluate the output voltage (d) of Er-doped-PVDF films.

The difference in the tangent loss (D) of the Er-doped PVDF films according to the frequency variance from 100 Hz to 1 MHz at room temperature is shown in Fig. 3 (b). The dielectric loss of the films exhibited a high dielectric stability over a wide range of frequencies. However, an abrupt increase at 100 kHz and 1 MHz may be due to heat generation followed by more intermolecular vibrations, resulting in an increase in dielectric loss.

Polymer piezoelectric materials have been extensively used in the preparation of energy-generating devices. The power generator device of transparent Er-doped PVDF films was prepared through the construction of electrical generators, as described in a previous study [4]. The piezo-response (open-circuit voltage (OCV) through the upper and lower electrodes) was monitored using a digital oscilloscope.The results are shown in Fig. 3 (c), where a continuous weight impact was applied to the upper surface, as illustrated in [4]. The positive and negative peaks of the OCV related to the weight impact and release are shown in Fig. 3 (c). After the impact tests, the average output voltages were determined to be – 1.83 V and 1.55 V, for the negative peak voltage and for the positive peak voltage, respectively. These results indicate that the Er-doped PVDF films exhibit better piezoelectric properties. The piezoelectricity of the Er-doped PVDF may be due to the effect of the well-crystallized polar β phase in the PVDF films, as confirmed through XRD (see Fig. 1).

The preparation of Er-doped PVDF films with transparency within the visible spectral region, flexibility, and piezoelectricity demonstrates that the joining of hydrated metal nitrate offers a new and suitable method for providing smart materials and structures for optoelectronic sensors and Internet of Things (IoT) devices.

IV. CONCLUSIONS

Transparent and piezoelectric PVDF films were fabricated onto the cleaned SLSG substrates throughEr-doping on pure PVDF solution. From the results of the crystalline structure investigated by using XRD, a strong peak at approximately 2θ = 20.6 to 20.7°, which corresponds to the super-positioning of the (110) and (200) reflections of the polar β phase of PVDF, could be detected for the Er-doped PVDF film on SLSG substrates. The high transmittance at the visible spectral region of the Er-doped PVDF films was attributed to the homogeneous surface structure exhibiting a low surface roughness, as confirmed through SPM, which eliminates light scattering on the surface. From the result of the piezo-response, the average output voltages were determined to be – 1.83 V and 1.55 V, for the negative peak voltage and for the positive peak voltage, respectively. These results indicate that the Er-doped PVDF films exhibit better piezoelectric properties.Piezoelectricity combined with the optical transmittance at visible spectral region of Er-doped PVDF confirms that the film is an attractive option for optoelectronic applications.

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