Nigerian Journal of Physics (NJP)
ISSN online: 3027-0936
ISSN print: 1595-0611
DOI: https://doi.org/10.62292/njp.v33i4.2024.355
Volume 33(4), December 2024

Investigation of Impacts of Annealing on the Properties of Poly (3,4-ethylene dioxythiophene)/poly (styrene sulfonate) (PEDOT:PSS) Films

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ABSTRACT

Poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonic acid) (PEDOT:PSS) holds a promise in the electronics and optoelectronics world owing to its promising electrical conductivity, exciting optical transparency, and improved structural network. It has found diverse applications in various technological fields and electronics devices, such as photovoltaics devices, light-emitting diodes, and photodiodes. However, the optical, surface morphology and structural properties of PEDOT:PSS films are significantly influenced by post-treatment processes, among which annealing plays a vital role. Annealing influences the surface property, phase separation, and molecular orderliness of PEDOT:PSS films, which invariably impacts their charge transport and optical behaviours. In this study, we evaluate the effects of thermal treatment on the optical, structural, and surface morphology properties of poly(3,4-ethylenedioxythiophene/poly styrene sulfonate) (PEDOT:PSS) thin film particularly for solar energy conversion application. The optical, structural, and surface morphology properties of PEDOT:PSS films as a function of annealing temperatures were studied by UV - Visible spectroscopy, X-ray diffraction, and scanning electron microscopy techniques respectively. An increase in annealing temperature improves the photons transmittance characteristic of the films. The X-ray diffraction pattern of the annealed film exhibits slight markedly improvement in the peak intensity suggesting improvement in the order of molecular structure and the SEM images reveals an increase in surface roughness of the annealed films improving the pathway for charge carrier mobility. These results highlight the significance of annealing treatments on the characteristic performance of PEDOT:PSS films for diverse electronic applications.

Keywords:
PEDOT:PSS films,
Annealing,
Electronics.

INTRODUCTION

PEDOT–PSS aqueous dispersion is Poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonate) (PEDOT: PSS) hold promise as an attractive conductive polymer for electronics application owing to its remarkable optical, mechanical and electrical properties. It has attracted huge attention in the field of optoelectronic technology such as solar cells (Alemu et al., 2012), and light-emitting diodes(Friend et al., 1999) because of some striking characteristics such as optical transparency in the visible region, relatively low material cost, simple solution processing, and structural robustness (Heywang & Jonas, 1992; Alemu et al., 2012; Elschner et al., 2010 & Ouyang et al., 2005).

PEDOT: PSS is synthesized via polymerization of PEDOT in the presence of the water-soluble polyelectrolyte (styrene sulfonic acid) (PSS) to form aqueous colloidal suspension. (Hu et al., 2011; Groenendaal et al., 2000). This aqueous suspension is made of solution containing a hydrophobic PEDOT-rich conductive core (a benzoid coiled like structure) surrounded by an insulating hydrophilic PSS-rich shell to stabilize PEDOT. Moreover, excess PSS is assembled at the composite layer surface, which tends to limit the conductivity of the PEDOT polymer (Yun et al., 2020; Hwang et al., 2006). The molecular structure of the polymer is shown in Figure 1 Ordinarily, PEDOT polymer is insoluble in water and other organic solvents.

(Lee et al.,2013). Doping of the polymer with PSS poly-electrolyte stabilize its water dispersibility and improve electrical conductivity (Park et al.,2013). PEDOT: PSS is usually employed as a hole transport layer and active material in optoelectric devices (Litzov et al., 2013).

However, the hygroscopic characteristics of the composite PEDOT/PSS dispersion pose a great challenge to film quality, having a propensity to induce series resistance (Kim et al., 2011; Kirchmeyer & Reuter, 2005; Nardes et al., 2008; Yang et al., 2006). Besides, the relatively low electrical conductivity of PEDOT: PSS aqueous dispersion cause by the insulating influence of the chemical dopant PSS chain in the PEDOT: PSS matrix also limit its widespread applications. Several approaches have been explored to improve the properties performance of PEDOT: PSS film. Many group of researchers reported the various solvents treatment on PEDOT: PSS dispersion such as DMSO, ethylene glycol etc. as effective approaches to substantially improve the film charge transport network. They revealed that solvent assisted strategy induced conformational changes in the PEDOT: PSS chain, transition from coiled dedoped state(benzoid) to linear doped state (quinoid) leading to optical and electrical conductivity enhancement of the PEDOT: PSS film. (Debjani et al., 2006; Chien et al., 2017; Kim et al.,2002; Thomas et al., 2015 &Wang et al.,2005). The influence of thickness control on PEDOT: PSS properties were investigated by Friedel et al., (2009). They demonstrated that thickness variation improved crystallinity, surface roughness and optical absorbance as well as electrical connectivity of the PEDOT: PSS film. Post thermal treatment approaches of the film also consider to influence the electrical, structural and morphological properties of PEDOT: PSS film(Friedel et al., 2009; Jönsson et al., 2003). The annealing processing parameter is a subject of debate as reported to either decrease or increase conductivity PEDOT: PSS film (Kim et al., 2008; Pingree et al., 2008). Nevertheless, further studies need to be carried out to understand the mechanism of improving the properties performance of the PEDOT: PSS material through explicit annealing processing.

Hence, in this work, the effects of annealing temperature on the structural, optical and surface morphology behavior of PEDOT: PSS for solar energy conversion is extensively investigated.

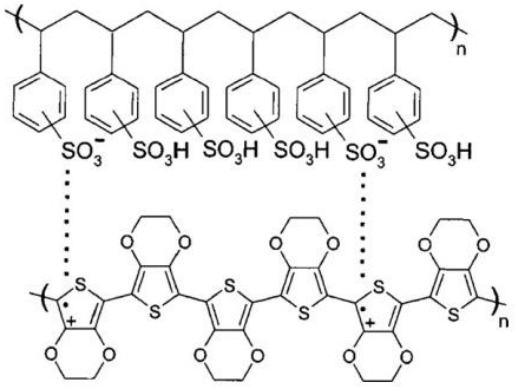

Figure 1: Schematic diagram of PEDOT (up) and PSS (down) Nardes et al., (2008)

MATERIALS AND METHODS

PEDOT/PSS water dispersion (Clevios P HC V4, H. C. Starck GmbH) was purchased from Sigma-Aldrich (Germany) used as purchased. It is filtered to ensure smooth film. Prior to deposition, glass substrate (2cm × 2cm) was cleaned ultrasonically with methanol, acetone, and isopropanol for 30 min each then dried in electric oven for 15 min. PEDOT/ PSS aqeous solution was spincoated on the pre-cleaned glass substrate at spin speed 2000 rpm for 30s. in ambient condition. Subsequently, the obtained films were subjected to post-thermal treatment at different temperatures in an electric oven ranging from 100 ℃ to 200 ℃ for 60 minutes.

Characterisation

Powder X–ray diffractometer model X Pert with utilized monochromatic Cu-kα radiation source 40 kV and 30 mA (CuKa = 1.542 A) at 2θ in the range of 5–15° was used to evaluate the structural properties of PEDOT:PSS thin films. The optical transmittance of the films were measured using UV-vis spectrophotometer, model Avantes-Avalight-DH-5-BAL in the wavelength range 200-900 nm. The surface morphology properties of the films were examined by a scanning electron microscope (SEM, Philips XL-30). The films thickness were estimated from gravimetry method.

RESULTS AND DISCUSSION

Optical Studies of PEDOT:PSS Thin films

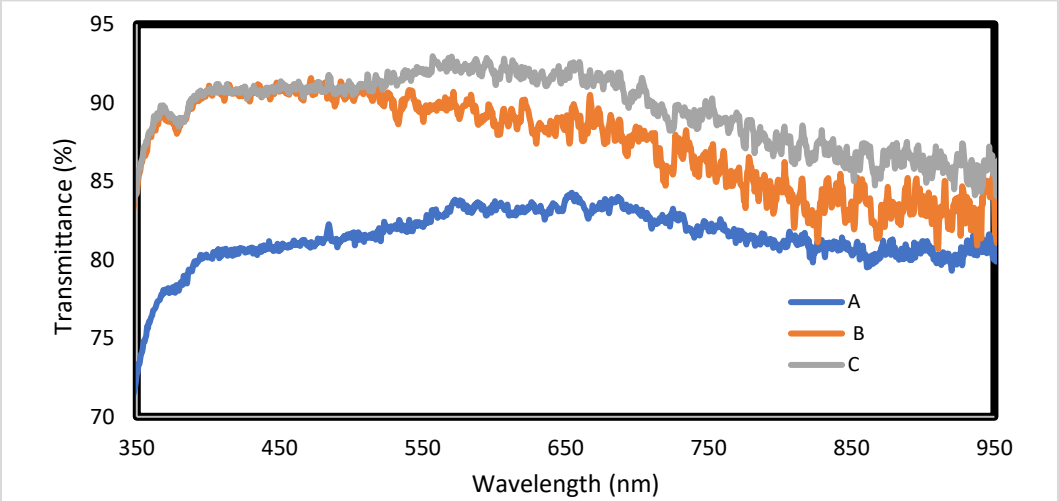

Figure 2: Transmittance spectra of PEDOT:PSS thin films on glass substrate at different temperatures conditions.(A-as-deposited, B- 100 ^{o}C , and C- 200 ^{o}C)

Figure 2 shows the percentage of incident photons transmitted through PEDOT:PSS thin films at each wavelength as a function of annealing temperatures. (as-deposited, 100 ^{o}C , and 200 ^{o}C), The peaks in the spectra demonstrate the increase in their optical transmittance behavior at the wavelength range from 350 to 950 nm (Figure 2). This corroborate the optical transparency of PEDOT:PSS thin films to the incident photons in the visible range at elevated temperature as reported in the previous literature, thereby enhancing their ability to transmit photons. The optical transmittance of the PEDOT:PSS films improved upon annealing. At wavelength 600 nm, the unannealed sample exhibits 83 % transmittance while the annealed PEDOT: PSS samples (100 and 200°C) exhibit 87 and 93 % increase respectively. This can be attributed to induced structural and morphology change of the films in relation to annealing temperature treatment, which is similar to the work of (Sivakumar et al., 2017). Annealing treatment can facilitate shrinkage of water-soluble polyelectrolyte PSS region modifying the PEDOT:PSS annealed surface morphology and cause structural rearrangement within the film network via phase segregation of PSS phase from PEDOT alignment. Thus the impact of annealing temperature treatment on optical feature of the PEDOT: PSS films enhance photons transmission efficiency, which in turn contribute to photocurrent generation in the photovoltaic device.

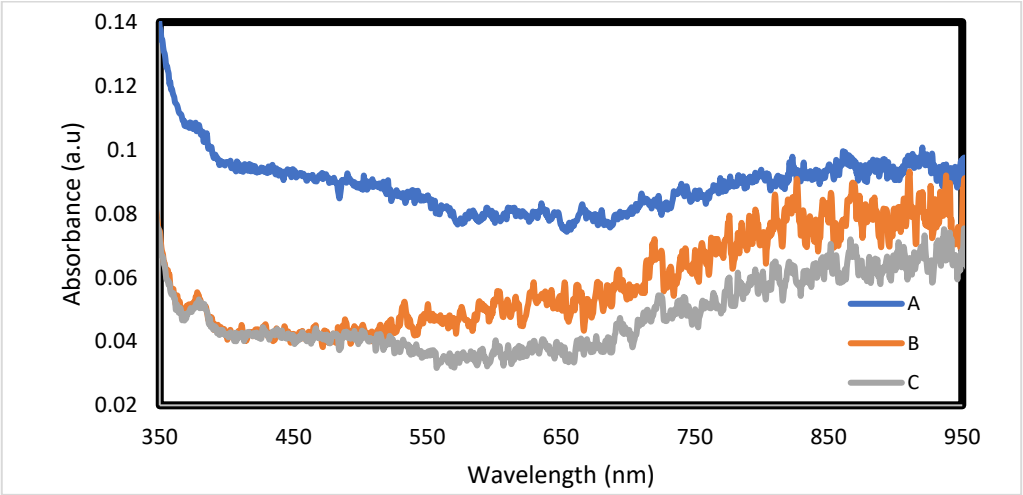

Figure 3: Absorbance spectra of PEDOT:PSS films as a function of annealing temperatures. (A- as-deposited, B- 100 ^{o}C, and C- 200 ^{o}C)

In Figure 3, the amount of incident photons absorbed by PEDOT:PSS films at different wavelength as a function of annealing temperatures were illustrated. The annealed films exhibited a remarkable decrease in the optical absorption in the wavelength range 550-950 nm as compared with the unannealed film (Figure 3). Besides, the prominent rise in optical absorption of PEDOT: PSS film in the UV region (≈ 350 nm) correspond to the π-π* electronic transition of PEDOT: PSS polymeric molecules presumably due to the photoexcitation phenomenon (Kažukauskas et al., 2010; Vázquez-López et al., 2020).

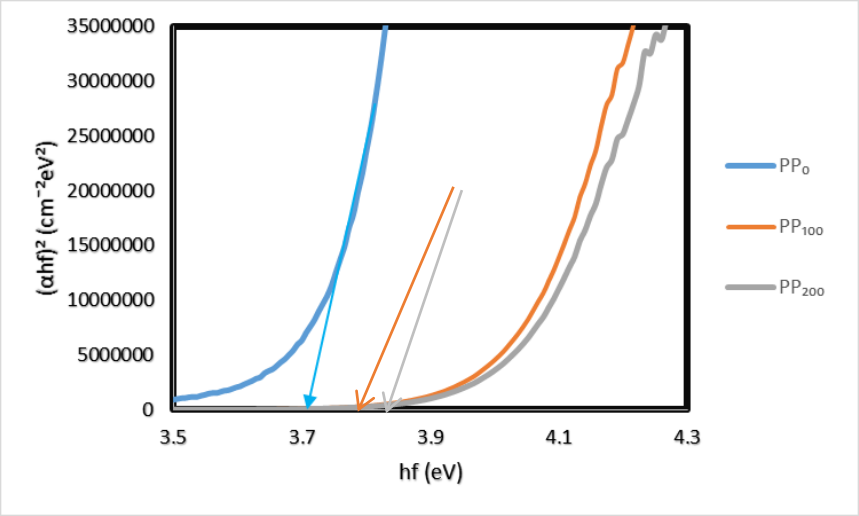

Figure 4: Plots of $(\alpha hf)^2$ vs photon energy of PEDOT:PSS thin films at different annealing conditions; As-deposited = (PP_0), 100 ℃ = (PP_{100}), and 200 ℃ = (PP_{200})

Figure 4 shows the Optical bandgap of as-deposited, and annealed PEDOT:PSS films at 100 and 200 ℃. The optical bandgap (Eg) can be estimated from the linear extrapolation of the curve to the hf axis at $(\alpha hf)^2 = 0$. The optical bandgap of the PEDOT:PSS thin films were obtained from the Tauc's plot, which derivable from the expression:

$(\alpha hf)^n = A(hf - Eg)$

where α is the absorption coefficient, hf is the photon energy, Eg is the optical band gap, A is the proportionality constant of n depends on the radiative transition probability and n is given as ½ for directed allowed band-gap. The Eg of the films annealed at 200 ℃ (4.05 eV), and 100 ℃ (3.95 eV) increase in comparison with as-deposited sample (3.7 eV). which in agreement with the optical transparency characteristics of the annealed films. This can be attributed to thermally induced change of PEDOT: PSS morphology and crystal structure similar to the observations of Friedel *et al*., (2009); Carter et al.,(2023).

Surface morphology studies of PEDOT:PSS Thin Films

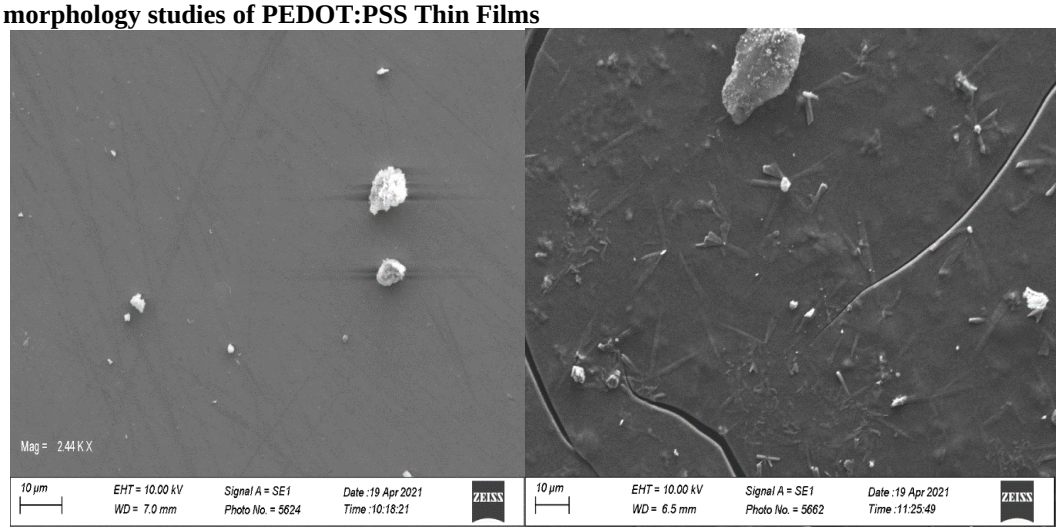

Figure 5: SEM micrographs of (a) Unannealed and (b) annealed PEDOT:PSS films

Figure 5 shows a surface morphological change of unannealed and annealed PEDOT: PSS films. It was observed that the surface roughness of the unannealed film was modified by thermally induced change in film surface property.

Annealing influenced the colloidal particles size in the PEDOT: PSS structure leading to coalescence of PEDOT: PSS particles by softening of PSS sites. Moreover, The conductivity of PEDOT: PSS film is associated with the particle size distribution. At elevated temperature, the grain size is increased causing a reduction of inter-grain barriers, which consequently lead to the formation of crystalline PEDOT: PSS structure (Carter et al., 2023; Aasmundtveit et al., 1999). Annealing temperature treatment of PEDOT:PSS sample improves agglomeration of the PEDOT: PSS particles as well as surface roughness of the PEDOT: PSS structure when compared with unannealed film ascribed to rearrangement of PEDOT: PSS chain. The increase in grain size may be due in part to the removal of residual solvent in PEDOT: PSS grain and an induced phase segregation, reducing grain boundary defects resulted in charge carrier mobility enhancement in the PEDOT chain. (Koidis, et al., 2011; Cruz-Cruz et al., 2010; Kurukavak & Polat, 2020; Sivakumar et al., 2017).

Structural analysis of PEDOT:PSS Films

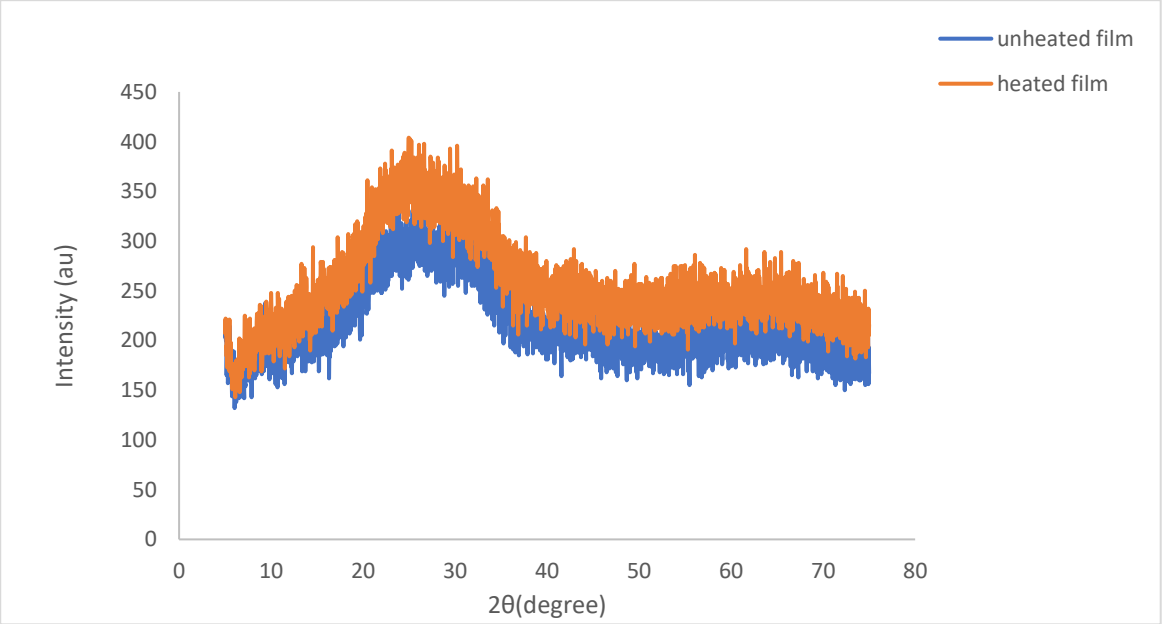

Figure 6: Powder X-ray Diffractometer (PXRD) diffraction of annealed (200 °C) and unannealed PEDOT:PSS films

The Structural properties of annealed and unannealed PEDOT PSS films spin-coated on glass substrates are analyzed by Powder X-Ray Diffractometer (PXRD), as shown in Figure 6. The diffraction peak at two theta (2θ) position = 26° was obtained for both the unannealed and annealed (200 ºC) PEDOT PSS films. No discernible peaks were observed in the XRD diffraction patterns of both samples probably due to amorphous nature of organic material molecular packing which may be linked to the presence of residual PSS, in agreement with previous reports (Kim ET AL., 2020; Rwei ET AL., 2019; & Liu ET AL.,2009). However, the annealing treatment increases the film characteristic peak intensity indicating an improvement on the crystallization feature of the PEDOT:PSS film.

CONCLUSION

The effects of annealing on the optical, structural, and surface morphological properties of the obtained PEDOT:PSS films for energy conversion application were studied. The optical transmittance behavior of the films improve with increase in annealing temperatures. The molecular orderliness and connectivity of the film improve slightly upon heat treatment. SEM image reveals increased electrical conductivities associated with improved degree of roughness in annealed film. Hence, the impact of annealing temperature treatment improve the potential applications of PEDOT:PSS films in optoelectronic devices.

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