Tuned high dielectric constant, low dielectric loss tangent with positive and negative values for PPy/MWCNTs/TiO2/Al2O3/n-Si

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Abstract
The paper presents structural and dielectric properties of Polypyrrole-MWCNTs/TiO2/Al2O3/n-Si emphasizing that one of the superior characteristics is the appearance of negative dielectric constant and dielectric loss tangent at both high and low frequencies. It may worth mentioning that the need to develop electronic devices based on new materials combination has motivated the development of such structures as supercapacitors and diodes. The structural characterization of PPy-MWCNTs/TiO2/Al2O3/n-Si was investigated using X-ray diffraction, FTIR, Raman spectroscopy, and scanning electron microscope. The oxide film thickness (dox), the density of state (NSS), admittance (Ym), electric field (Em), depletion layer width (Wd), and Dr (eV) were examined using the C/C0^2/C0 relationship. At low frequencies, the values of Wd, Φh increase, however as frequency rises, the Wd, NSS, and Rs decrease. The dielectric constant (ε) takes only negative values at a high frequency of 2x10^7 Hz, whereas it takes both negative and positive values at frequencies of 10^7, 100, and 10 Hz. The dielectric loss tangent (tanδ) has positive and negative values at frequencies 10^7, 10^6, 100, and 10 Hz.

1. Introduction
In microelectronics, although high-power-density dielectric capacitors provide rapid charging and discharging, they also have the disadvantage of having a low energy density [1]. It’s still critical to find an alternative dielectric material with a high energy density. Aimed at dielectrics, the energy density is determined by together of the electrical breakdown strength and dielectric constant [2]. Consequently, resources with a high dielectric constant have been widely deliberate in the previous [3,4], to obtain a controllable...
dielectric capacitor, we need to process the dielectric materials several times. Several studies have been dedicated to polymer dielectrics with great processing properties, then it has been found that the slight polarization covalent dipoles yield a comparatively little dielectric constant. The little dielectric constant bounds the growth of neat polymer dielectrics [5]. To increase the dielectric constant of polymer resources, the composite dielectrics must be manufactured by mixing a great dielectric constant of ferroelectric ceramic particles with the polymers [6]. Inappropriately, the great weight content of ferroelectric ceramics can lead to a decline in the processing presentations of the composites. Ceramic particles with a great electrical conductivity must be regularly spread in the polymers as in the conductor/polymer composite dielectrics [7]. The weight content of conductive particles remains actual low in most suitcases. The great dielectric constant of the
composites is due to the influence of conductive fillers and remains frequently tracked by together of high dielectric loss and high conductivity [8,9]. The great electrical conductivity remains negative when the high energy density conflicts with high collapse strength. Asymmetry point must originate between the low dielectric loss and the high dielectric constant aimed at obtaining a great energy density in composites. Thus, it is significant to investigate the dielectrics of polymer/conductor composites in the field of electrostatic energy storage. Recently, studying the dielectric properties of materials and composites plays a pivotal role in electronic device manufacturing. Dielectric properties such as a high dielectric constant ($\varepsilon$), low dielectric loss (tan$\delta$), and high electrical breakdown intensity ($E_b$) are extremely required for several requests containing energy storage. Together polymers and ceramics have been extensively used as energy storage dielectrics. Generally, ceramics, for example, the ferroelectric display a higher $\varepsilon$ than polymers [10–14], though the polymers display a greater $E_b$ than the ceramics [15–19]. Moreover, polymers are elastic and can be treated at low temperatures, since it is a pioneering material for capacitors manufacturing. In recent years, dielectric composites that combine the properties of ceramics, MWCNTs, and polymers have been commonly used to develop high dielectrics [20–24]. The electrical and dielectric properties of polymer with desired high dielectric constant and low dielectric loss can be modified by improving their microstructure and controlling the regulatory of nano-fillers [25–28]. In this paper, we synthesized a composite of polypyrrole with MWCNTs then deposited it on the surface of TiO$_2$/SiO$_2$/n-Si. This structure has a high dielectric constant and low dielectric loss emphasizing the appearance of negative dielectric constant and dielectric loss tangent at both high and low frequencies, in contrast to what is preserved as the appearance of a negative value only at high or low frequencies [29,30]. The main aim of this study is to fine-tune the dielectric constant and dielectric loss tangent so that high-energy storage such as supercapacitors and electronic devices as diodes can be manufactured [31–35]. The structure of Polypyrrole-MWCNTs composite/TiO$_2$/Al$_2$O$_3$/n-Si has been fully characterized by X-ray diffraction pattern, FTIR, Raman spectroscopy, and scanning electron

Figure 2. X-Ray diffraction pattern of PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$/n-Si.
In this paper, the impacts of multi-layers on the electrical interface states and series resistance characteristics of Au/PPy-MWCNTs/Al2O3/TiO2/Al capacitors are reported, by analyzing Capacitance – Voltage (C – V), conductance (G – V). The density of state (N_{SS}), the oxide film thickness (d_{ox}), admittance (Y_m), electric field (E_m), depletion layer width (W_d), and ΔΦ_b (eV) were examined using the $C^{-2} - V$ relationship. The values of $W_d$, $Φ_b$ increase at low frequencies, but as frequency increases, the $W_d$, $N_{SS}$, and $R_s$ decrease. At a high frequency of $2 \times 10^7$ Hz, dielectric constant $ε'$ takes only negative values, while at frequencies of $10^7$, 100, and 10 Hz, $ε'$ takes both negative and positive values. Negative permittivity indicates that the electric displacement and electric field vectors are in opposite directions, but it does not imply that the electric energy stored in such a material is negative. The negative dielectric constant was observed at sufficiently high and
Figure 4. (a-à,b-b,c-c,d-d,e-è,f-f, g-g, h-h) $\varepsilon$ and $\tan\delta$ vs T at different voltages and frequencies of PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$/n-Si.
Figure 4. Continued.
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low frequencies and it was attributed to the interfacial polarization, interface traps, recombination process, and series resistance. At low frequencies, both interfacial polarization and interface states can easily follow the same external signal. At frequencies of $10^7, 10^6, 100,$ and $10$ Hz, the dielectric loss tangent ($\tan\delta$) has also positive and negative values.

2. Results and discussion

The Au/PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$/n-Si/Al structure was manufactured by mixing multi-wall carbon nanotubes with polypyrrole with a ratio of 90:10 percentages respectively. PPy and MWCNTs were bought from Sigma Aldrich with a purity of 99.9%. Aluminum oxide thin film (Al$_2$O$_3$) was deposited on the surface of the silicon using certain drops of its suspension in water by a spin coater technique, titanium dioxide (TiO$_2$) thin film was deposited onto the Al$_2$O$_3$ by the similar procedure. Lastly, drops of PPy – MWCNTs composite were deposited on the surface of the TiO$_2$ film, the construction after that became PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$. Two electrodes of gold and aluminum were deposited on the upper and lower surfaces to measure electrical and dielectric properties.
The surface topography and particle size of MWCNTs and PPy-MWCNTs composites were described using SEM [36–40]. Figure 1(a,b) shows the surface morphology of MWCNTs and PPy-MWCNTs composites, respectively. The tubular shape of carbon nanotubes with a diameter of around 15 nanometers is described in Figure 1a, and it was also observed in the PPy-MWCNTs composite after being coated with a thin layer of Polypyrrole with a larger diameter as seen in Figure 1b. The X-ray diffraction peaks of PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$/n-Si are seen in Figure 2. The peak at 2$\Theta$ = 25.3$^\circ$ is related to both Polypyrrole and MWCNTs [23–25]. The peak at 2$\Theta$ = 43.7$^\circ$ is corresponding to MWCNTs, while peaks at 2$\Theta$ = 48.1$^\circ$ and 58.46$^\circ$ are corresponding to TiO$_2$, though at 2$\Theta$ = 26.5$^\circ$ connected to Al$_2$O$_3$, whilst at 2$\Theta$ = 37.8$^\circ$ connected to TiO$_2$ and Al$_2$O$_3$. The Raman spectroscopy of PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$/Si is seen in Figure 3, the Raman spectrum of pure MWCNTs has two distinct peaks, the G band at 1576 cm$^{-1}$ and the D band at 1354 cm$^{-1}$ as seen in Figure 3b. The D band in the Raman spectroscopy of PPy-MWCNTs composite changes to a wideband as the MWCNTs/PPy nanocomposite is formed. Furthermore, as MWCNTs are mixed with the Polypyrrole matrix, the D and G bands change significantly, and one extra peak is observed at 1057 cm$^{-1}$ due to the
presence of PPY, as seen in Figure 3a. This is due to the doping of PPY from the carboxyl group of functionalized MWCNTs and the $\pi - \pi$ contact amid PPY and MWCNTs. The other peaks from 380 to 976 are related to TiO$_2$ and Al$_2$O$_3$.

### 3. Dielectric properties

Using a Novocontrol high-resolution alpha analyzer, the dielectric properties were measured throughout a frequency range of 10 Hz–20 MHz, at temperatures ranging from 233 to 323 K, and voltages ranging from $-2$ V to 2 V. We provide this instrument with the essential information in terms of temperature range, voltages, and frequency, and it measures the dielectric characteristics automatically. Though a high dielectric constant is important for high energy storage dielectrics, finding the right balance between a high dielectric constant and low dielectric loss is much more critical [41,42].

Figure 4 (a–a, b–b, c–c, d–d, e–e, f–f, g–g, h–h) clarifies dielectric constant ($\varepsilon'$) and dielectric loss tangent (tan\(\delta\)) as a function of temperature at different voltages and frequencies of Au/PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$/n-Si/Al heterostructure. At frequency $2 \times 10^7$ Hz, $\varepsilon'$ has negative values at all voltages and temperatures the $\varepsilon'$ decrease with temperature increase at about 300K, then increase with temperature as shown in Figure 4a, its values about ($-280$ to $-210$), though tan\(\delta\) has positive small values of ($0.77$ to $0.83$), it increases and

![Figure 4](image-url)
decrease with temperature as seen in Figure 4(a, à) [43–46]. At frequency $10^7$ Hz, $\varepsilon$ raises from (-2 V to 2 V) and decreases with temperature increase, the increase in $\varepsilon$ was attributed to the surface states localized at interfacial layer/semiconductor, surface polarization, and series resistance ($R_s$). Similar results observed are quite compatible with the different materials [47–50]. On the other hand, the dielectric constant is inversely proportional to the temperature where raising temperature provides thermal energy to the dipoles which in turn randomizes them. As a result, a lesser number of dipoles remain aligned in the direction of the electric component of microwave radiation, resulting in a lower dielectric constant. It is worth mention that $\varepsilon$ has both positive and negative values of (-600 to 1500), whilst $\tan\delta$ has positive and negative values of about (-60 to 15) as seen in Figure 4(b,b). At frequency $10^6$ Hz, both $\varepsilon$ and $\tan\delta$ increase with temperature increase and have positive values, though $\tan\delta$ takes positive and negative values at this frequency as seen in Figure 4(c,c). At all frequencies such as $(10^5,10^4,10^3)$ Hz, $\varepsilon$ and $\tan\delta$ have only positive values which increase as the temperature increase. At frequencies (100) Hz, $\varepsilon$ and $\tan\delta$ have both positive and negative values, we notice that the curve at a voltage $-2$ V has negative values, while the curves at voltages of (-1,0,1,2) V have positive values as seen in Figure 4(g-g). At a frequency of 10 Hz, although all $\varepsilon$ curves at the entire voltages range have negative values as shown in Figure 4h, on the other hand, all $\tan\delta$ curves have negative values except the curve at zero voltage which has positive values as illustrated in

Figure 4. Continued.
Figure 5. (a-à,b-b,c-c,d-d,e-è,f-f, g-ğ, h-h) $\varepsilon'$ and $\tan\delta$ vsV at different voltages and frequencies of PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$/n-Si.
Figure 5. Continued.
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Figure 5. Continued.
Figure 4h. With a variety of frequencies, \( \varepsilon' \) is reaching its maximum of about (15000 to \(-600000\)), though \( \tan\delta \) has minimum values of about (0.01 to 0.08). The boost of the dielectric constant for the of Au/PPy-MWCNTs/TiO\(_2\)/Al\(_2\)O\(_3\)/n-Si Al is owing to the polarity influence such as Maxwell–Wagner–Sillars (MWS) or interfacial polarity influence [46, 51]. Besides, the charge can be gathered at the borders between layers due to their boosted dielectric constant at low frequency [52,53].

Figure 5 (a-a,b,b,c-c,d-d,e-e,f-f, g-g, h-h) demonstrates the variation of \( \varepsilon' \) and \( \tan\delta \) as a function of applied voltage at fixed temperatures and frequencies of Au/PPy, MWCNTs/ TiO\(_2\)/Al\(_2\)O\(_3\)/n-Si/Al heterostructure. At high frequency \( 2 \times 10^7 \text{ Hz} \), \( \varepsilon' \) has negative values at all temperatures, while \( \tan\delta \) takes positive values, both \( \varepsilon' \), \( \tan\delta \) have positive and negative values at \( f = 10^7 \text{ Hz} \), the \( \varepsilon' \) raises with temperature decrease as shown in Figure 5b. At frequency \( 10^6 \text{ Hz} \), \( \varepsilon' \) and \( \tan\delta \) increase with temperature increase taking positive values in both positive and negative regions of the voltage additionally \( \varepsilon' \) and \( \tan\delta \) increase with voltage in the positive and negative voltage region. At frequency \( 10^5 \text{ Hz} \), \( \varepsilon' \) increases as
Figure 5. Continued.

the temperature rises, whereas \( \tan \delta \) is seen more regular compared to \( \varepsilon \), both have positive values as illustrated in figures (d,d). At frequencies, 104 Hz and 103 Hz, \( \varepsilon \) and \( \tan \delta \) have only positive values which increase as the temperature increase. At low frequencies (100, 10) Hz, \( \varepsilon \) and \( \tan \delta \) have positive and negative values, \( \varepsilon \) has a mean value of \( (1.8 \times 10^3 \text{ to } -8 \times 10^5) \) at a low frequency while \( \tan \delta \) has a minimum value of \( (0.03 \text{ to } -0.01) \) at high frequency. The behavior of \( \varepsilon \) and \( \tan \delta \) can be credited to the specific distribution of \( N_{ss} \) and Maxwell Wagner type interfacial polarization [54,55].

Figure 6 (a, a, b, b) shows the dependence of \( \varepsilon \) and \( \tan \delta \) with voltages at different frequencies and temperatures of Au/PPy-MWCNTs/TiO\(_2\)/Al\(_2\)O\(_3\)/n-Si/Al. As shown \( \varepsilon \) creates a reverse peak for each frequency at zero voltage, the values of \( \varepsilon \) increase with increasing frequencies in both positive and negative regions of the voltage reaching its maximum of \( 2.8 \times 10^3 \) as seen in Figure 6a. At high frequencies, \( \tan \delta \) takes a minimum positive and negative values of about (-0.6 to 0.2) as seen in Figure 6a. At low frequencies, both \( \varepsilon \) and \( \tan \delta \) show positive and negative values, the dispersion in the \( \varepsilon \) and \( \tan \delta \) was attributed to the local surface states at interfacial layers/semiconductor, surface polarity and series resistance (\( R_s \)) [47,48]. In other words, at high frequencies, the influence of
interfacial polarity reaches a constant value as the electron hopping loses the capability of tracking alternate fields afterward a certain frequency of exterior field [46]. As a result, we can say that $\varepsilon'$ and $\tan\delta$ can be affected by the four types of polarity operations (ionic, dipolar, electronic, and interfacial) at low frequencies. At very high frequencies, the influence of ionic and electronic shares becomes the dominant mechanism, while the others can be more active at lower frequencies. In addition, as exposed in Figure 6(a), $\tan\delta$ is nearly independent of the voltage at high frequencies, it is recognized that the value of $\tan\delta$ and $\varepsilon'$ depends on several factors for example the temperature of substrates, frequency, the growth or preparation methods, annealing, thickness and homogeneities, applied voltage or electric field [56,57].

Figure 7 (a–e) illustrates the variation of $\varepsilon'$ with ln$f$ at different temperatures and voltages of Au/PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$/n-Si/Al. At high frequencies, $\varepsilon'$ has negative values reached to $-1500$, whilst at mid frequencies, it takes positive values of about $5.5 \times 10^3$, it takes also negative values at low frequency as displayed in Figure 7a while it takes negative values at both high and low frequencies as seen in Figure 7b. It takes the values
5.7 \times 10^3, 1.44 \times 10^4, 2.8 \times 10^4, 1.65 \times 10^4 and 1.38 \times 10^4 at the voltages (-2,-1,0,1,2) V respectively depending on the applied voltage. At low frequencies, $\varepsilon$ has negative values another time, this is a novel in this paper where the negative values of $\varepsilon$ occurred at both high and low frequencies. It also shows that the magnitude of $\varepsilon$ decreases as the frequency increases throughout the range. The decline in $\varepsilon$ at high frequencies can be assumed as: the ac field is applied to samples; at minor frequencies, all the dipoles can align themselves with practical frequency throughout the first cycle and reoriented in the opposite direction in the next cycle of the practical frequency. Then, when the frequency rises, dipoles cannot realign themselves, resulting in an additional dielectric dispersion at low frequencies, which becomes independent at higher frequencies.

Figure 8 (a,b,c,d,e),(a’,b’,c’,d’,e’) describes the $\varepsilon$- $\varepsilon$ of Au/PPy/MWCNTs/TiO$_2$/Al$_2$O$_3$/ n-Si/Al heterostructure at different voltages and temperatures. The size of the semicircular increase with the voltage of (-2 V, 2 V, 1 V, 1 V, 0 V) respectively as shown in Figure 8 (a,b,c,d,e). The semicircle at a voltage of 2 V increases as seen in Figure 8b when compared to the same semicircle in Figure 8a, while the semicircles at (2,-2)V are merged as seen in Figure 8d, whereas it increases with temperature in Figure 8(a–e). On the other hand, figures (a’,b’,c’) show how the radius of the semicircle

![Figure 5. Continued.](image-url)
Figure 6. (a–a′, b–b′) ε and tan δ vs V at different frequencies and temperatures of PPy-MWCNTs/TiO₂/Al₂O₃/n-Si.
Figure 7. (a,b,c,d,e) $\varepsilon^*$ vs $f$ at different temperatures and voltages of PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$/n-Si.
increases with decreasing voltages (2,1,0) V, whereas Figure 8 (d’.e’) show how the radius of a semicircle decreases as the voltage decreases (2,1,0) V. The constructed heterostructure performance was linked to an electrical circuit model derived from the parallel assembly of a constant phase element (CPE) and resistance (R_p) combined with R_s [58,59].

4. Capacitance–voltage (C–V)

(C–V) measurements of the structure were stated and verified at room temperature using a frequency range of 10 Hz–20 MHz, the C–V relation of diodes can be expressed by [60–62];

$$C^{-2} = \frac{2}{qe_sA^2N_p} \left( V_{bi} - \frac{KT}{q} - V \right)$$

(1)

$$N_p = \frac{2}{qe_sA^2} \left[ d\left( \frac{1}{C^2} \right)/dV \right]$$

(2)
where \( N_p \) is the concentration of holes in the valence band, \( V \) is the voltage, \( A \) is the active diode area, and \( \varepsilon_s \) is the permittivity of diode material [38]. \( V_0 \) is determined by plotting of \( 1/C^2 \) vs. \( V \). The potential \( V_{bi} \) is calculated from \( V_0 \) by

\[
V_{bi} = V_0 + \frac{kT}{q}
\]

The barrier height \( \Phi_b \) from the C–V measurement is agreed by

\[
\phi_{CV} = V_{bi} + E_F - \Delta \phi_b
\]

and \( E_F \) is the Fermi level which is given by [38]

\[
E_F = \frac{kT}{q} \ln \left( \frac{N_C}{N_p} \right)
\]
where $N_c$ is the concentration of electrons in the conduction band, $m^*$ is the effective electron mass which equals $1.08 \times m_e$ for Si, it is expressed by [38]:

$$N_C = 2 \left[ \frac{2\pi m^*_e m_0 kT}{\hbar^2} \right]^{3/2}$$

(6)

Wherever $\hbar$ is Plank's constant. $\Delta \Phi_b$ is the image force-induced barrier lowering, it is assumed by [62,63]:

Figure 8. Continued.
\[ \Delta \varphi_b = 2 \left[ \frac{qE_m}{4\pi \varepsilon \varepsilon_0} \right]^{1/2} \]  

(7)
The $C^{-2}$ vs $V$ characteristics shown in Figure 9 can be used to determine certain electrical parameters of Au/PPy/MWCNTs/TiO$_2$/Al$_2$O$_3$/n-Si/Al structure for example $V_D$, $N_A$, $E_F$, $\Delta \phi_b$, $W_D$, $\phi_b$ (C–V). Extrapolation of the straight line to the voltage axis yielded the $V_d$ values for each frequency, and their values are assumed in Table 1. The disparity of $\phi_b$ and $W_d$ with frequency is exposed in Figure 10(a–c), while $W_d$ values increase at low frequencies, they decrease as frequency increases. The $\phi_b$ values have the same behavior as $W_d$, which increases at low frequencies and decreases marginally as frequencies increase. Figure 11 (a and b) show the variation of $N_{ss}$, $R_s$ versus frequency, the $N_{ss}$ and $R_s$ values reduce with raising frequency [64]. At lower frequencies, the $N_{ss}$ that is affected by the practical signal can send and receive charges in response to it. The boundary state

$$E_m = \left[ \frac{2qN_pV_0}{\varepsilon_r\varepsilon_0} \right]^{3/2}$$

$$W_d = \left[ \frac{2\varepsilon_sV_d}{qN_d} \right]^{1/2}$$

Figure 8. Continued.
capacitance seems directly in parallel with the exhaustion capacitance, ensuing in a higher entire value of the capacitance. Instead, the boundary state density is almost free of the frequency at higher frequencies [64–66]. As seen in Figure 12a, Na values decrease as frequency increases, while in Figure 12b increases as frequency increases. This performance can be described by whether the border state charges contribute to the capacitance of the diode or the charge at the boundary states can track ac sign due to a variety of states of different lifetimes [64, 67]. Figure 13 displays that the Wd, Nss, Na, Ef were strongly dependent on the frequency. The values of φb, Wd, Nss, Na, Ef were drawn against lnf as seen in previous figures, all values of φb, Wd, Nss, Na, Ef are a robust function of frequency. Table 1 also assumes the additional variables calculated from C−2 − V curve.

5. Conclusion

The paper presented the possibility of tuning the dielectric constant and dielectric loss tangent so that the current structure can be used in manufacturing high-energy storage devices like

![Figure 9](image_url) C−2 vs. V at different frequencies and room temperatures of PPy-MWCNTs/TiO2/Al2O3/n-Si.

**Table 1.**

| Frequency (Hz) | 10⁷ | 10⁶ | 10⁵ | 10⁴ | 10³ | 10² | 10¹ |
|---------------|-----|-----|-----|-----|-----|-----|-----|
| Na (cm⁻³)     | 2.81 × 10¹⁹ | 2.81 × 10¹⁹ | 2.81 × 10¹⁹ | 2.81 × 10¹⁹ | 2.81 × 10¹⁹ | 2.81 × 10¹⁹ | 2.81 × 10¹⁹ |
| Nv (cm⁻³)     | 1.05 × 10¹⁹ | 1.05 × 10¹⁹ | 1.05 × 10¹⁹ | 1.05 × 10¹⁹ | 1.05 × 10¹⁹ | 1.05 × 10¹⁹ | 1.05 × 10¹⁹ |
| Nss (cm⁻³)    | 1.54 × 10¹⁸ | 2.52 × 10¹⁷ | 1.49 × 10¹⁷ | 1.34 × 10¹⁷ | 1.46 × 10¹⁷ | 1.99 × 10²¹ | 1.69 × 10²⁴ |
| Vb (V)        | 3.00           | 3.2             | 2.2             | 1.2             | 1.2             | 1.2             | 1.2             |
| Vd (V)        | 3.00           | 3.2             | 2.2             | 1.2             | 1.2             | 1.2             | 1.2             |
| E-Fermi (eV)  | 0.05           | 0.11            | 0.11            | 0.05            | 0.14            | 0.14            | 0.14            |
| φb (eV)       | 3.08           | 3.34            | 2.34            | 1.28            | 1.09            | 1.2             | 1.82            |
| Coo (F)       | 1.80 × 10⁻⁷    | 1.10 × 10⁻⁸     | 1.30 × 10⁻⁸     | 1.20 × 10⁻⁷     | 1.00 × 10⁻⁵     | 3.20 × 10⁻³     | 1.90 × 10⁻³     |
| dso (nm)      | 6.19 × 10¹⁴    | 1.01 × 10¹⁵     | 8.58 × 10¹⁶     | 9.29 × 10¹³     | 1.11 × 10²      | 4.85 × 10⁻¹     | 5.87 × 10⁻¹     |
| Nss (eV·cm⁻²) | 2.06 × 10¹⁰    | 7.68 × 10¹⁰     | 3.31 × 10¹⁰     | 4.37 × 10¹⁰     | 3.15 × 10¹⁰     | 1.69 × 10¹⁰     | 1.26 × 10¹⁰     |
| Rs (Ω)        | 6.30 × 10⁻⁴    | 1.15 × 10⁻⁴     | 2.67 × 10⁻²     | 2.02 × 10⁻²     | 2.72            | 5.22 × 10⁻²     | 7.02 × 10⁻²     |
| Ym (cm)       | 1.13 × 10⁻³    | 6.91 × 10⁻⁴     | 8.18 × 10⁻²     | 7.55 × 10⁻²     | 6.58 × 10⁻³     | 1.45 × 10⁻¹     | 1.19 × 10⁻¹     |
| Em (V/cm)     | 1.40 × 10⁻³    | 5.84 × 10⁻³     | 4.49 × 10⁻¹     | 3.53 × 10⁻¹     | 8.62 × 10⁻¹     | 3.18 × 10⁻¹     | 1.23 × 10⁻¹     |
| Wd (cm)       | 1.69 × 10⁻¹    | 4.31 × 10⁻¹     | 5.60 × 10⁻¹     | 4.90 × 10⁻¹     | 1.10 × 10⁻¹     | 2.97 × 10⁻¹     | 1.35 × 10⁻¹     |
| φb (eV)       | 1.31 × 10⁻⁵    | 8.48 × 10⁻⁴     | 7.43 × 10⁻⁴     | 6.59 × 10⁻⁴     | 1.03 × 10⁻³     | 6.25 × 10⁻³     | 1.35 × 10⁻³     |
supercapacitors highlighting the novel appearance of negative dielectric constant and dielectric loss tangent at both high and low frequencies. Polypyrrole with MWCNTs composite/TiO2/Al2O3/n-Si has been fully characterized using different techniques as X-ray diffraction pattern, FTIR, Raman spectroscopy, and scanning electron microscope. The surface topography and particle size of MWCNTs and PPy-MWCNTs composites show a tubular shape of carbon

Figure 10. (a,b,c) Wd, $\phi_b$ and Wd $\phi_b$ vs frequency of PPy-MWCNTs/TiO2/Al2O3/n-Si.
nanotubes with a diameter of about 15 nm, its diameter increased after forming a composite with polypyrrole. Temperatures, frequencies, and voltages have a significant impact on the dielectric constant and dielectric loss tangent, as a result, we can tune the magnitude of \( \varepsilon' \) and \( \tan\delta \). The thickness of the oxide film \( (d_{\text{ox}}) \), the density of state \( (N_{\text{SS}}) \), admittance \( (Y_m) \), electric field \( (E_m) \), depletion layer width \( (W_d) \), and \( \Delta\Phi_b \) (eV) were determined using the \( C^{-2} - V \) relationship. The values of \( W_d, \Phi_b \) increase at low frequencies, but as frequency increases, the \( W_d, N_{\text{SS}}, \text{and } R_s \) decrease. At a high frequency of \( 2 \times 10^7 \) Hz, dielectric constant \( \varepsilon' \) takes only negative values, while at frequencies of \( 10^7, 100, \text{and } 10 \) Hz, \( \varepsilon' \) takes both negative and positive values. At frequencies of \( 10^7, 10^6, 100, \text{and } 10 \) Hz, the dielectric loss tangent \( (\tan\delta) \) has also positive and negative values, thus, we can conclude that the negative values of \( \varepsilon' \) and \( \tan\delta \) repeat two times in high and low frequency.

Figure 11. (a,b,c) \( N_{\text{SS}}, R_s, N_{\text{SS}}R_s \) vs frequency of PPy-MWCNTs/TiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}/n-Si.
Figure 12. (a,b,c) $\phi_0$, $\eta$, $N_a$ vs frequency of PPy-MWCNTs/TiO$_2$/Al$_2$O$_3$/n-Si.
Figure 13. (a,b,c,d) Wd, Nss, \( \phi_{fb} \), Na, Ef vs frequency of PPy-MWCNTs/TiO\(_2\)/Al\(_2\)O\(_3\)/n-Si.
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