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Structural, optical and impedance spectroscopy study of thin film of polyaniline (PANI/ZnO) nanocomposite

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Abstract

Modern organic electronic and power electronic devices gained attention due their superior performance and efficiency with reduced cost. While nanocomposites of these organic semiconductors have high potential to further enhance these properties. In this work, thin films of zinc oxide–polyaniline (ZnO–PANI) nanocomposite with different compositions of ZnO (50, 60 and 70 wt%) are deposited by spin coater onto the surface of p-Si. The phase identification of the samples is identified through x-ray diffraction analysis. Pure ZnO showed wurtzite crystalline while PANI and nanocomposites of ZnO–PANI showed amorphous structure. The optical absorption band gap was evaluated from ultraviolet–visible spectroscopy absorption studies and band gaps were calculated from Tauc’s plots. The ultraviolet–visible spectroscopy showed that by increasing ZnO content in the nanocomposite, the band gap increases from 3.25 eV to 3.3 eV and 3.4 eV for 50–50, 60–40 and 70–30 wt% respectively. The AC electrical properties of the nanocomposites were studied by using impedance spectroscopy. The parameters extracted from the impedance plots and conductivity values showed that 50–50 wt% is more conductive while that of 70–30 wt is more resistive.

Introduction

Organic semiconductors have received considerable interest in many electronic devices due to their commercial applications in solar cells, light emitting diodes, Schottky diodes, transistors and photodetectors [1–4]. These materials exhibit some beneficial properties such as large area, light weight, low cost, low temperature fabrication and easily processed in comparison to their counterparts [5]. Therefore, due to these properties they are becoming an area of interest in the development of electronic and optoelectronic devices. Furthermore, these materials can be easily deposited by thermal vacuum evaporation, spin coating, inkjet printing and drop casting techniques [5, 6]. The attention has also been given to these materials due to their compatibility with flexible substrates such as plastic, polymer and paper for the fabrication of flexible organic electronic devices [7, 8].

Presently, the metal/organic semiconductors interfaces have gained more attention in modern electronic technology [9]. The electrical properties of metal/organic semiconductors heterojunctions can be fabricated in the form of bulk and thin films by employing various materials [10, 11]. These junctions play a vital role in the development of many devices like Organic Photovoltaics (OPVs), Organic Light-Emitting Diodes, Organic Field-Effect Transistors, lasers and memory devices [12–15].

Intrinsically conducting polymers are attracting more attention in many technological applications such as photonics and optoelectronics [15–17]. Nowadays, a number of polymers like polypyrrole (Ppy), polypyrrole (PTh), polyaniline (PANI), poly(p-phenylene vinylene) (PPV) and poly (3,4-ethylidioxythiophene) (PEDOT)
are synthesized and employed as active materials in sensors, diodes, transistors, and solar cells [16, 17]. Among these materials, polyaniline (PANI) is of particular interest due to its high conductivity, ease of preparation, simple polymerization, environmental friendly and good thermal stability [18]. It is widely used in batteries, electrochemical devices, electromagnetic shielding devices and biosensors [19, 20]. Recently, several reports on nanocomposites of PANI with the inorganic materials such as Ag, TiO₂, MnO₂, Au, CaWO₄, MnWO₄ and ZnO were published [21–24]. These nanocomposites exhibit some unique electrical, optical, catalytic, structural and mechanical properties due to the interaction of two different chemical components.

Zinc oxide (ZnO) is a semiconducting material having direct band gap (3.37 eV) and large excitation binding energy (60 meV) at room temperature. It is non-toxic and n-type semiconductor having good conductivity [25]. Due to its interesting properties, it is expected to play an important role in the development of future optoelectronic and electronic devices such as field effect transistors, electro optics, field emission displays, transducers, UV detector and piezo electronic materials [9, 18, 26]. Recently, a technological interest is given to ZnO-PANI nanocomposites. The use of PANI with inorganic materials produces materials with complementary properties. Therefore, nanocomposites of ZnO-PANI are intensively studied among various composites in order to explore its applications in many fields such as microelectronics, electrophotonic devices and photoelectrochemical devices [19].

Impedance Spectroscopy (IS) is a technique used for measuring electrical parameters of the materials. [27]. IS allows us to calculate and differentiate the contributions of many components i.e. bulk, electrode and grain boundary [26, 28]. In IS, the ac electrical properties are measured over a range of frequencies, commonly 10 to 10⁷ Hz and various regions of the material are recognized according to their electrical relaxation times [29–31]. In IS, the electrical properties can be represented in any of the four interrelated basic formalisms: the electric modulus M*, the impedance Z*, the admittance A* or Y* and permittivity e*. This allows a more in-depth study of the electrical properties of a material [30].

The main purpose of this work is to investigate the electrical microstructure of p-Si/ZnO-PANI nanocomposite thin films using impedance and modulus spectroscopy for three different compositions. Moreover, the structural and optical properties of the p-Si/ZnO-PANI thin films are investigated through x-ray Diffraction (XRD) JEOL, Japan (JDX-3532) and LAMBDA 1050 UV/VIS spectrometer.

### Experimental

The native oxide layer from the p-silicon substrate was removed by dipping it into the dilute solution of HF and H₂O in ratio of (1: 10). Then the cleaned substrate was dried in nitrogen (N₂) atmosphere. Polyaniline was purchased from Sigma-Aldrich (USA) and ZnO nanoparticles from Neutrino Company (China). The received materials were used without further purification. Solution of various concentrations of Polyaniline powder and zinc oxide nanoparticles were prepared in N-methyl-2-pyrolidone, then the solution was stirred for 5 h to obtain homogenous solution. Thin films of nanocomposites with different concentration were deposited on the surface of the p-Si substrate by using spin coating method at 800 rpm for 30 s/30 s. Then the metallic electrode of aluminum having thickness of 100 nm was thermally grown on the nanocomposite thin film. During the deposition of electrode, 10⁻⁵ mbar pressure was maintained in the vacuum chamber. The electrical measurements were taken at room temperature under dark condition using a computer-controlled LCR Hi-Tester (HIOKI 3532-50, Japan). Schematic of prepared sample is shown in figure 1.
Results and discussion

X-ray diffraction analysis

The x-rays diffraction (XRD) analysis was performed to study the structure of ZnO-PANI nanocomposite thin films. The x-ray diffraction pattern of ZnO, PANI and nanocomposite of ZnO-PANI were shown in the figure 2.

The characteristic peaks of ZnO come at \(2\theta = 31.73^\circ, 34.37^\circ, 36.21^\circ, 47.48^\circ, 56.53^\circ, 62.77^\circ, 67.86^\circ\) and \(69^\circ\) which relates to plane \((100), (002), (101), (102), (110), (103), (112)\) and \((201)\) respectively. The inset in figure 2 shows that the x-rays diffraction pattern of PANI, having a broad peak at \(2\theta = 22.6^\circ\), which corresponds to \((200)\) plane.

Figure 2 represents the characteristic peaks for crystalline ZnO of hexagonal wurtzite structure which clearly shows that the pattern of ZnO-PANI nanocomposite doesn’t remain the same shape after \(36.21^\circ\) as observed for pure ZnO nanoparticles. This shows that the crystalline structure of zinc oxide altered after treating with polyaniline molecules. However, ZnO-PANI nanocomposite peaks were shifted to lower intensities by compositing with PANI chains, which shows the amorphous nature of ZnO-PANI nanocomposite \([1]\). The nanocomposite patterns exhibit the characteristic peaks of both ZnO and PANI up to \(36.21^\circ\) which approves the presence of ZnO and PANI in the nanocomposite for each composition. It is clear from these plots that all the compositions are in resemblance with the zinc oxide pattern up to 36.21 Bragg’s angle. But the peak intensities increased with the increase of zinc oxide percentage in the nanocomposites.

4.3 UV-visible absorbance spectroscopy

The UV–vis absorbance spectrum of the nanocomposites was shown in the figure 3. The figures show the UV-Visible spectra of the pure PANI and ZnO. The left figure shows the PANI spectra and right side insert image shows ZnO spectra. According to Wood and Tauc \([2]\) the optical band gap is related with the photon energy and absorbance as:

\[
h\alpha \propto (h\nu - E_{\text{gap}})^n
\]

Where \(h\nu\) is the incident photon energy, \(\alpha\) is the absorbance, \(E_{\text{gap}}\) is the band gap and \(n\) is a constant which depends on the nature of transitions \((n = 1\) for direct semiconductors and \(4\) for indirect semiconductors) \([3]\).

In order to calculate the energy gap \(E_{\text{gap}}, (h\nu\alpha)^2\) was calculated and the plots of \((h\nu\alpha)^2\) versus incident photon energy \(h\nu\) were plotted for three different nanocomposites and are shown in figure 4. Thus, the energy gaps \(E_{\text{gap}}\) were obtained by extrapolating the linear part of the curves or tails to join the energy axis. The \(E_{\text{gap}}\) value at \((h\nu\alpha)^2 = 0\) was calculated for all the three compositions. The band gap values 2.84, 2.86, and 2.9 eV were calculated from the Tauc plots for 50–50, 60–40 and 70–30 wt%, respectively. These values suggest that the band gap energy increases by increasing the zinc oxide percentage in the nanocomposites. This trend in the increase of band gap and the calculated values are in accordance with the reported behavior of \([3]\). These wide band gaps of the selected nanocomposites revealed that they are suitable to use in the organic electronic devices for the potential use in semiconductor industry and next generation power electronics \([4]\).

Figure 2. The XRD patterns of ZnO–PANI nanocomposites with the standard XRD pattern of ZnO (PDF Card No # 89-1397) and the inset shows the XRD pattern of pure PANI.
Electrical properties

Impedance spectroscopy

Complex impedance analysis

Figure 5 shows the complex impedance plots \( Z' \) versus \( Z'' \) at 300 K for three different compositions i.e. (50–50, 60–40 and 70–30 by wt%). These plots give information in the form of arcs or semicircles and each arc denotes an electroactive region with a related relaxation time, \( \tau = RC \), where, \( R \), \( C \) and \( \tau \) are the resistance, capacitance and relaxation time of the charge carriers, respectively. The figure 4 shows two different sized semicircular arcs for all compositions in the complex plane. These indicate the presence of two electroactive

Figure 3. UV–vis spectrum of three different nanocomposites along with the absorbance of PANI and ZnO.

Figure 4. Tauc’s plots for three different ZnO-PANI nanocomposites.
regions in the nanocomposite; grain and grain boundary. The arrow direction represents the increase in frequency ($\omega$). At lower values of frequencies, the arc with $Z'$-axis gives the total resistance ‘R’ of the sample. The depressed semicircle represents the bulk nature while the enlarged semicircle represents the grain boundary nature in the sample [5]. This result suggests, that grain boundary is more resistive as compared to grain. The radius of each arc exhibited a decreasing trend with changing composition, showing that the resistivity of the sample increases with increasing the percentage of zinc oxide in the compositions. From this discussion we conclude that the composition of (50–50 wt%) is less resistive, while the most resistive composition is (70–30 wt%).

Modulus analysis is another approach to calculate electrical properties of the material and enlarge the most conductive effect present in the sample. The data of figure 5 is replotted in the electric modulus complex plane and was shown in figure 6. The resistive nature of the sample is almost vanished in the modulus analysis and single semicircular arcs were seen for all compositions. The x-axis denotes the real part, while the y-axis shows the imaginary part of the modulus plane plot. In these plots it is clearly shown, that the contribution of zinc oxide to the conductivity, decreases with increasing its percentage in the compositions. This formalism is in consistence with the results shown in figure 5, i.e., representing that 50–50 wt% has the highest conductivity and 70–30 wt% has the lowest conductivity in the selected compositions.

Figure 7 shows the spectroscopic plots ($Z'$-log($f$)), measured for three different nanocomposites. These plots represent a frequency independent region where $Z'$ decreases slowly with the increase in frequency. The magnitude of $Z'$ decreases by increasing frequency. It is also observed that $Z'$ decreases with the decrease in the
content of ZnO which confirms that 70–30 wt% is more resistive while that of 50–50 wt% is less resistive nanocomposite. At higher frequencies, $Z'$ seems to fuse for all nanocomposites, representing the possible release in space charge [6].

To analyze the electrically inhomogeneous nature of the samples, having dissimilar electro-active regions, the combined imaginary components of impedance and electric modulus plots can be utilized. The combined spectroscopic plots for $Z''$ and $M''$ are beneficial because one can investigate the most resistive regions and also analyze the conductive region. Figure 8 shows the combined spectroscopic plot of $Z''$ and $M''/\varepsilon_0$. The $Z''$ spectroscopic plot shows single relaxation phenomenon, highlighting the most resistive region at low frequency. While in the modulus formalism, we noticed a single relaxation at high frequencies representing the most conductive behavior in the sample. This formalism is further utilized for the calculations of $R$ and $C$ values from the peaks using the associated value to the height of the corresponding peak. The corresponding values of resistance $R = 2Z''$ and capacitance $2\mu F_{\max} RC = 1$ were calculated and these values were tabularized in table 1.

It is noticed from the table 1 that the resistance values increases by increasing the ZnO concentration, which confirms that 50–50 wt% is more conductive while that of 70–30 wt% is more resistive. Also, the capacitance values vary in a small ratio or nearly constant with the increasing percentage of zinc oxide in the compositions. It is observed that the capacitance lies in the range of $10^{-12}F$ to $10^{-12}F$ for 50–50 and 60–40 wt% which confirms the bulk/grain nature while that of 70–30 wt% lies in the range of $10^{-11}F$ which confirms the grain boundary nature and these values resembles with the standard proposed by Irvin et al [7].

![Figure 7. Spectroscopic plots of $Z'$-log($f$) for different ZnO-PANI nanocomposites.](image)

![Figure 8. Combined spectroscopic plot of $Z''$ and $M''/\varepsilon_0$.](image)
Figure 9 shows the frequency variation of the ac conductivity ($\sigma_{ac}$) for different compositions. For each composition the graph shows (at lower values of frequency) a frequency independent region followed by a region where $\sigma_{ac}$ increases with increasing ZnO content in the nanocomposite. This represents that conductivity follows Jonscher’s power law given as $\sigma_{ac} = \sigma_{dc} + A\omega^n$, $0 \leq n \geq 1$. Where $\sigma_{dc}$ is dc conductivity (frequency independent), A is the temperature dependent factor and n is the slope of the region II. The frequency at which the slope changes is called hopping frequency. From the table 2 it is clear that the conductivity value is greater for 50–50 wt% and for 70–30 wt% it is smaller; hence it is again in accordance with the above results.

Table 1. Values of fitted parameters i.e. resistance and capacitance of p-Si/PANI-ZnO/Al at 300 K.

| Composition | $R_1$(Ω) | $C_1 = R_1^{-n/\omega}(\omega/\epsilon)^{-n/\epsilon}$ (F) | $n$ | $R_2$(Ω) | $C_2 = R_2^{-n/\omega}(\omega/\epsilon)^{-n/\epsilon}$ (F) | $n$ |
|-------------|----------|-------------------------------------------------|----|----------|-------------------------------------------------|----|
| 50–50       | $5.08 \times 10^6$ | $2.75 \times 10^{-12}$ | 0.96 | $2.32 \times 10^6$ | $1.54 \times 10^{-13}$ | 0.89 |
| 60–40       | $6.10 \times 10^6$ | $3.75 \times 10^{-12}$ | 0.92 | $4.99 \times 10^6$ | $1.81 \times 10^{-13}$ | 0.91 |
| 70–30       | $9.28 \times 10^6$ | $3.49 \times 10^{-11}$ | 0.87 | $7.86 \times 10^6$ | $1.58 \times 10^{-13}$ | 0.96 |

Table 2. Data of $\sigma_{ac}$, A and n for the p-Si/PANI-ZnO/Al at 300 K.

| Composition | $\sigma_{ac}$ (S m$^{-1}$) | A | n |
|-------------|-----------------|---|---|
| 50–50       | $4.21 \times 10^{-7}$ | $2.15 \times 10^{-12}$ | 0.98 |
| 60–40       | $2.31 \times 10^{-7}$ | $3.63 \times 10^{-11}$ | 0.95 |
| 70–30       | $1.08 \times 10^{-7}$ | $5.12 \times 10^{-12}$ | 0.91 |

Figure 9 shows the frequency variation of the ac conductivity ($\sigma_{ac}$) for different compositions. For each composition the graph shows (at lower values of frequency) a frequency independent region followed by a region where $\sigma_{ac}$ increases with increasing ZnO content in the nanocomposite. This represents that conductivity follows Jonscher’s power law given as $\sigma_{ac} = \sigma_{dc} + A\omega^n$, $0 \leq n \geq 1$. Where $\sigma_{dc}$ is dc conductivity (frequency independent), A is the temperature dependent factor and n is the slope of the region II. The frequency at which the slope changes is called hopping frequency. From the table 2 it is clear that the conductivity value is greater for 50–50 wt% and for 70–30 wt% it is smaller; hence it is again in accordance with the above results.

**Conclusion**

ZnO-PANI nanocomposites were successfully prepared by spin coating method with good electrical and optical properties. XRD results confirmed that the addition of the ZnO nanoparticles to the PANI slightly changed the structure of PANI. The conductance of nanocomposites decreases with increasing ZnO content in the samples.

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