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M.H. Abbas, Saif H. Hameed, Ahmed Hashim

Ameliorating and Tailoring the Morphological and Optical Properties of PEO-MnO_2-$SrTiO_3$ Solid State Nanocomposites for Electronics Fields

University of Babylon, College of Education for Pure Sciences, Department of Physics, Babylon, Iraq,
mohhph@yahoo.com, ahmed_taay@yahoo.com*, pure.saif.mahmoud@uobabylon.edu.iq

In this work, polymer nanocomposites films of (PEO-MnO_2-$SrTiO_3$) were manufactured using the casting method with varying weight percentages of nanoparticles (MnO_2-$SrTiO_3$) are 1.7%, 3.4%, and 5.1%, respectively. The morphological and optical properties of (PEO-MnO_2-$SrTiO_3$) films were investigated. The results exhibited that by increasing the percentages of MnO_2-$SrTiO_3$ the optical properties improved. The results showed that with increasing concentration, the morphology on the surface of PEO-MnO_2-$SrTiO_3$ appears homogeneous and more cohesive. The absorption of PEO doped with MnO_2-$SrTiO_3$ was increased of 75% with wavelength equal to 380 nanometer and 76% with wavelength equal to 680 nanometer, by increasing the content of MnO_2-$SrTiO_3$ nanoparticles to reach of 5.1%. The transmittance decreased from 43% to 41%. Absorption coefficient increased from 6453 cm^{-1} at E_{ph}=4.41 electron volt to reach 8589 cm^{-1} for MnO_2-$SrTiO_3$ nanoparticles content equal to 5.1%. The energy gap for the allowed indirect transitions decreased from 3.7 eV to reach 3.3 eV while content of the nanoparticles increased to reach of 5.%. The energy gap of forbidden indirect transition decreased from 3.7 eV to 3.2 eV while the nanoparticles content of MnO_2-$SrTiO_3$ increased to reach of 5.1%. The optical factors were enhanced with increasing the content of MnO_2-$SrTiO_3$ nanoparticles content. The optical conductivity increased from 3.1×10^{12} S^{-1} at the wavelength of 800 nanometer for pure PEO to 1.6×10^{13} S^{-1} when the addition of nanoparticles equal to 5.1%. The obtained results indicated that the PEO-MnO_2-$SrTiO_3$ films may be employed for different optical and electronics applications.

Keywords: PEO, Energy Gap, Nanocomposites, MnO_2, Optical Properties, $SrTiO_3$, Absorbance.

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Introduction

Nanocomposites received great interest both academia and industry [1]. In practice, adding a small percentage of nanoparticles to a polymer matrix significantly improves its physical properties [2]. Nanocomposites consist of two parts, matrix and filler. Conventional composites use glass fiber, or carbon composites as fillers. Nanocomposites depend largely on the properties of the filler (geometry, size, and type of filler), the host matrix (crystallinity, polymer chemistry, and natural thermoplastic), the degree of filler, and the degree of dispersion and agglomeration [3]. Nanocomposites are used to create new polymeric materials by strengthening polymers use of semiconductors and magnetic nanoparticles [4,5]. Nanomaterial's have high-precision dimensions, can bring about significant improvements in electrical and mechanical properties, radiation resistance, and heat resistance due to nanometer-sized dispersion of inorganic fillers in the organic matrix [6]. Polyethylene oxide (PEO) has a very high flexibility that makes it suitable awide range of important physical and chemical applications such as. Its water solubility, biocompatibility, and ability to form complexes with different materials that make it valuable in pharmaceutical, personal care, textiles and paper industries [7]. Polyethylene oxide (PEO) is used in electrochemical and biological applications, PEO structures nanoparticles with nanocomposites show providing thermal stability [8,9]. PEO is peculiarly selected in this work. Due to its high refractive index, high absorption and low optical energy gap, PEO is used as an additive polymer in some nanocomposites [10-12]. Figure 1 shows the chemical structure of polyethylene oxide (PEO).

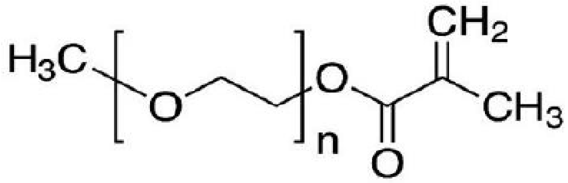

Fig.1. Chemical composition of polyethylene oxide (PEO). [14]

Due to its high flexibility, excellent physical properties and low cost, PEO is often used in clinical applications. It has been recently discovered, that PEO polymer has excellent properties such as relatively low cost, mechanical flexibility and corrosion resistance [14,15]. Strontium titanate $SrTiO_3$ (STO) is a semi electric material with suitable optical energy ga. [16]. $SrTiO_3$ is a diverse group of multifunctional perovskite oxides and is often viewed as one of the way for varying combination of a new devices. $SrTiO_3$ (STO) chip is widely used in the growth of large numbers of cells. $SrTiO_3$ (STO) has a very large dielectric constant used in electronic devices and sensors [17,18]. Due to its outstanding biosensors, MnO_2 (manganese dioxide) has received great research development [19,20]. Due to its environmental safety and low cost, it is a major material in supercapacitors [21,22]. Different methods are used to prepare $MnO_2/SrTiO_3$ nanocomposites in recent studies to improve the electrochemical utilization of MnO_2 [23,24]. For recent years, super capacitors based on MnO_2 as electro active materials have received great attention [25]. MnO_2 is scientifically attractive in various application fields such as catalysts, ionic sieves, molecular sieves, artificial oxidase, and adsorption of toxic metals, dry cell components, electrochemical battery electrodes, and inorganic dyes. In ceramics, the electrodes of super capacitors are highly efficient metal oxide [26,27]. This work aims to study the optical and microscopic properties of PEO/MnO_2-$SrTiO_3$ films when specific proportions of MnO_2-$SrTiO_3$ are mixed into the PEO matrix.

I. Materials and Methods

PEO films were prepared with various contents of (MnO_2-$SrTiO_3$) nanoparticles use the casting process. Preparation of PEO/MnO_2-$SrTiO_3$ films was investigated by dissolving 1 g of PEO into 40 ml from chloroform using a special magnetic stirrer for two hours. MnO_2-$SrTiO_3$ were added into PEO solution by concentrations (1.7, 3.4, and 5.1) wt.%. The Measuring of optical properties for (PEO-MnO_2-$SrTiO_3$) films was examined by using spectrophotometer (Shimadzu, UV-1800 A) with wavelength ranges between (300-800) nanometer. The Determination of absorption coefficient (α) for nanocomposites by using the well-known Beer–Lambert relation [28].

$$a = 2.303\ A/t \quad (1)$$

Where A: is the absorbance of sample, t: the sample thickness.

Optical properties such as refractive index (n) and reflectivity were calculated using equations [29].

$$R = (n-1)^2 + k^2/(n+1)^2 k^2 \quad (2)$$

Where:

$$n = \left(1 + R^{1/2}\right)/\left(1 - R^{1/2}\right) \quad (3)$$

The allowed direct and indirect optical transitions for the energy gap are calculated by Tauc's equation. [30]

$$ahv = B_0(hv - Eg^{opt})^r \quad (4)$$

where hv and E_g are the photon energy and the energy gap. Where the numbers 2, 3, 1/2, and 3/2 are taken for the indirectly allowed, indirectly forbidden, directly allowed, and directly forbidden electronic transitions respectively [31]. The extinction coefficient (k) is measured by the equation [32]

$$K = a\lambda/4\pi \quad (5)$$

The imaginary (ε_1) and real (ε_2) parts of the dielectric constant were measured, by the following equation [33].

$$\varepsilon_1 = n^2 - k^2 \quad (6)$$

$$\varepsilon_2 = 2nk \quad (7)$$

The optical conductivity (σ_{op})can be defined by the equation [34]:

$$\sigma_{op} = anc/4\pi \quad (8)$$

II. Results and Discussion

Fig. 2 shows the microscopic images of PEO-MnO_2-$SrTiO_3$ nanocomposite films. From these images, we notice the homogeneity of the mixture distribution of the PEO polymer with the nanoparticles of MnO_2-$SrTiO_3$. At low content of NPs, the NPs form a clusters inside the polymer matrix. When the content of NPs increases the NPs shaped a network paths within polymer matrix[35,36].

Figures 3 and 4 show the variations in the absorption and transmittance spectra of MnO_2-$SrTiO_3$ doped PEO with contents of (0-5.1) % with respect to the wavelength of photon. The absorbance values increase while decrease in the transmittance with the increase of nanoparticles and this performance is due to the formation of charge transfer complexes [37]. The absorption of PEO doped MnO_2-$SrTiO_3$ increases from 75% for wavelength equal to 380 nanometer to 76 percent for wavelength equal to 680 nanometer when the content of MnO_2-$SrTiO_3$ nanoparticles increases from 0% to 5.1%. The films includes high absorbance and low transmittance at low wavelength due to the high energies at these spectra. The decreases of transmittance from 43% to 41%. Absorption performance and transmittance spectra may be due to increase the charges carriers numbers and reduce of optical energy gap [38].

To know the shape of the electronic transition and determine the value of the energy gap, the absorption coefficient (α) was calculated. Fig 5 shows demeanor of photon energy (E_{ph}) with absorption coefficient(α) for PEO-MnO_2-$SrTiO_3$ films with NPs contents (0–5.1) %. The increases of value of the absorption coefficient(α) for PEO from 6453 cm^{-1} to 8589 cm^{-1}, at Eph = 4.41 electron volt and MnO_2-$SrTiO_3$ content equal to 5.1 %, which indicates the occurrence of indirect electronic transfer. Due to the increased photon intensity, they lead to high α value, which means that the required intensity is sufficient for the electron movement from high to low, and the high α values of PEO-MnO_2-$SrTiO_3$ in the UV spectrum make the films suitable for different optoelectronic fields [39].

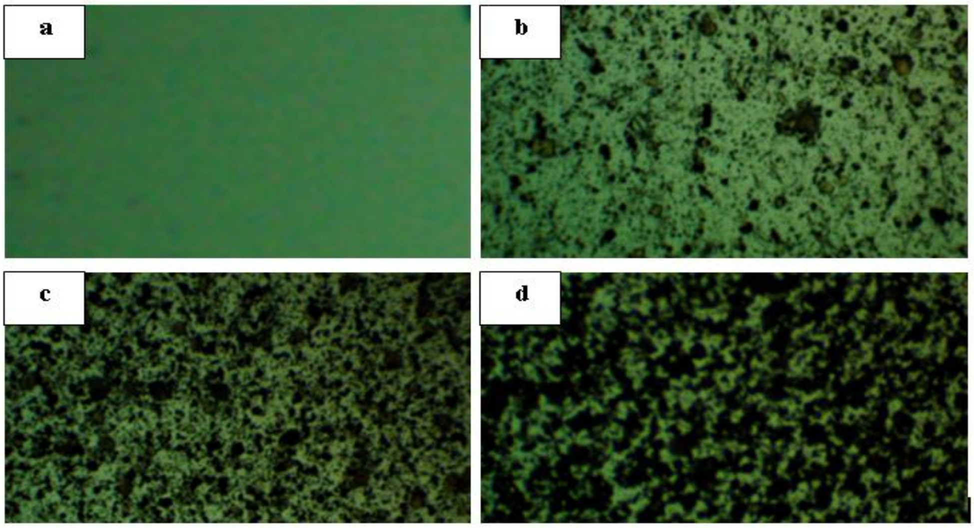

Fig. 2. Microscopic images (×100) of the PEO-MnO2-SrTiO3 films: a- pure PEO b- 1.7 percent of MnO_2-$SrTiO_3$ c- for 3.4 percent of MnO_2-$SrTiO_3$ d- 5.1 percent of MnO_2-$SrTiO_3$.

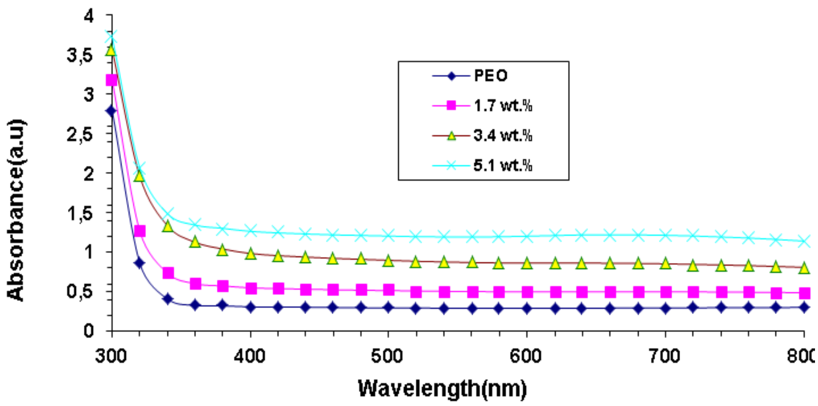

Fig. 3. Absorbance behavior of PEO-MnO_2-$SrTiO_3$ films with wavelength.

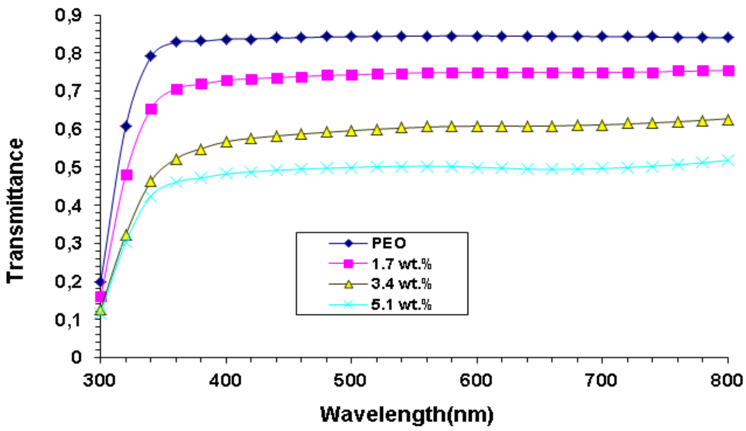

Fig. 4. Transmittance behavior of PEO-MnO_2-$SrTiO_3$ films with wavelength.

Figures 6 and 7 illustrate the energy gaps (E_g) to forbidden indirect transitions, and allowed of PEO-MnO_2-$SrTiO_3$ films. The energy gap decreases from 3.7 eV to 3.3 eV, in the case of allowed indirect transitions. When the content of MnO_2-$SrTiO_3$ nanoparticles increases to 5.1 %, for PEO-MnO_2-$SrTiO_3$, the energy gap decreases from 3.7 eV to 3.2 eV. In the case of forbidden indirect transitions,when the MnO_2-$SrTiO_3$ nanoparticles content increases from 0% to 5.1percent,the energy gaps are reduced due to the formation of multiple levels, which causes electrons to move from the upper part of the valence band to the lower part of the conduction band. The likelihood of widespread transmission of cases is also greatly reduced. Due to increased local levels, values Eg decrease, and this decrease in Eg is associated with some disadvantages creation in the matrix. Produced defects create localized phases in example [40] leading to reduced example when the proportion of MnO_2-$SrTiO_3$ increases in the medium.

The extinction coefficient is calculated using the relationship (5). Fig.8 shows the relationship between extinction coefficient of PEO-MnO_2-$SrTiO_3$ and the wavelength. The extinction coefficient(k) increases with increasing concentration of MnO_2-$SrTiO_3$ nanoparticles due to the scattering of photons and the increase in optical absorption in the nanocomposites. With increasing wavelength, the extinction coefficient value of polymer increases due to the direct proportionality between the extinction coefficient value and the absorption coefficient value [41]. The extinction coefficient value increases from 4×10^{-3} to 1×10^{-2} at 800 nm wavelength with the increase of MnO_2-$SrTiO_3$ NP content from 0% to 5.1%.

The index of refraction for PEO-MnO_2-$SrTiO_3$ films explained in Fig.9. The n values increase from 1.81 to 2.59 at a wavelength of 800 nm as the content of MnO_2-$SrTiO_3$ nanoparticles increases from 0 % to 5.1%. These results can be due to increase of density of the films [42,43].

The real and imaginary dielectric constant variations with wavelength for PEO-MnO_2 $SrTiO_3$ films at different contents of (0–5.1) wt.% are showed in Figures 10 and 11. With increasing concentrations of MnO_2-$SrTiO_3$ nanoparticles, the real and imaginary parts of the dielectric increase due to the motion and rotation of the dipoles. The enhanced dielectric constant valuesare due to the relatively high polarization of nonpolar bonds. Due to the increase in refractive index and extinction coefficient, the values of the real and imaginary parts increase with the concentrations of nanoparticles [44].

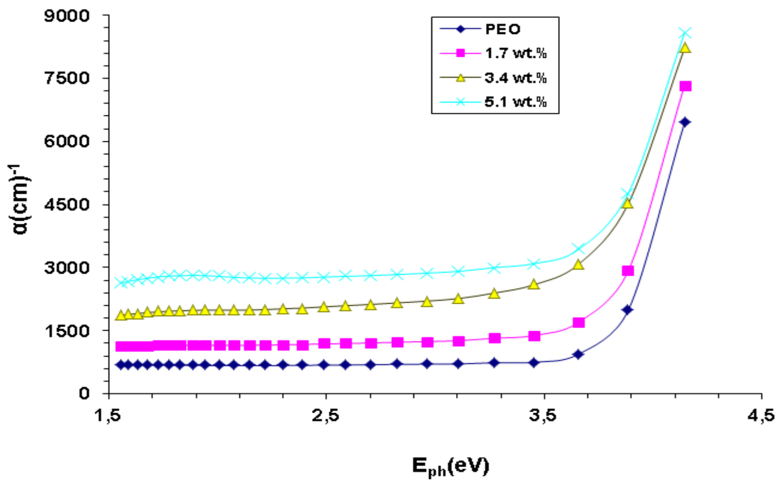

Fig. 5. Absorption coefficient of PEO-MnO_2-$SrTiO_3$ performance of the films.

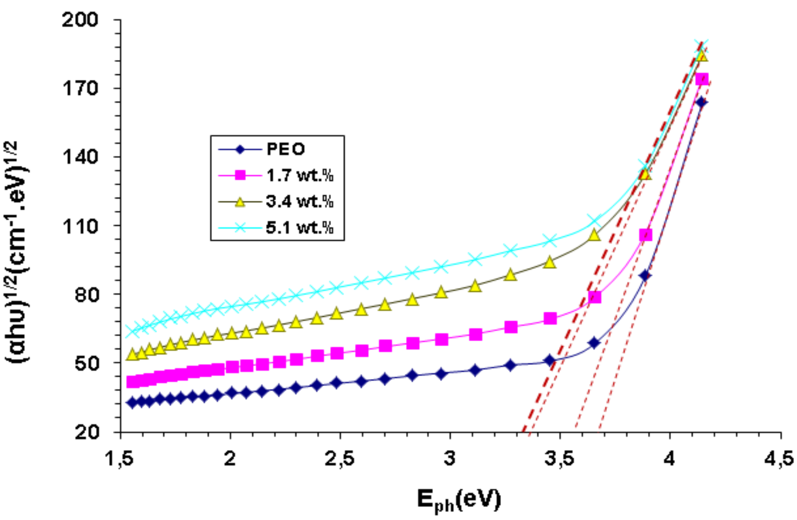

Fig. 6. Relationship of $(\alpha h\nu)^{1/2}$for PEO-MnO_2-$SrTiO_3$ nanocomposites with the photon energy**.**

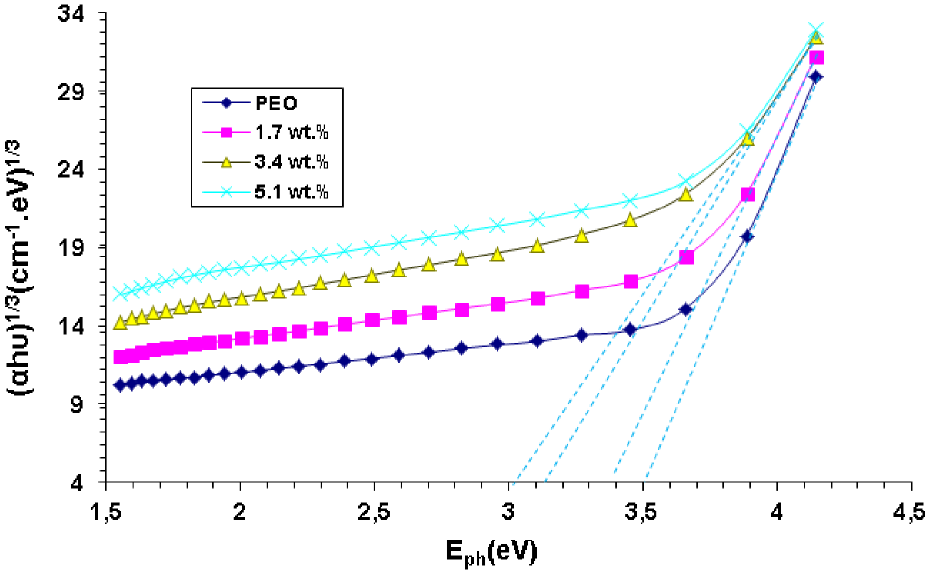

Fig. 7. Relationship of $(\alpha h\upsilon)^{1/3}$ for PEO-MnO_2-$SrTiO_3$ with the photon energy.

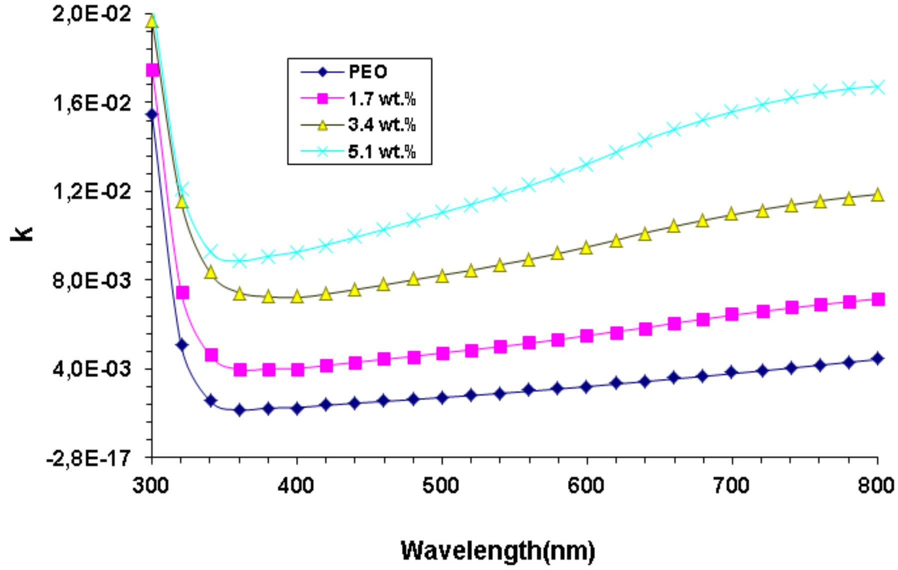

Fig. 8. Variation of the extinction coefficient for (PEO-MnO_2-$SrTiO_3$) versus the wavelength.

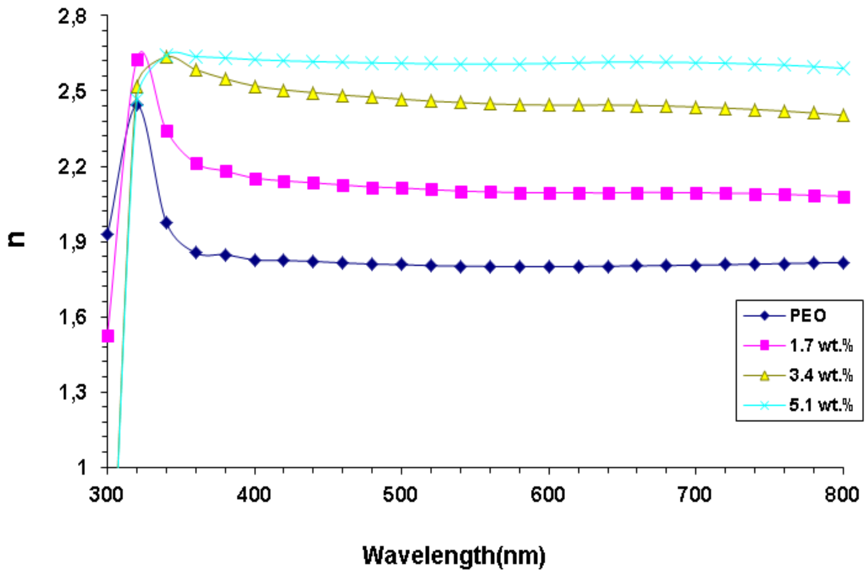

Fig. 9. Relationship of the refractive index to PEO-MnO_2-$SrTiO_3$versus the wavelength.

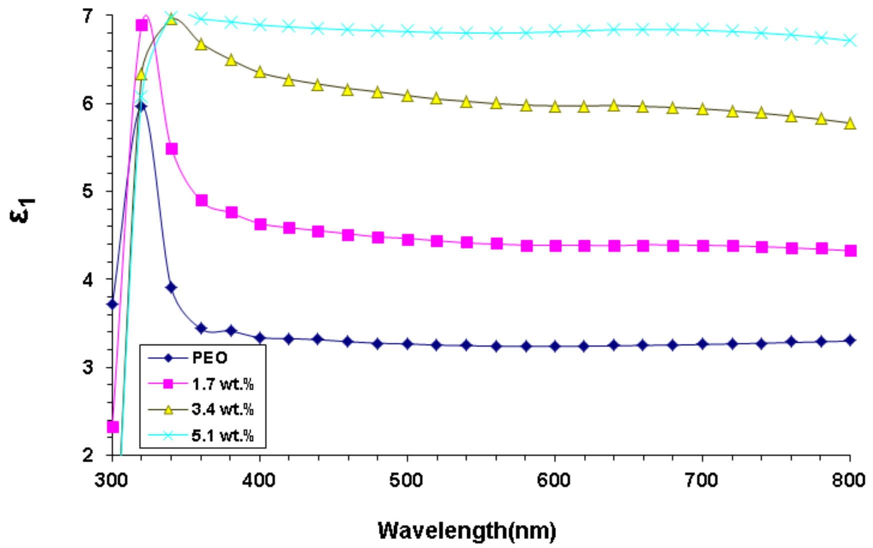

Fig. 10. Behavior of real dielectric constant for PEO-MnO_2-$SrTiO_3$ films with wavelength.

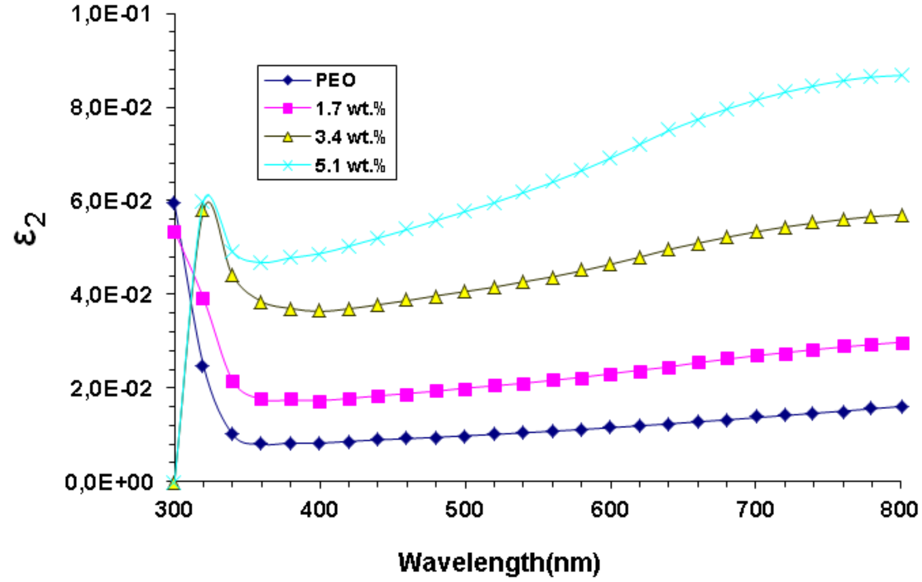

Fig. 11. Imaginary dielectric constant variation for PEO-MnO_2-$SrTiO_3$ films with wavelength.

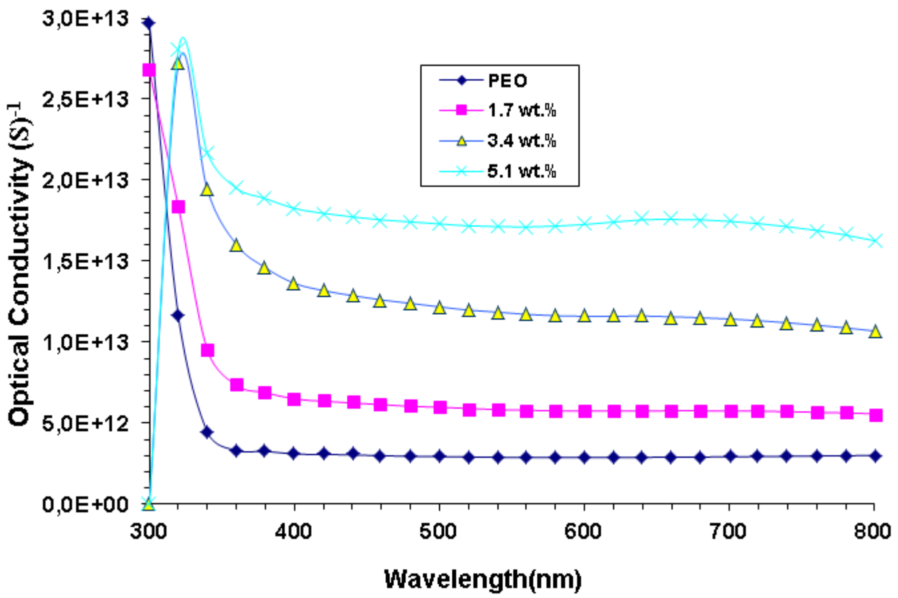

Fig. 12. Relationship of optical conductivity to PEO-MnO_2-$SrTiO_3$ with wavelength.

The optical conductivity behavior with wavelength for PEO-MnO_2 $SrTiO_3$ films is demonstrated in Figure 12. Due to the excitation of electrons, the absorption coefficient rises as the photon energy increases, this leads to an increase in the optical conductivity from 3.1×10^{12} S^{-1} for the polymer PEO to 16×10^{12} S^{-1} at wavelength 800 nm when the ratio of nanoparticles equal to 5.1%. The reason for the increase in optical conductivity is due to the formation of new additional levels for the energy gap, which leads to the transfer of the electron from the valence band to the conduction band [45,46].

Conclusions

This study includes of (PEO-MnO_2-$SrTiO_3$) nanocomposites fabrication using casting method. The morphological and optical properties of (PEO-MnO_2-$SrTiO_3$) films were studied. The results showed that the PEO absorption is improved about 75% and 76% at wavelength of 380 nm and 680 nm with increasing the content of MnO_2-$SrTiO_3$ NPs to 5.1%. Absorption coefficient increased from 6453 cm^{-1} to 8589 cm^{-1} at E_{ph}=4.41 eV. The allowed energy gap was decreased from 3.7 eV to reach 3.3 eV. Extinction coefficient, refractive index, and dielectric constant were enhanced with increasing the content of MnO_2-$SrTiO_3$ NPs to 5.1%. The optical conductivity increased from 3.1×10^{12} S^{-1} to 1.6×10^{13} S^{-1} at wavelength of 800 nm and 5.1% MnO_2-$SrTiO_3$ NPs. Final results showed that the PEO-MnO_2-$SrTiO_3$ films could be used for optoelectronics applications.

***Abbas M. H.** – PhD, Assistant Professor.*
***Hameed Saif H.** – MSc, Assistant Lecturer.*
***Hashim Ahmed** – PhD, Professor.*

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М.Х. Аббас, Сайф Х. Хамід, Ахмед Хашим

Покращення та керування морфологічними й оптичними властивостями твердотільних нанокомпозитів PEO–MnO_2–$SrTiO_3$ для електронних застосувань

Університет Вавилону, Коледж освіти з чистих наук, кафедра фізики, Вавилон, Ірак, ahmed_taay@yahoo.com

У роботі методом лиття отримано плівки полімерних нанокомпозитів PEO–MnO_2–$SrTiO_3$ з різним масовим вмістом наночастинок (1,7 %, 3,4 % та 5,1 %). Досліджено їх морфологічні та оптичні властивості. Показано, що зі збільшенням концентрації MnO_2–$SrTiO_3$ поверхня плівок стає більш однорідною та щільною, а оптичні характеристики суттєво покращуються. Встановлено зростання поглинання до 75–76 % у видимому діапазоні спектра та зменшення пропускання з 43 % до 41 % при максимальному вмісті наночастинок. Коефіцієнт поглинання збільшується до 8589 $см^{-1}$, тоді як ширина забороненої зони для дозволених і заборонених непрямих переходів зменшується відповідно до 3,3 еВ та 3,2 еВ. Оптична провідність зростає з $3,1 \times 10^{12}$ $с^{-1}$ для чистого PEO до $1,6 \times 10^{13}$ $с^{-1}$ при вмісті наночастинок 5,1 %. Отримані результати свідчать про перспективність використання плівок PEO–MnO_2–$SrTiO_3$ в оптичних та електронних пристроях.

Ключові слова: PEO, нанокомпозити, MnO_2, $SrTiO_3$, оптичні властивості, ширина забороненої зони.