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Research Article

Fabrication and Characterization of Nickel Chloride Doped PMMA Films

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Films of PMMA and PMMA doped with $NiCl_2$ with different contents were prepared using the casting technique. The optical properties of all films were investigated using spectrophotometric measurements of absorbance and transmittance in the wavelength range 200–800 nm. The change of the calculated values of the optical energy gaps with increasing $NiCl_2$ content has been interpreted in terms of the structural modifications of the PMMA matrix. The optical energy gap decreased from 3.6 to 3.05 eV with increasing the $NiCl_2$ concentration to 0.4%. The effect of doping on the optical constants of films such as refractive index, extinction coefficient, real and imaginary parts of dielectric constant, optical conductivity, and skin depth has been reported. All these constants were increased with increasing $NiCl_2$ concentration with the exception of skin depth which is different result.

1. Introduction

Optical properties of polymer films are very important for many technological applications [1], ranging from protective coatings to paintings, microelectronic, semiconductors, and optoelectronic devices depending on the reflectance and transmittance properties of the films during their preparation [2, 3]. PMMA as a polymeric waveguide has attracted much attention for use as optical components and in optoelectronics devices due to their low cost and volume productivity. Recently, some researchers reported optical components such as an optical switch, a coupler, a splitter, and a transceiver [4, 5].

PMMA is considered as an excellent host material for doping due to their good transparency (the transmission for visible light is very high), resistivity, mechanical strength, and optical homogeneity which can play an important role in building up advanced optical materials [6]. It is one of the earliest and best known polymers. PMMA was seen as a replacement for glass in a variety of applications and is currently used extensively in glazing applications. The material is one of the hardest polymers and is rigid, glass-clear with glossy finish and good weather resistance [7].

Owing to the influence of doping on the properties of polymeric materials, the controlled preparation of PMMA of different doping materials and concentrations is always the researcher's purpose; these doping processes cause a remarkable change in their properties [8, 9]. The present work is a part of a systematic study of the effect of doping of $NiCl_2$ on PMMA on improving their physical properties. Therefore, we study the effect of the doping level (W) using both the optical absorption measurements and the determination of the optical constants and energy gap. The accurate determination of the optical constants of these materials is important, in order not only to know the basic mechanisms underlying these

phenomena but also to exploit and develop their interesting technological applications.

2. Experimental Details

Films of poly(methyl methacrylate) PMMA doped with different weight concentration of nickel chloride ($NiCl_2$) salt (0.1, 0.2, 0.3, and 0.4%) have been prepared by the dispersed polymer and $NiCl_2$ dissolve in 100 mL chloroform with stirring the solution, using a magnetic stirrer for about 30 min at room temperature for complete dissolving. Different polymer solutions (volumetric solutions) were casted as a layer, dried at room temperature for 24 hours. Layer thickness was measured using indicating micrometer 0.25 μm; all layers were found to be in the range of 20 ± 1 μm; these layers were clear, transparent, and free from any noticeable defect showing light bluish color.

Optical transmittance and absorbance were recorded in the wavelength range of 200–800 nm using computerized UV-VIS spectrophotometer (Shimadzu UV-1601 PC). Optical transmittance and absorbance were reported in order to study the effect of doping on the parameters under investigation.

3. Results and Discussion

The optical properties of films by means of optical absorption in the UV-VIS region of 200–800 nm have been investigated. Figure 1 shows the dependence of absorbance (A) on wavelength (λ) of all films before and after being doped by $NiCl_2$ salt with different concentrations (0.1, 0.2, 0.3, and 0.4%). It is observed that in the visible region all films have very low transparent; then absorbance is rapidly decreased with increasing wavelength. This behavior may be attributed to perfection and stoichiometry of the films. Also it can be observed from the figure that the absorbance increased with increasing the doping concentration of $NiCl_2$ to 0.4%; this result agrees with the previous work [10]. It has been observed that the absorption peaks appear at wavelengths 240, 242, 248, 249, and 251 nm as the concentration of dopant varies from 0 to 0.4 mol/L in PMMA matrix, respectively. The shifting occurring in the spectra may be due to the polarity of solvent used in the synthesis or may be due to the dispersion of rare earth oxide particles in the PMMA matrix [11].

From the transmittance (T) data and according to Tauc [12] relation, the most satisfactory representation is obtained by plotting the quantity $(\alpha h\nu)^2$ as a function of $(h\nu)$. The plot of $(\alpha h\nu)^2$ versus $h\nu$ for different dopant percentage in polymer samples is shown in Figure 2. The observed behavior suggests allowed direct transition for amorphous material [13]. The values of optical energy gap E_{opt} obtained from the extrapolation of the linear region are found to be decrease for all samples 3.6, 3.5, 3.29, 3.19, and 3.05 eV with increasing the doping percentage of $NiCl_2$ 0.1, 0.2, 0.3, and 0.4%, respectively. The decrease in E_{opt} with increasing $NiCl_2$ concentration can be understood by considering the mobility gap variation in the doped polymer [14]. The figure shows a linear dependence for pure PMMA in one region representing one optical absorption edge as mentioned before in previous work

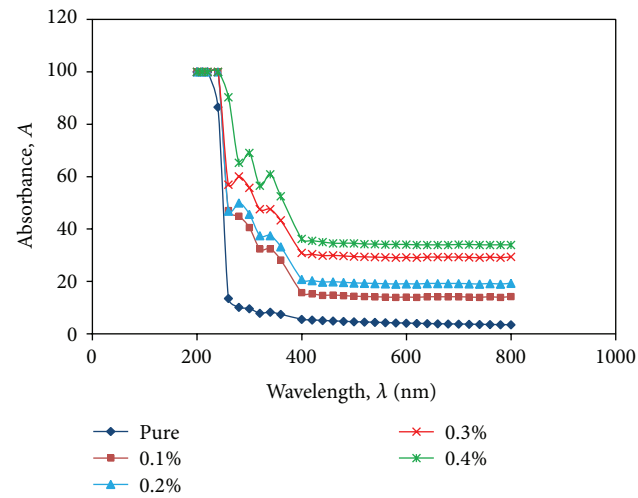

Figure 1: The variation of absorbance with wavelength for pure and doped PMMA films.

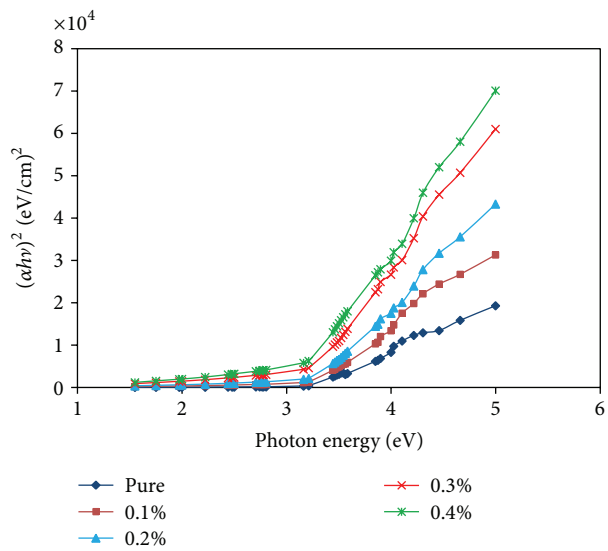

Figure 2: The $(\alpha h\nu)^2$ versus photon energy for pure and doped PMMA films.

[9, 15–17]. The value obtained in this work is close to others previously reported for the allowed direct transition.

The refractive index (n) is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films. The refractive index of the films was determined from the following relation [18]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - K^2}, \quad (1)$$

where R represent the reflectance and k is the extinction coefficient ($k = \alpha\lambda/4\pi$) where α is the absorption coefficient. The n and k values of dependence of wavelength are shown in Figures 3 and 4, respectively, for all samples before and after being doped. As seen in these figures, the n and k values increase with increasing the doping concentration of

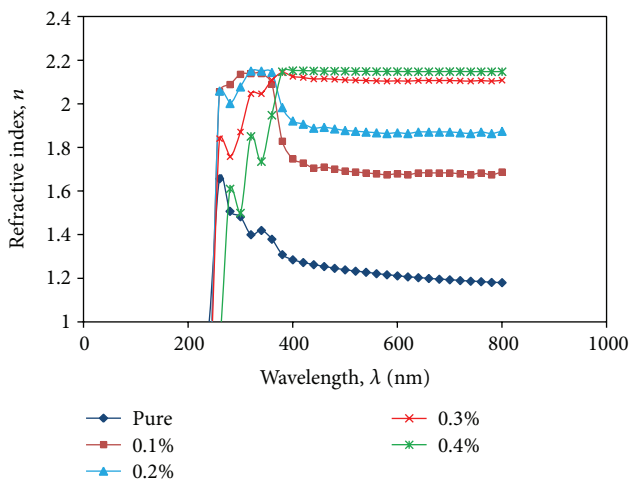

Figure 3: The variation of refractive index with wavelength for pure and doped PMMA films.

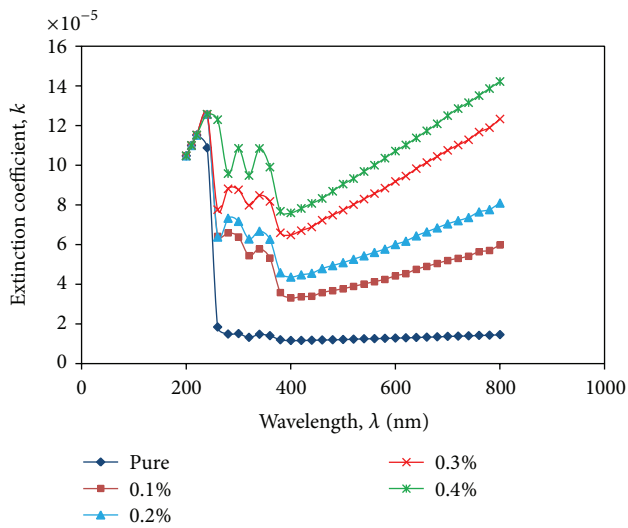

Figure 4: The extinction coefficient versus wavelength for pure and doped PMMA films.

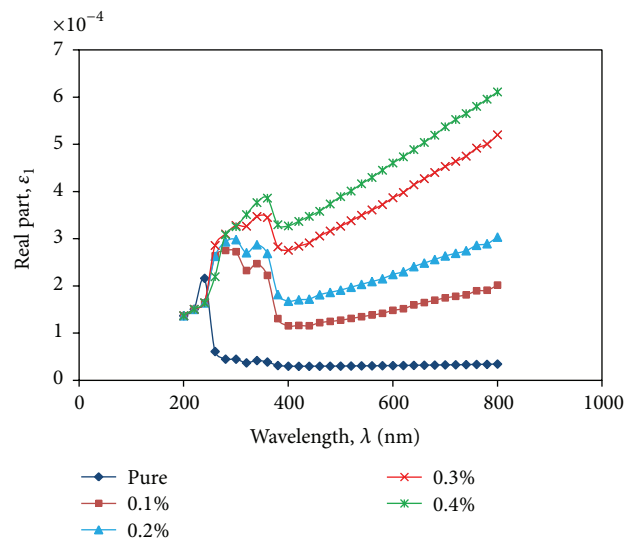

Figure 5: The variation of real part of dielectric constant with wavelength for pure and doped PMMA films.

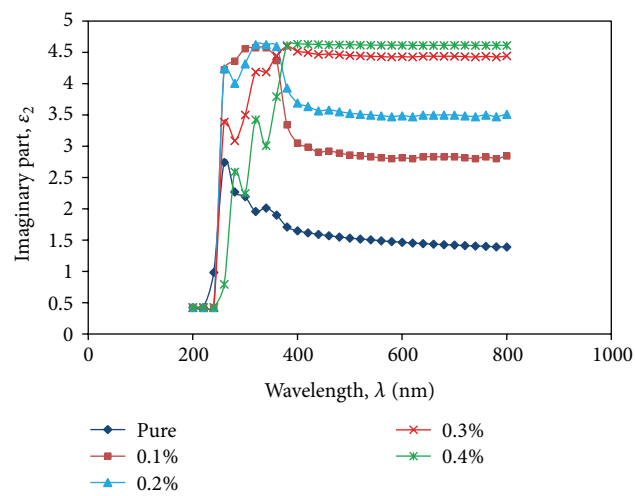

Figure 6: The variation of imaginary part of dielectric constant with wavelength for pure and doped PMMA films.

$NiCl_2$; this result agrees with the previous work [19]. Such behavior corresponds to the density of absorbing centers such as impurities absorption, excitation transition, and other defects in the crystal lattice dependent on the conditions of sample preparation.

The dielectric constant is defined as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$; real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric constant are related to the n and k values. The ε_1 and ε_2 values were calculated using the following formulas [20]

$$\varepsilon_1 = n^2 - k^2, \qquad \varepsilon_2 = 2nk. \tag{2}$$

The ε_1 and ε_2 values of dependence of wavelength are, respectively, shown in Figures 5 and 6 for pure and doped films. The ε_1 values are higher than ε_2 values. It is seen that the ε_1 and ε_2 values increase with increasing wavelength and with the doping concentration of $NiCl_2$. The values of dielectric constant at 400 nm for 0, 0.1, 0.2, 0.3, and 0.4% $NiCl_2$ content were 1.75, 3.08, 3.71, 4.45, and 4.60, respectively, for real part and 0.000035, 0.000123, 0.000177, 0.000285, and 0.000342, respectively, for imaginary part. Moreover, this increase by the variation of ε_1 mainly depends on n^2 because of small values of k^2 while ε_2 mainly depends on k value which is related to the variation of absorption coefficients [21].

The optical conductivity (σ) was calculated using the following relation [22]:

$$\sigma = \frac{\alpha n c}{4\pi}, \tag{3}$$

where c is the velocity of light.

Figure 7 shows the variation of optical conductivity with the wavelength. It was observed that the optical conductivity

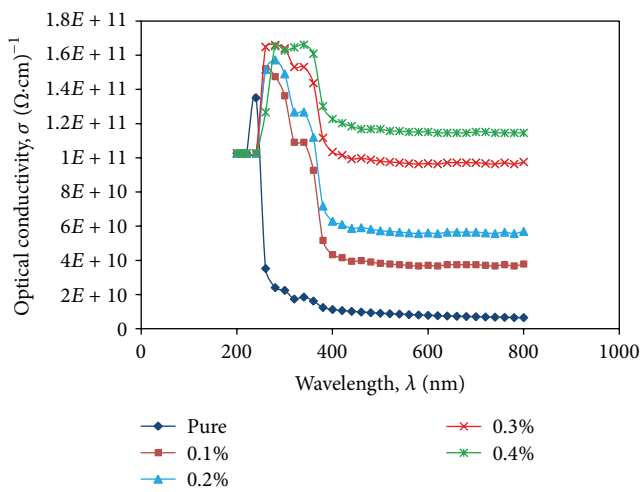

Figure 7: The optical conductivity versus wavelength for pure and doped PMMA films.

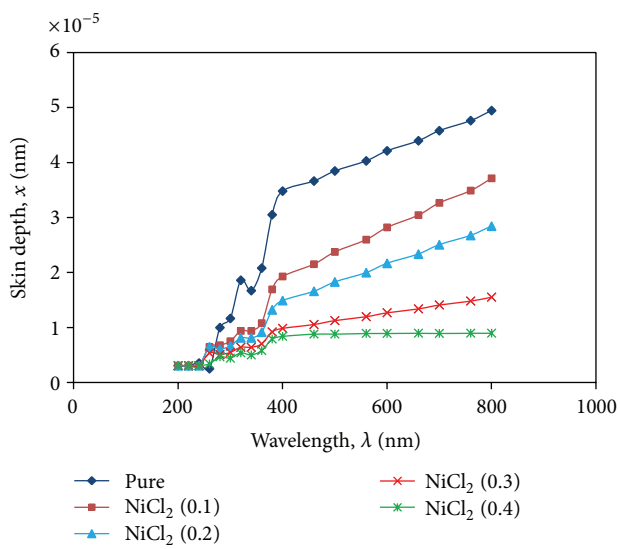

Figure 8: The skin depth versus wavelength for pure and doped PMMA films.

increases as the doping percentage of $NiCl_2$ in the PMMA increases to 0.4%. It can be noticed from the figure that the optical conductivity for all films increased in the low wavelengths region and decreased in the high wavelength region; this decrease is due to the low absorbance of the films in that region.

The skin depth (x) could be calculated using the following relation [23]:

$$x = \frac{\lambda}{2\pi k}. \quad (4)$$

Figure 8 shows the variation of skin depth as a function of wavelength for all films. It is clear from the figure that the skin depth increases as the wavelength increases; this behavior could be seen for all samples, but the skin depth decreases as the doping concentration increases, so the skin depth is a transmittance related.

4. Conclusion

PMMA and $NiCl_2$ doped PMMA films were prepared by using casting technique. Both pure and doped samples were characterized. Results indicate that the optical band gap and the optical parameters are strongly dependent on doping with $NiCl_2$. The optical band gap decreased from 3.6 to 3.05 eV with increasing the doping concentration to 0.4%. The refractive index, extinction coefficient, the real and imaginary parts of dielectric constant, and the optical conductivity were calculated and they are tending to increase with increasing the doping concentration of $NiCl_2$; on the other hand, the skin depth decreases with increasing the doping concentration. These present observations can help improve the understanding of the optical parameters of $NiCl_2$ films.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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