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Study Optical Properties of PVP Films Doped with Nanoparticles Ag by Using Nd:YAG Laser

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Abstract

The doped PVP with nanoparticle silver metal using Nd:YAG laser ablation solute in ethanol. The spin-coating techniques with concentrations (0,3,5,7,9,11wt%) are achieved by (20 ml) ethanol using magnetic stirrer The solution doped with (1ml) of collide nanosilver particle.. An increment of UV-Vis absorption has produced maximum peak absorbance spectra at about 0.7 to 0.85 values with a high shifting after doping with nanoparticle silver. The indirect Eg_{opt} of pure and doped PVP films were found to be decreased about 2.56,2.54,2.52.2.50,2.47eV, and 4.18,4.14,4.15,4.16,4.12,4.17 eV for indirect allowed transitions as increase concentration respectively, whereas the indirect forbidden band gaps were determined as 2.73, 2.67, 2.66, 2.65, 2.63 eV and 4.175,4.18,4.15,4.158,4.1,4.165 eV with increase concentration after doping respectively. The prepared samples appeared near band edge peak absorption at about 350 nm.

***Keywords*:** polyvinylpyrrolidone (PVP); doping; structural; optical properties; optical energy gap; concentration; nanoparticle silver.

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1. Introduction

PVP was first synthesized by Walter Rappe and Patent was filed in 1939 for one of the most interesting derivatives of acetylene chemistry [1]. PVP was initially used as a blood plasma substitute and later in a wide variety of application in medicine, pharmacy, cosmetics and industrial production. PVP is soluble in water and other polar solvents. When dry it is a light flaky powder, which may absorbs up to 40% of its weight in atmospheric water .In solution, it has excellent wetting properties and readily forms film. This makes it good as a coating or an additive to coatings [2]. The authors in [3] Collide Au and polyvinylpyrrolidone composite thin film are fabricated by spin – coating to study the nonlinear optical properties of Au / PVP composite thin film. The authors in [3] studied the synthesis and characterization of (Ag/PVP) Nanoparticles using Gamma Irradiation Techniques. The authors in [4] studied the synthesis, structural and optical properties of PVP encapsulated CdS Nanoparticles. The authors in [5] studied the structural and optical properties of Li^{+} : PVP and Ag^{+} : PVP polymer films.

2. Experimental

PVP solution was prepared with different weight percentage (0 , 3 , 5 , 7 , 9 , 11%) . PVP was dissolved in a glass screw cup in (20 ml) ethanol using magnetic stirrer . The solution doped with (1ml) of colloid nanosilver particle. This colloidal solution was prepared by using second harmonic generator of Nd:YAG laser (532 nm). The samples were put on glass substrate to obtain a film by using spin coating technique under atomic pressure and (3000 r/min), the thickness of the film about (5 μm). A(UV-Vis spectrophotometer (UV-Vis-CECIL2700) was used to get the spectral absorbance and transmittance at room temperature.

3. Theoretical

The relationship between incident intensity and the penetrating light intensity is given by equation:

$$I=I_o e^{-\alpha t} \quad (1)$$

Where t is the thickness of the matter (cm) and α is the absorption coefficient (cm^{-1}) [7]:

$$\alpha t = 2.303 \log I_o / I \quad (2)$$

Where the amount of log I/Io represents the absorbance (A).The absorption coefficient can be calculated by:[8]

If the amount of absorption is $\alpha \geq 10^4 cm^{-1}$, the electronic transitions are direct. The amount of optical energy gap from this region can be evaluated by the relation [9]:

$$\alpha = 2.303 (A/t) \quad (3)$$

$$\alpha h\upsilon = A(h\upsilon - E_g)^m \quad (4)$$

Where $h\upsilon$ is the photon energy, A is the proportional constant, E_g is the allowed or forbidden energy gap of direct transition and m is a parameter that gives the type of electron transition. Specifically, m is ½ ,3/2,2,and 3 for transitions direct allowed, direct forbidding, indirect allowed and indirect forbidding respectively [10]. The indirect transition, which requires phonon assistance, the absorption coefficient has the following dependence on photon energy [11]:

$$\alpha h\upsilon = A(h\upsilon - E_g + E_p)^2 + B(h\nu - E_g - E_p)^2 \quad (5)$$

Where E_p is the energy of the photon associated with the transition, A and B are constants, depending on band structure. The optical absorption edge can be correlated to optical gap energy using Taucs equation [12]. The variation of $ln\alpha$ as a function of photon energy is given by:

$$\alpha = \alpha_o \exp(\frac{h\nu}{E_u}) \quad (6)$$

Where E_u is the Urbarch energy, it can be evaluated as width of the localized states. The optical band gap can be obtained by extrapolating the linear portion of plot $(\alpha h\upsilon)^{1/n}$ versus $h\upsilon$ to $\alpha = 0$. The refraction index consists of real and imaginary parts ($N = n\text{-}ik$), the relation between reflectivity and refractive index is given by the equation [13]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (7)$$

Where k is the extinction coefficient. The quality (R+T<1) at certain wavelength implies the existence of absorbing region. The refractive index can be expressed by the equation [14]:

$$n = \sqrt{\frac{4R - k^2}{(R-1)^2}} - \frac{(R+1)}{(R-1)} \quad (8)$$

The extinction coefficient can be calculated by using the equation [15]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (9)$$

Where λ is the wavelength of the incident ray. The relation between the complex dielectric constant and the complex refractive index N is expressed by:

$$\varepsilon = N^2 \quad (10)$$

We can conclude that [16]:

$$(n\text{-}ik)^2 = \varepsilon_1 - i\varepsilon_2 \quad (11)$$

The real and imaginary complex dielectric constant can be expressed by the following two equations respectively:

$$\varepsilon_1=n^2-k^2 , \qquad \varepsilon_2=2nk \tag{12}$$

Also the finesses coefficient is given by [6]:

$$F=\frac{4R}{(1-R)^2} \tag{13}$$

The optical conductivity is related to light speed and can be expressed by the equation [17]:

$$\sigma_{opt.}=\frac{\alpha nc}{4\pi} \tag{14}$$

4. Results and Discussion

The experimental results show that there are differences in optical parameters before and after doping with silvers nanoparticle in two preparations volume percentages. Figure (1) shows the optical absorbance as a function of wavelength at different concentrations of PVP thin film. The absorbance increases as concentrations increasing, because the polymer chains fill the vacancies of the real solution, but when doped with nanoparticle silver, the position of the absorbance are shifted to the red side, the absorbance increased and another weaker peak appeared at 680nm wavelength as shown in Figure (2). .

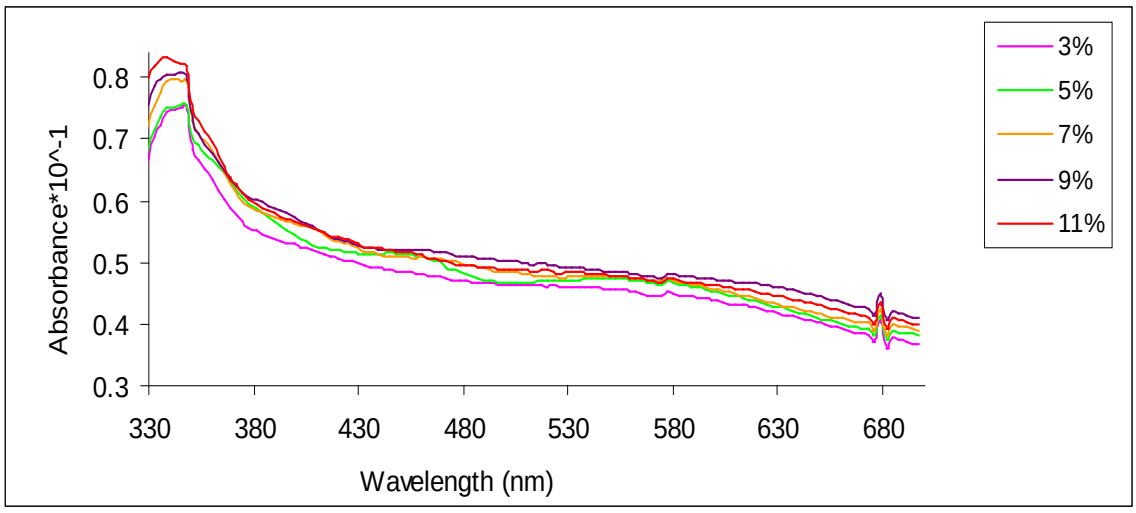

Figure1: The spectral absorbance at different concentrations of PVP thin film.

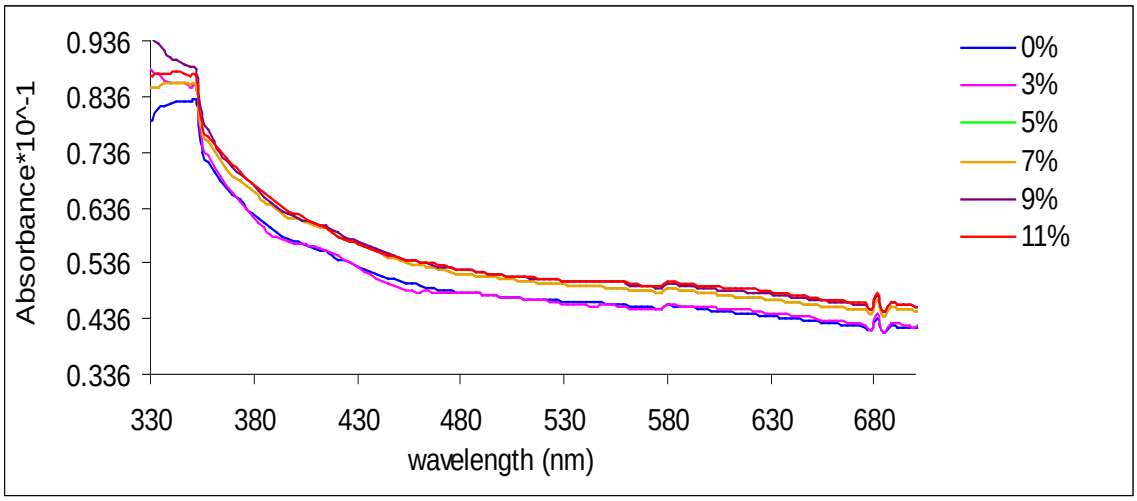

Figure 2: The spectral absorbance at different concentrations of PVP doped Ag thin film.

Figure 3 shows the spectral reflectance at different concentrations of PVP thin film. The position of the reflectance are shifting to the greatest wavelength as doping with nanoparticle silver as shown in Figure 4. The reflectance increase as the polymer solution contains nanoparticle silver. The intensity peak width increase after doping. So a simple change in structure of polymer after addition of dopant with roughly doping and concentration. This is because the filling Ag nanoparticle (5% , volume ratios) with the chain polymer. The free radicals will combine with silver ions. Combined there is a simple change in the structure of polymer has chemically occurred [17].

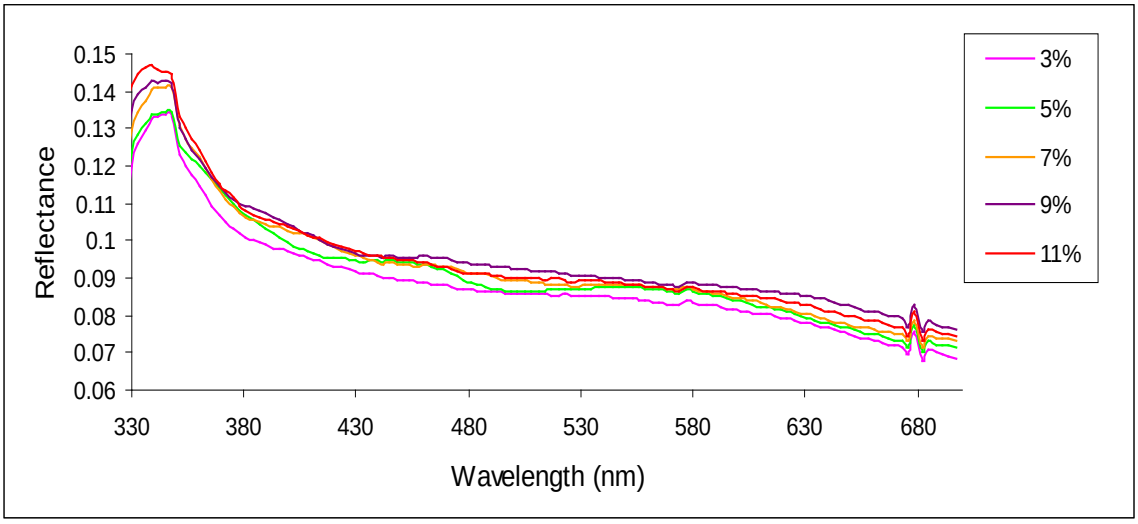

Figure 3: The spectral reflectance at different concentrations of PVP thin film.

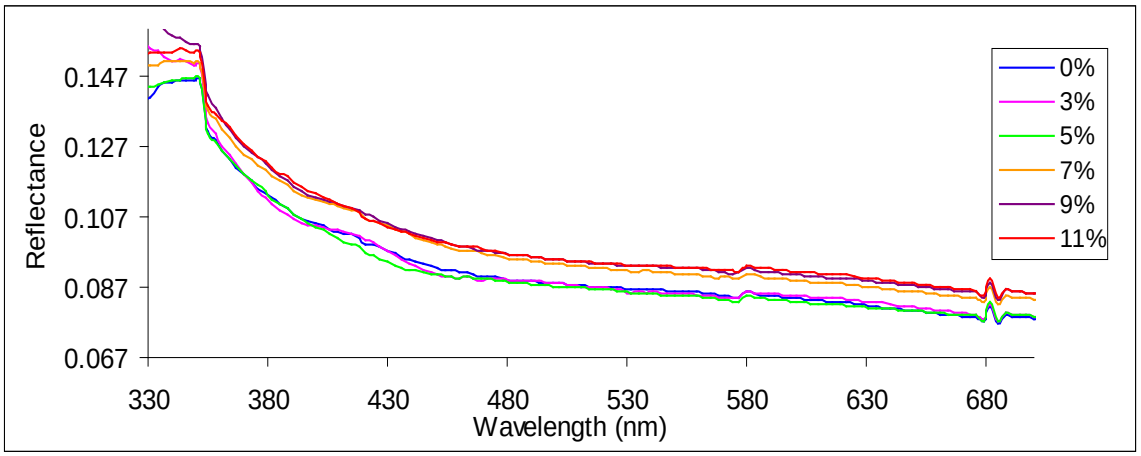

Figure 4: The reflectance at different concentrations of PVP doped Ag thin film.

Fig. 5 shows spectrum as a function of an optical transmittance films. The increased of PVP concentrations decrease the transmittance, because of the occupancy of the vacancies between the polymer chains. Fig.6 shows the decreasing of transmittance after doping with nanoparticles silver, the silver ions will occupy the residual positions of polymer chains especially at the shortest wavelengths.

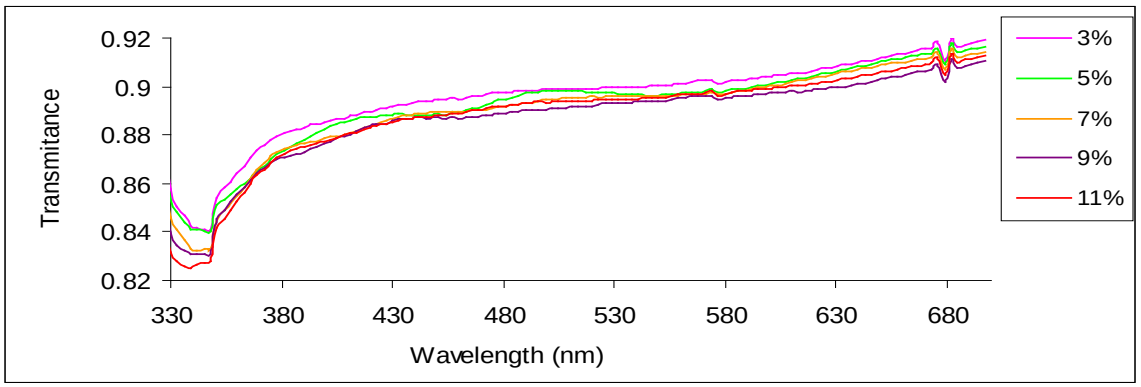

Figure 5: The spectral transmittance at different concentrations of PVP thin film.

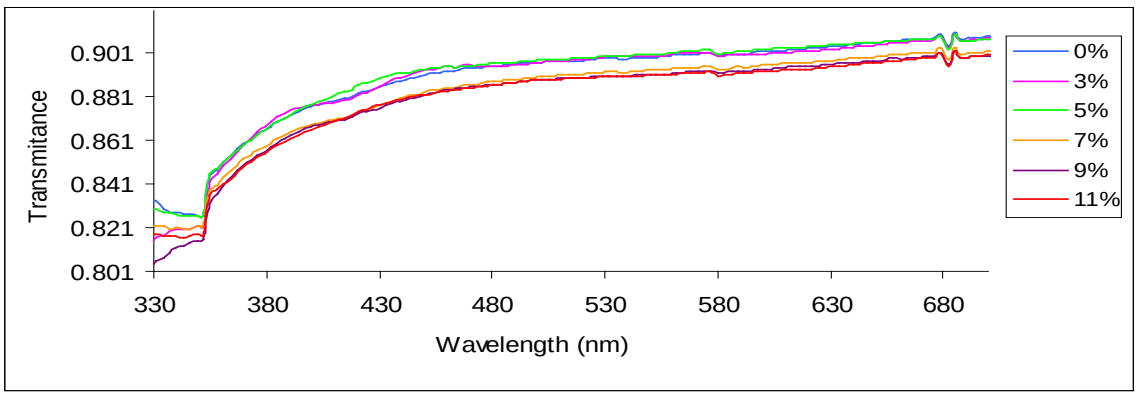

Figure 6: The transmittance at different concentrations of PVP doped Ag thin film.

The absorption coefficient also increases as photon energy increases slightly and the peak of this factor is 3.65 eV value. The absorption coefficient increases with increasing the concentration. This is depended on the absorbance value as shown in Figure 7 .But after doping with nanoparticle silver, there are shifting in peaks of the higher absorption coefficients as shown in Figure 8 .The absorption coefficients increase to 0.9 after doping. This can be used in solar cells

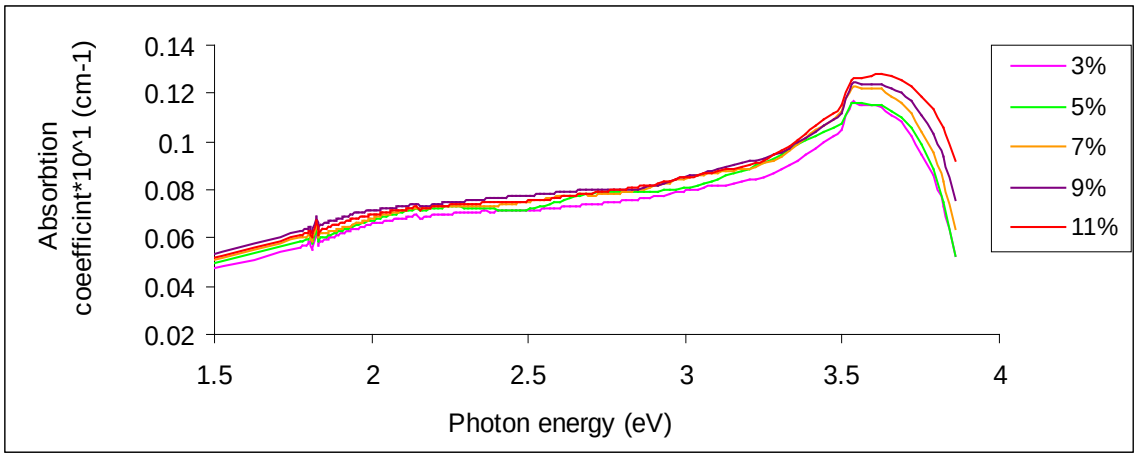

Figure 7: The absorption coefficient as a function of photon energy at different concentrations of PVP thin film.

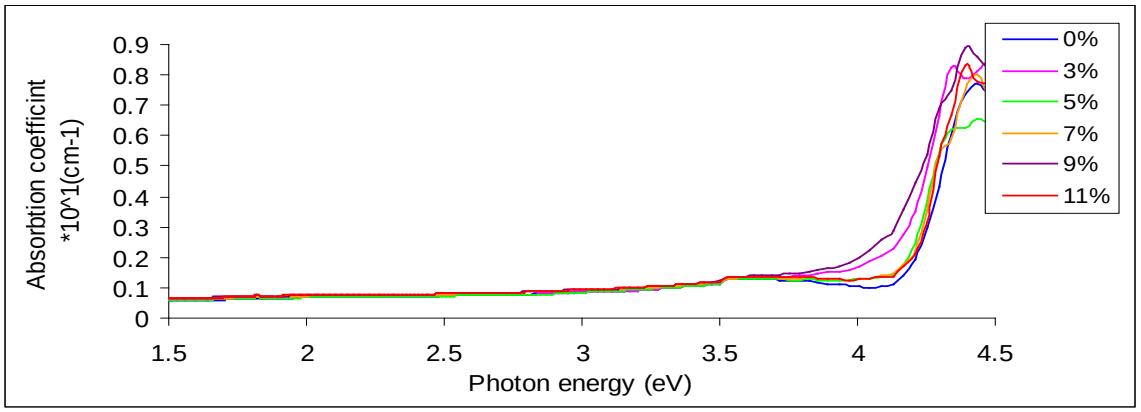

Figure 8: shows the absorption coefficient as a function of photon energy at different concentrations of PVP doped nanoparticle Ag thin film.

Figures.9 and 10 show the extinction coefficient as a function of wavelength at different concentrations of PVP before and after doped thin film with nanoparticle silver contained by laser. The peaks is higher after doping at 355 and 680 nm.

Figures 11 and 12 show refractive index as a function of wavelength at different concentrations of PVP before and after doping thin film. The refractive indices decrease with wavelength increase.

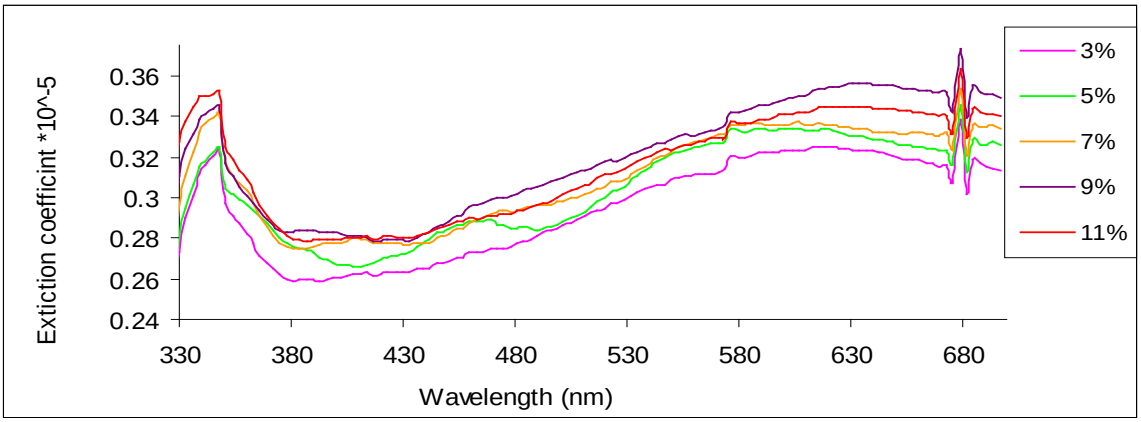

Figure 9: Extinction coefficient as a function of wavelength at different concentrations of PVP thin film.

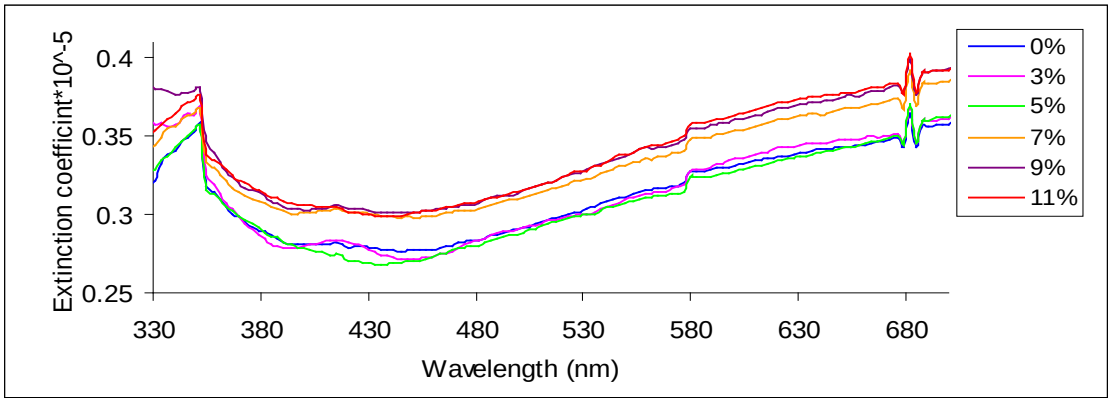

Figure 10: Extinction coefficient as a function of wavelength at different concentrations of PVP doped nanoparticle Ag thin film.

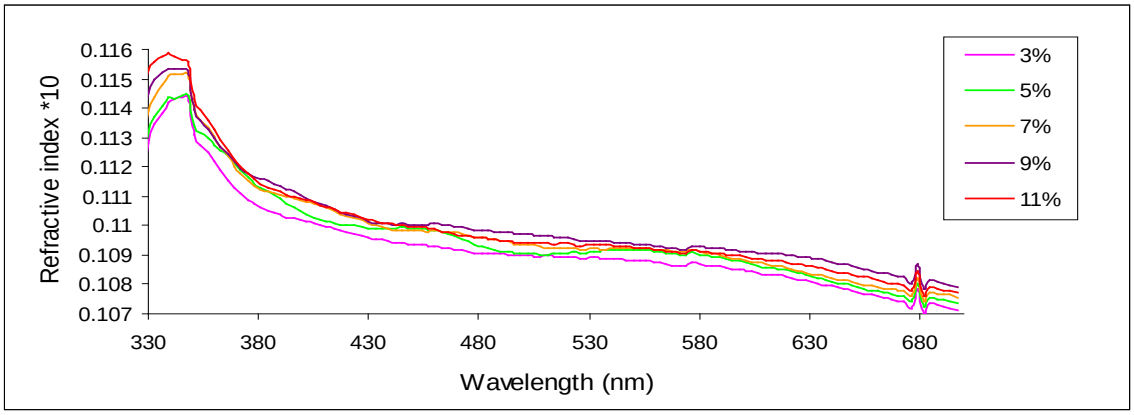

Figure 11: Reflective index as a function of wavelength at different concentrations of PVP thin film.

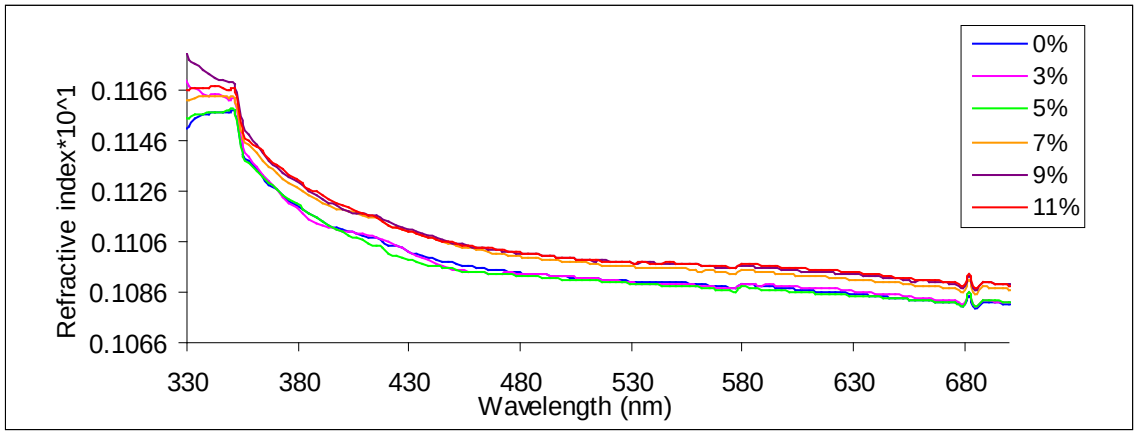

Figure 12: Refractive index as a function of wavelength at different concentrations of PVP doped Ag thin film.

Figures 13 and 14 show real dielectric coefficient as a function of wavelength at different concentrations of pure PVP and doped thin film with nanoparticle silver. The real dielectric coefficient increase after doping, because of the combing of silver nanoparticl with polymer bonds.

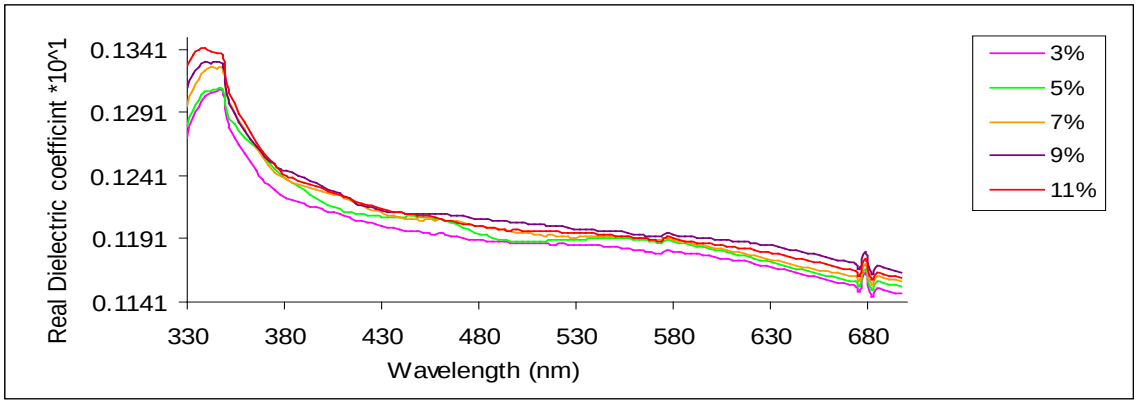

Figure 13: Real dielectric coefficient as a function of wavelength at different concentrations of PVP thin film.

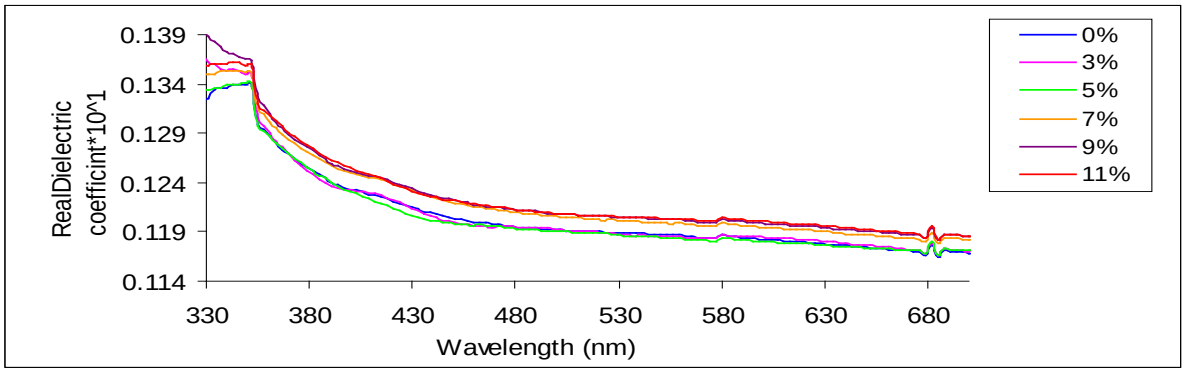

Figure 14: Real dielectric coefficient as a function of wavelength at different concentrations of PVP doped Ag thin film.

Figures 15 and 16 show imaginary dielectric coefficients as a function of wavelength at different concentrations of PVP before and after doping thin film.

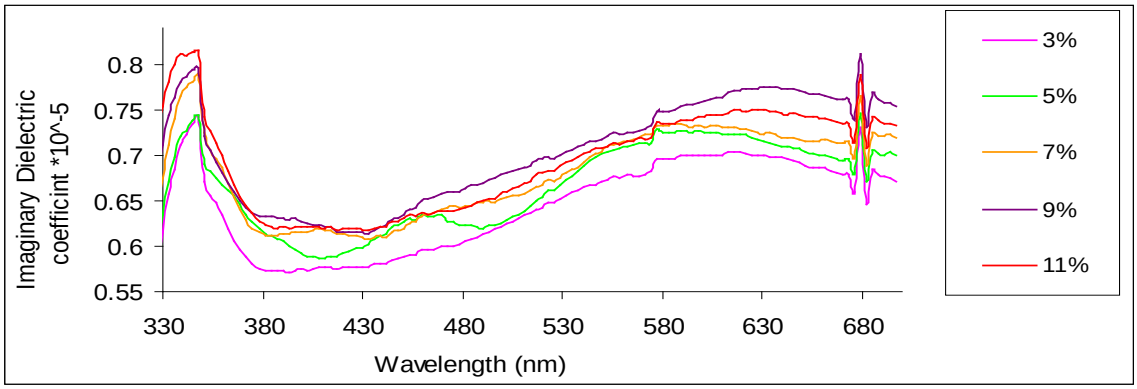

Figure 15: Imaginary dielectric coefficient as a function of wavelength at different concentrations of PVP thin film.

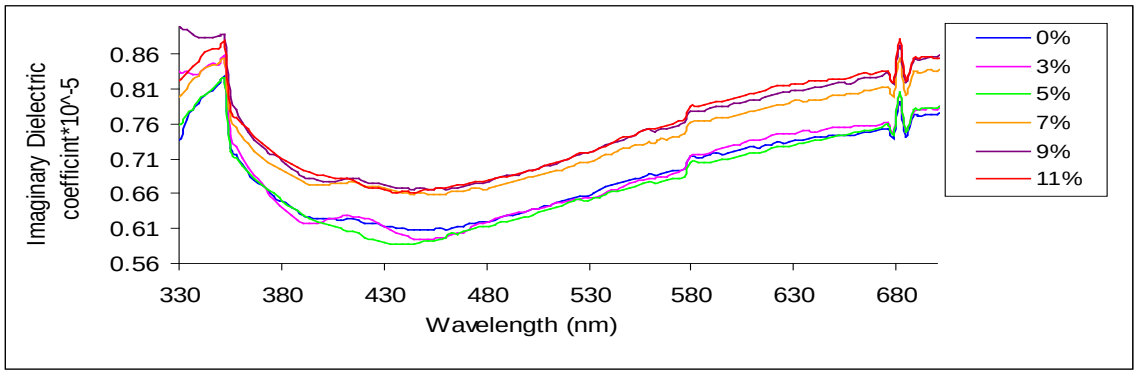

Figure 16: shows imaginary dielectric coefficient as a function of wavelength at different concentrations of PVP doped Ag thin film.

Figures 17 and 18 show $(\alpha h\upsilon)^{1/2}$ as a function of photon energy at different concentrations of PVP before and after doping thin film for allowed energy.

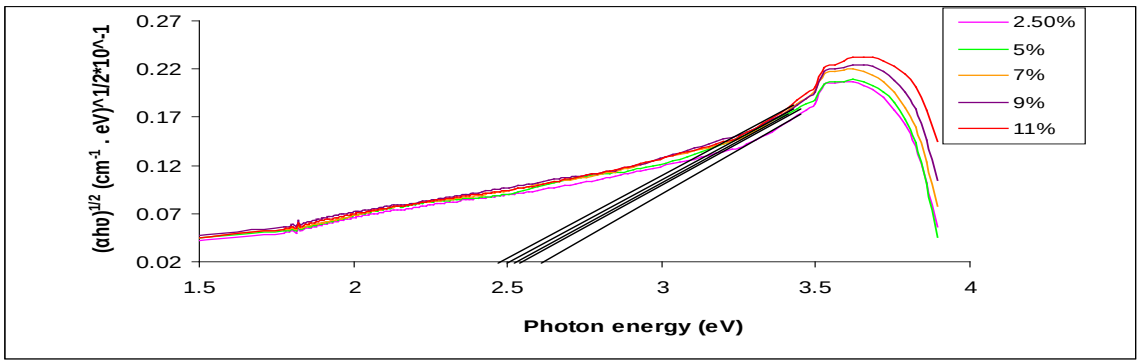

Figure 17: $(\alpha h\upsilon)^{1/2}$ as a function of photon energy at different concentrations of PVP thin film.

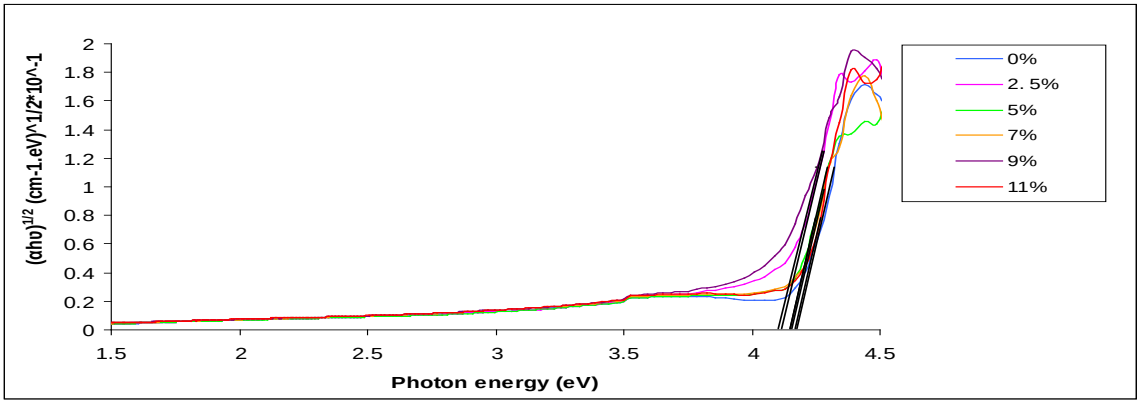

Figure 18: $(\alpha h\upsilon)^{1/2}$ as a function of photon energy at different concentrations of PVP doped Ag thin film.

Figs 19 and 20 show $(\alpha h\upsilon)^{1/3}$as a function of photon energy at different concentrations of PVP before and after doping thin film with nanoparticles silver. The forbidden energy gap is high after doping because the silver ions capture electrons

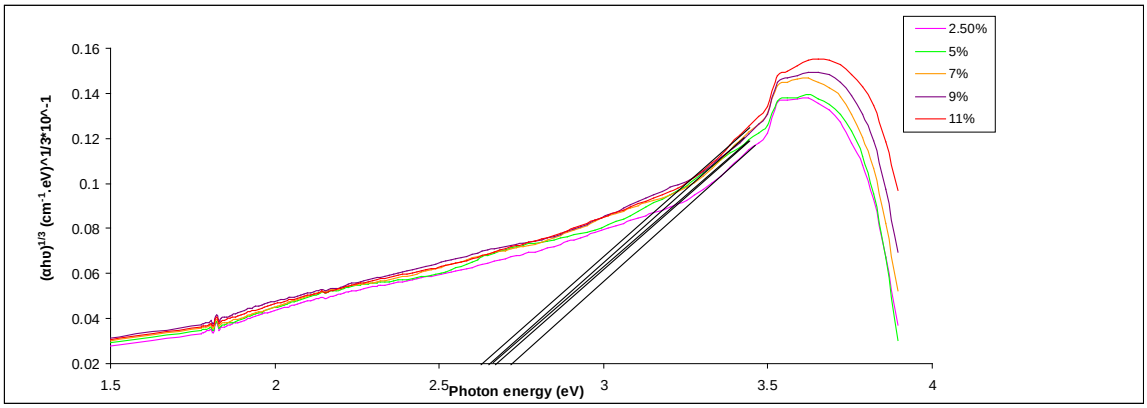

Figure 19: $(\alpha h\upsilon)^{1/3}$ as a function of photon energy at different concentrations of PVP thin film.

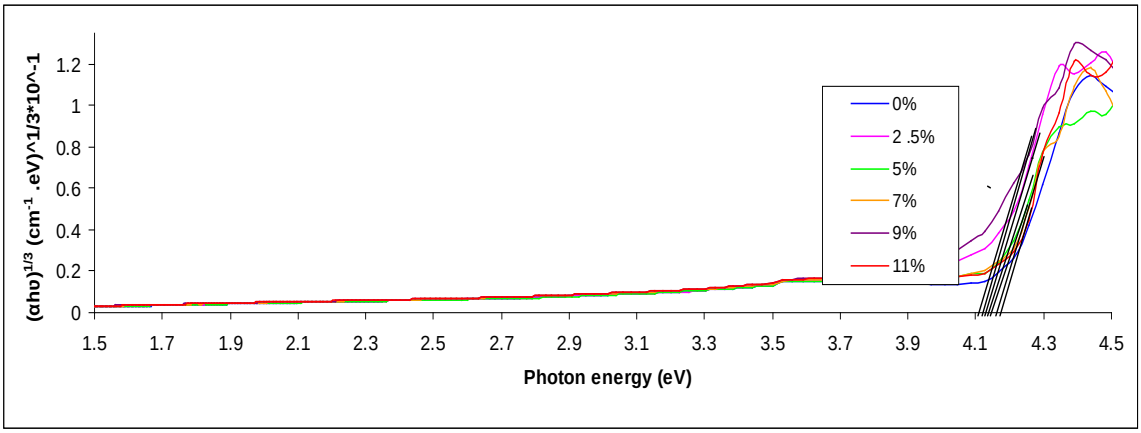

Figure 20: $(\alpha h\upsilon)^{1/3}$ as a function of photon energy at different concentrations of PVP doped Ag thin film.

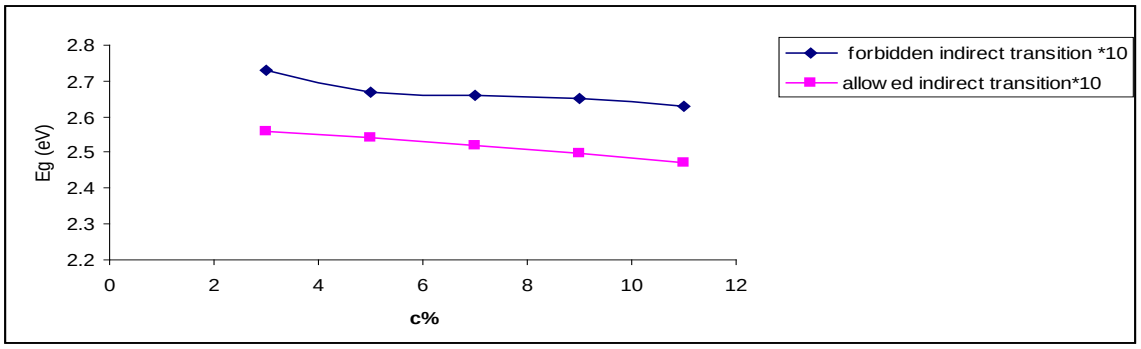

Figure 21: The dependence of Eg on doping levels for allowed and forbidden Indirect transitions of PVP thin film

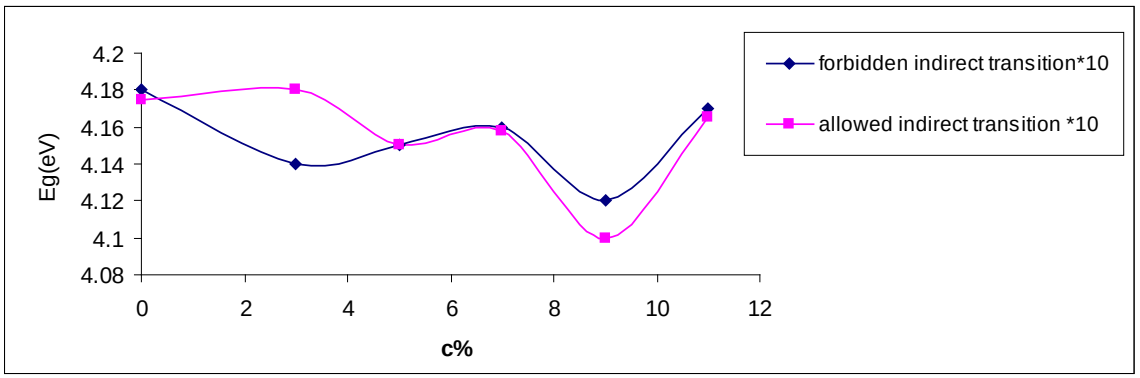

Figure 22: The dependence of Eg on doping levels for allowed and forbidden indirect transitions of PVP doped Ag thin film.

Figures 23 and 24 show finesses coefficient as a function of wavelength at different concentrations of PVP thin film before and after doping with nanoparticle silver.

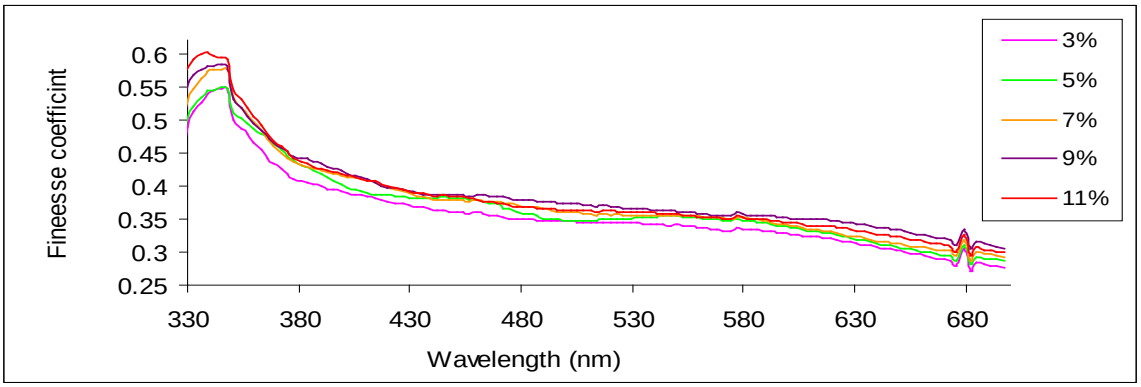

Figure 23: Finesses coefficient as a function of wavelength at different concentrations of PVP thin film.

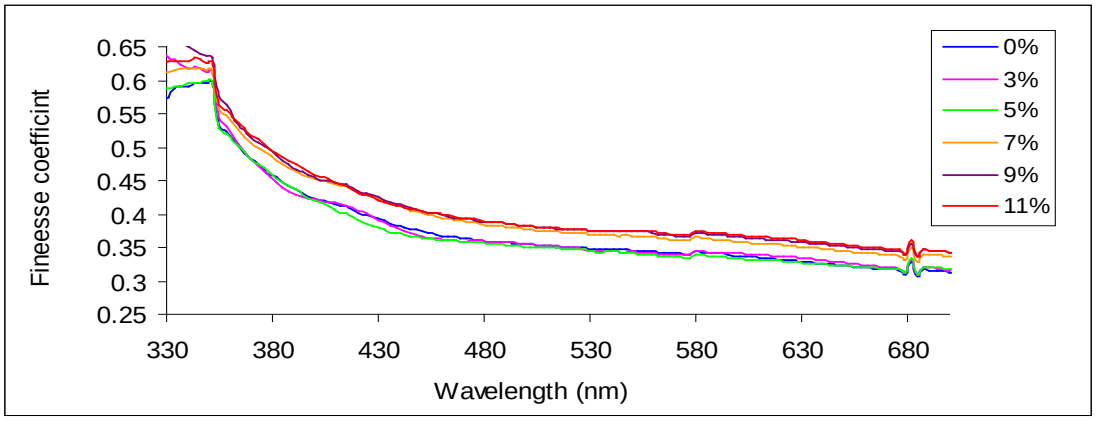

Figure 24: Finesses coefficient as a function of wavelength at different concentrations of PVP doped Ag thin film.

Figures 25 and 26 show optical conductivity as a function of wavelength at different concentrations of PVP before and doped Ag thin film.

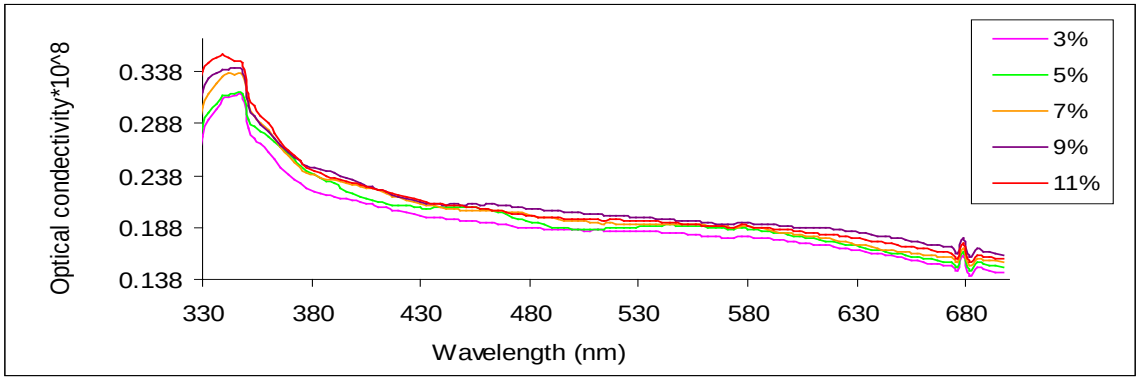

Figure 25: Optical conductivity as a function of wavelength at different concentrations of PVP thin film.

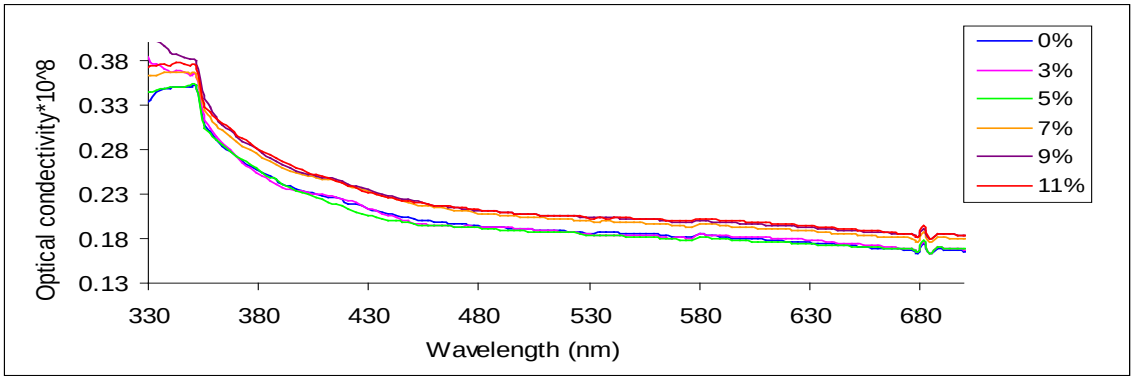

Figure 26: Optical conductivity as a function of wavelength at different concentrations of PVP doped Ag thin film.

Figures 27 and 28 show the spectrum peaks as a function of concentrations of PVP doped Ag thin film.

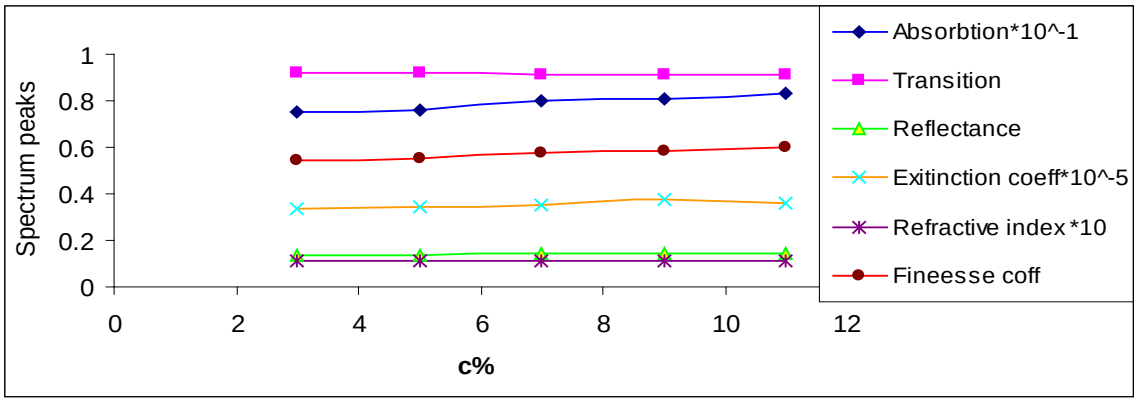

Figure 27: The spectrum peaks as a function of concentrations of PVP thin film.

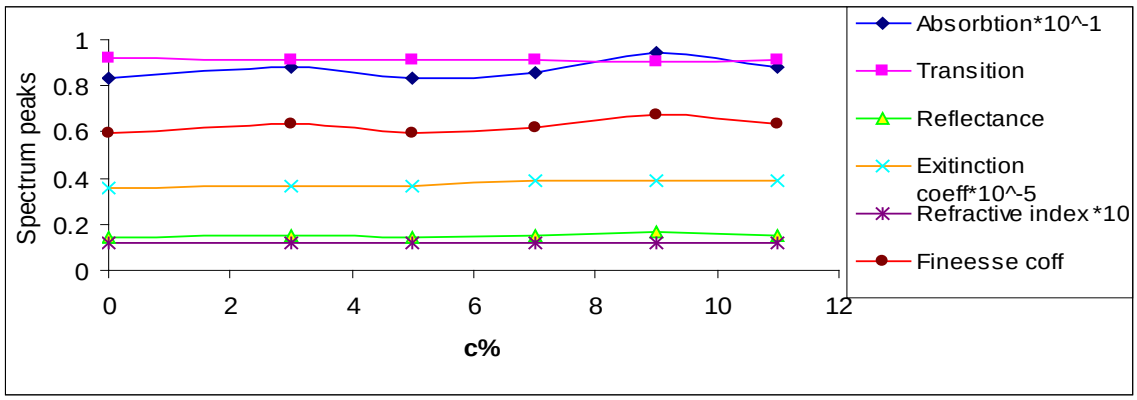

Figure 28: The spectrum peaks as a function of concentrations of PVP doped Ag thin film.

5. Conclusions

The results describe that the optical properties has a maximum values at 350nm and the absorbance values is higher after increase concentration of polymer and doping with nanoparticle silver. The other parameters change after doped with nanosilver by using laser.

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