Structural and Optical Analysis of Rhodamine 6G Thin Films Prepared by Q-switched Nd: YAG Pulsed Laser Deposition

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Abstract

Optical properties of Rhodamine 6G(R6G) thin film were presented in this work. R6G films are deposited on substrate of glass via the approach of the Q-switching Nd: YAG pulsed laser deposition (PLD) with wavelength 1064 nm, pulse duration 10 ns under vacuum condition of 10^{-3} torr. The growth films are presented and the measures have shown that films have high coefficient of absorption with increase films thickness. The direct band gap energy has been specified and found about 3.2eV for the B-band and 1.9eV for the Q-band with red shift when the thickness of film increased from 180nm to 250 nm. In addition, the Refractive index and dielectric constant highly depends on film thickness. XRD measurements show polycrystalline structure for powder, while have amorphous structure when converting to thin films.

Key Words: Rhodamine 6G (R6G), Optical Properties, Structural Properties, Dielectric Constant, Energy Gap.

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Introduction

The development of the dye laser has turned attention an important new filed of applications for organic dyes like the chemical sensors, solid-state dye laser, antenna systems, optic storage devices, solar cells, etc. and this has led to interest in the theory of optical properties of dyes [1, 2]. Laser dyes can be defined as organic complexes which radiatively relax post the optic excitation, which emits in visible or IR range. Organic dyes are pigments appear to be colored because they absorb some wavelength of light more than others [3]. Rhodamine 6G are well-known laser dyes whether the red range of the electromagnetic spectra [4]. Is a highly fluorescent Rhodamine family dye and has a bronze/red powder of the chemical formula $C_{28}H_{31}ClN_2O_3$ [5]. Even though highly soluble, and used as a gain medium. The dye is of a considerably high photo stability, low cost, high fluorescence quantum yields (00.95) [6], and its lasing dye range between 570 and 660nm with a maximal value of 590nm [7]. In this article we review briefly the relation between laser pulses and optic and structural characteristics for the Rhodamine 6G laser dye to use as a window for photovoltaic solar cell applications.

Experimental

Rhodamine 6G laser dye with molecular formula ($C_{28}H_{31}ClN_2O_3$) powder and molecular weight 479.02 g/mol used in the present work has been obtained from the chemical company (99%purity). It has been utilized for preparing a thin film with different thickness by pulsed laser deposition technique.

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This powder has been pressed under a 7 tons press in duration of 9 min for forming a target with a diameter of 9mm and thickness of 5mm. The resulted target has been maximally homogenous and dense for ensuring the best deposit quality. PLD has been performed within a vacuum chamber (10^{-3}torr).The focused Q-switching Nd: YAG laser beam incident on aimed surface deposit an angle = 45°with wavelength 1064nm, pulse width 10nsec, repetition rate 6Hz and spot size 3mm. R6G was deposited on glass substrate. The laser deposition chamber setup has been depicted in fig. (1).

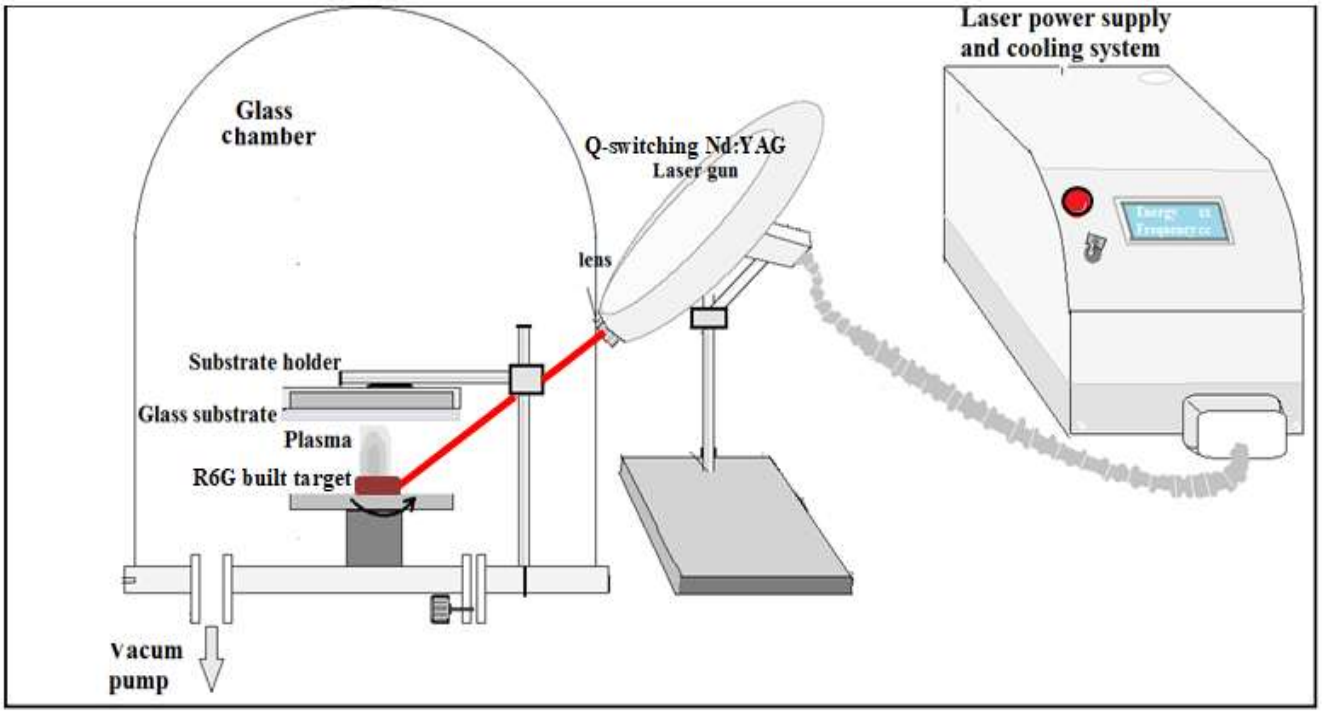

Fig. 1. Schematic for pulse laser deposition experimental set up

The film thickness has been measured with the use of an approach of laser inter-ferometer. The film's structural analysis were performed with the use of the X-ray diffractometer (XRD) utilizing (XRD6000) which is supplied with (Shimadzo6-2006, with a radiation of Cu-Kα which has wave length λ= 1.5406 Å). UV-Vis spectro-photometer of SHIMADZU UV1800type) UV-Visible recorder spectro-photometer has been utilized for the measuring of the spectrum of absorbance and transmittance in ranging between (200nm and 1100nm) for the R6G thin film. Optic measure makes up the most significant ways to determine the structure of the band of the semi-conductors and the thin films' optical constants give the knowledge about the properties of material and determining it is of a high level of importance for the utilization in any those devices.

Results and Discussions

The XRD spectrum of R6G powder and thin films grown on the glass substrates for shoots number of pulse laser to give film thickness (180) nm are shown in figure (2). It is obvious from figure(2) that the diffraction patterns of R6G powder have scattering peak around 2θ of (11.8°, 22.6°, 23.5° and 25°) related to the plans directions (102),(030),(131)and(230)respectively, while XRD spectrum for R6G thin film on glass substrate shows hump centered around 2θ of (23°) may be attributed to the glass substrate or R6G thin film. This means R6G powder has polycrystalline of tetragonal structure [8]; while thin films have amorphous structure as shown in figure(2).

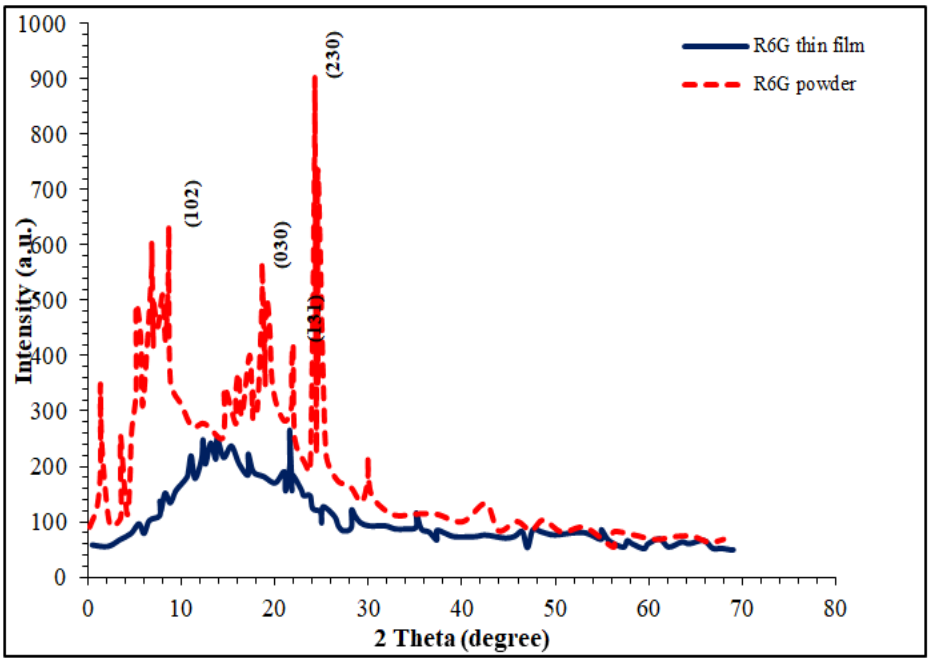

Fig. 2. XRD pattern of R6G powder and thin film

The absorption spectrum of R6G thin film deposited on the substrate of glass for shoots number of pulse laser (50,75,100) at film thickness(180, 210, 250)nm respectively are shown in figure (3). Figure shows all curves contain two bands, B-band at about (350 nm) attributed to σ-conjugated bithiophene substitutions, and Q-bands with two branches, Q1-band at about (512nm) is because of the transition between the bonding and the anti-bonding (π-π*), and Q2-band at about (545nm) due to corresponds to excitation peak [9]. Little Shift in peaks location toward the long wavelength with increased number of shoot pulses (film thicknesses). Increasing thickness cause to increase crystalline size, so reduce the strain in lattice and reduce the band energy and increase wavelength (red shift). The absorbance spectra increase with increase film thickness which is in a good agreement with Beer-Lambert Low.

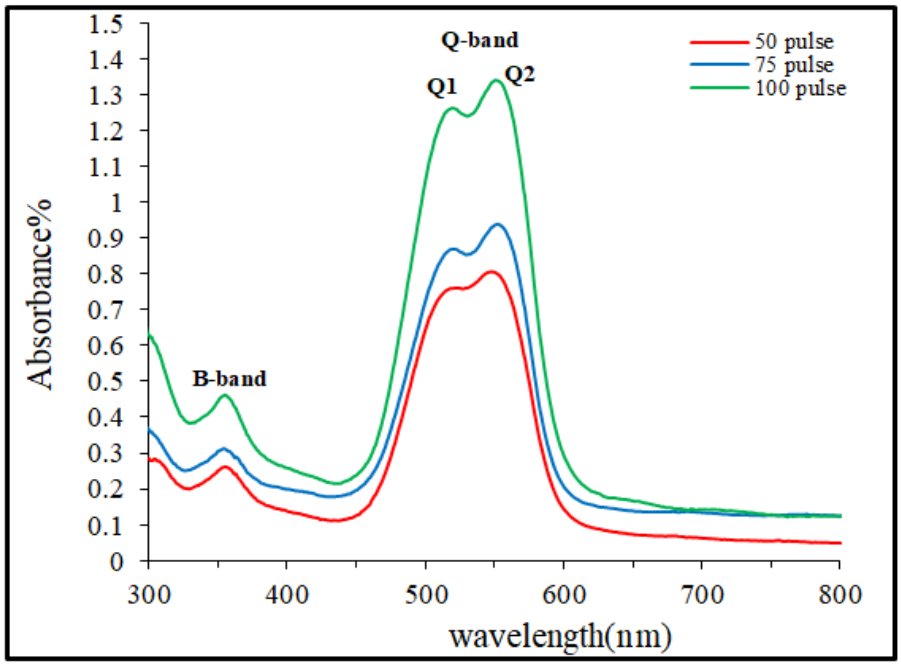

Fig. 3. Absorbance spectrum of R6G thin films at various numbers of shoot laser pulses

Figure (4a,b) illustrates the spectra of the optical transmittance and reflectance for different number of shoot laser pulses. From figure (4a) it is noted that at bigger value of the wave-length (λ>600) nm every film becomes transparent and no light gets absorbed or scattered, while at shorter wavelength (λ<600) nm existence of absorption may be noticed. The transmittance slightly increases with decreases of shoots for both B and Q bands and this is agreement with other literatures [10].figure (4b) simply shows that the reflectance increases slightly with increase the number of shoot laser pulses that means when increase the thickness of R6G thin films.

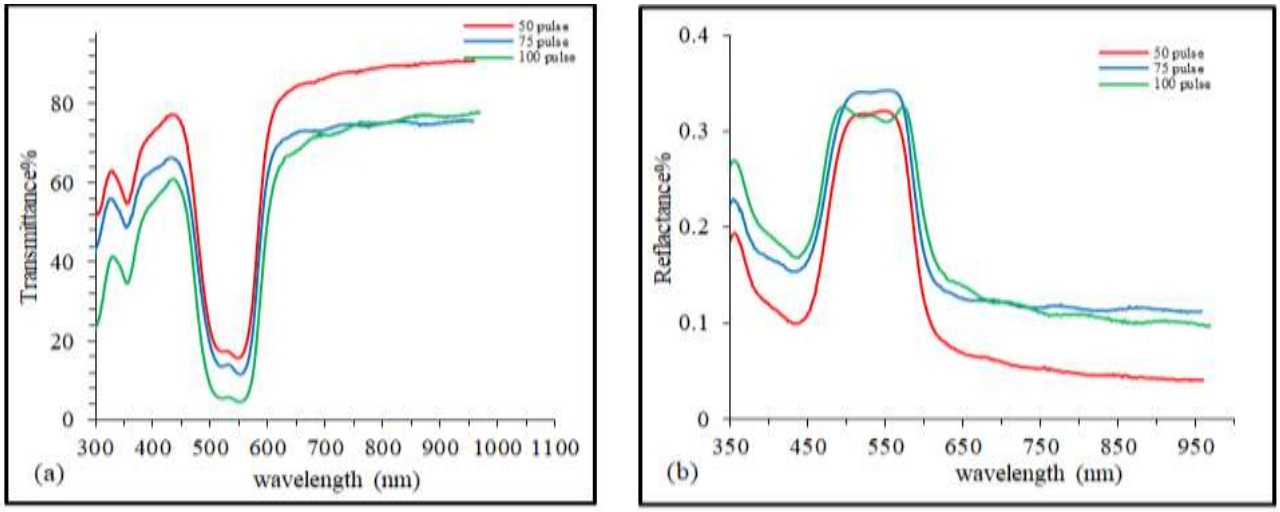

Fig.4. Rhodamine 6G thin films spectra atvarious numbers of shoot laser pulses, (a) Transmittance (b) Reflectance

With the assumption of the direct transition, the dependence of $(\alpha h\nu)^2$on the photon energy hν is plotted according to the Tauce formula[11,12] and the graph has been depicted in fig(5).

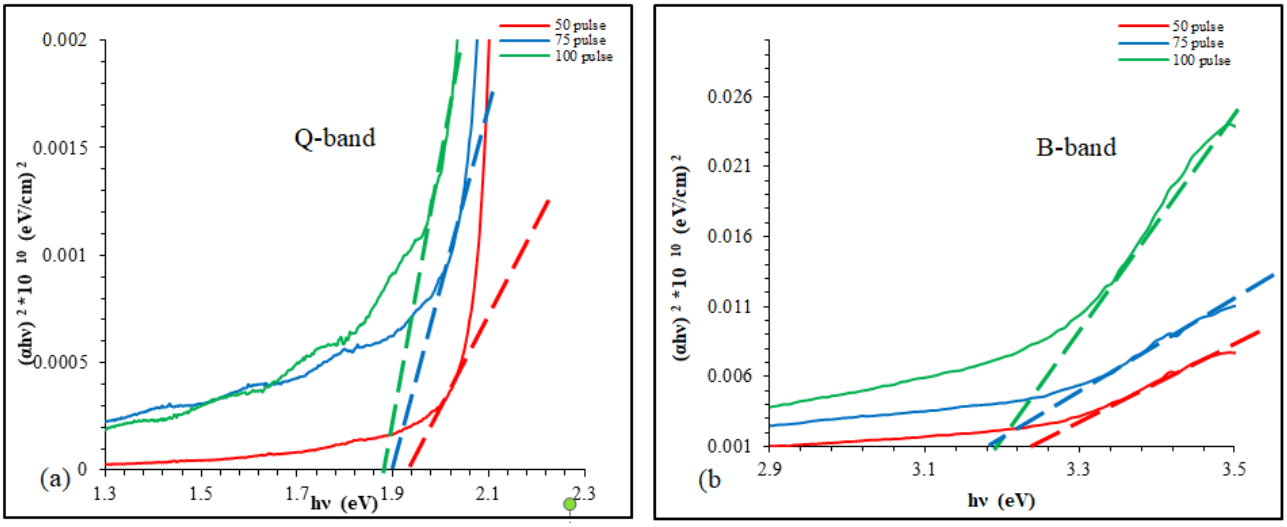

Fig. 5. Straight line extrapolation graph for obtaining the energy gap value for the R-6G thin film at number of shoot laser pulses for (a) B-band,(b) Q-band.

The linear part extrapolation in the plot that has been stated above to (αhν)=0 provides the values of

the energy gap of R6G thin films for different number of shoot laser pulses for B and Q bands, which were listed in table (1). It is seen from the figure that the energy gap value decreases with increasing the number of laser pulses and these value is a sufficient agreement with values which have been given by other researchers [13].

Table 1. Shows the energy gap for B-band and Q-band of R6G thin films at different number of shoot laser pulses

No. of shoot	Thin film thickness(nm)	Energy gap (eV) Q-band	Energy gap (eV)B-band
50	180	1.94	3.25
75	210	1.9	3.17
100	250	1.88	3.15

Refractive index (n) is one of the significant parameters for the optic materials applications and it's paramount for the determination of the film's optical constants. The refractive index was determined using the relation [14]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \text{--------- (1)}$$

where k represents the extinction coefficient ($k=\alpha\lambda/4\pi$). Fig. (6) illustrates the refractive index variation in the form of a wave-length function for the R6G thin films at different number of shoots, indicating that, the value of the refractive index increase with increasing the number of shoot laser pulses that mean with increasing the film thickness because the refractive index is a function of film thickness.

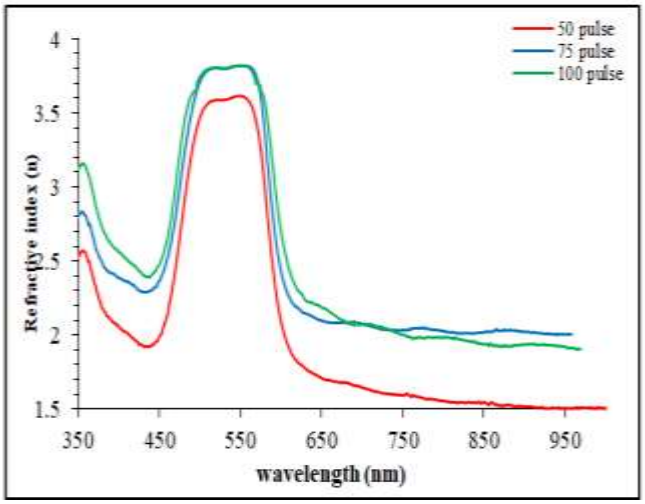

Fig. 6. The variations of the refractive index with the wave-length for R6G thin film at number of shoot laser pulses

The correlation between the coefficient of extinction (k) and wave-length for R6G at different number of shoots are shown in figure (7). From this figure can be observe that k values increase with increasing the thin film thickness and take high values in the range about (450-600)nm, whereas it is decreasing at longer wavelength (λ>600nm).

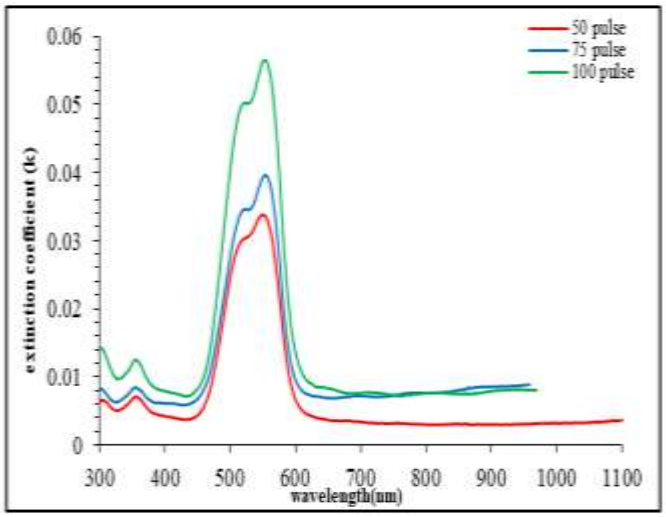

Fig. 7. The extinction coefficient's variation with the wave-length for R6G thin film at number of shoot laser pulses

The dielectric constant can be represented as $\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$, real and imaginary dielectric constant's parts are associated with to values of n and k. the values of each of ε_r and ε_i have been computed with the use of the following equations [15,16]:

$$\varepsilon_r = n^2 - k^2 \text{ --------(2)}$$

$$\varepsilon_i = 2nk \text{ ----------(3)}$$

The real (ε_r) and imaginary (ε_i) parts' variation values vs. the wave-length are shown in figure (8a,b). from figure (8a) it is clear that the dielectric constant's real part for R6G thin films increase with the increase in the thickness of the film, also the variation of (ε_r)is similar to the refractive index variation due to smaller k^2values compared to n^2, and the values of real part are higher than imaginary part. Figure (8b) shows the imaginary dielectric constant's part for the R6G thin films at different number of shoots. The variation of the (ε_i) is basically dependent on k variations associated with the absorption coefficient's variations. The dielectric constant's imaginary part increase with increasing number of shoots this caused by the increasing absorption coefficient's value as shown in figure 8.

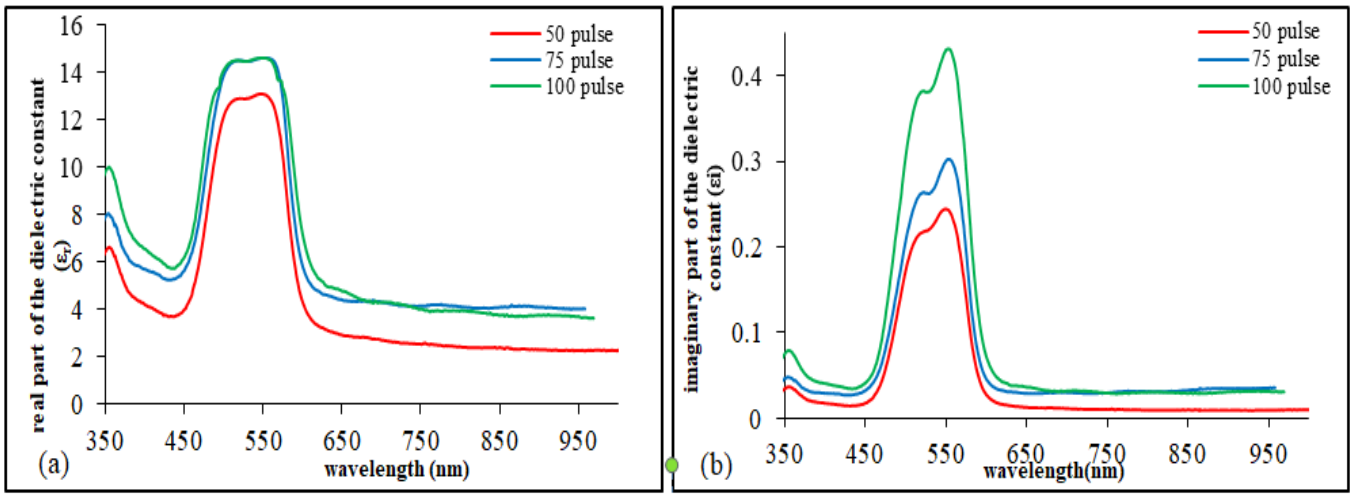

Fig. 8. (a) The variations of the dielectric constant's real part (ε_r) with wavelength for R6G thin film at various numbers of shoot laser pulses,(b) The variations of the dielectric constant's imaginary part (ε_i) with wavelength for R6G thin film at no. of shoot laser pulses.

Conclusion

Optical and structural characteristics of the R6G thin film at different number of shoots laser pulses are calculated using the PLD method. It was found that the thickness of films increase with increasing laser pulses. XRD of R6G in powder form has polycrystalline structure; while for thin films with various thicknesses have amorphous structure. From UV-Vis transmittance, absorbance spectra it can be observe that the optical transition to be direct transition. Energy band gap was determined and found has a little change when the thickness of film increased. The refractive indexes and dielectric constant of films have direct proportional with thickness. The absorbance peaks increased and shifted to large wavelength with a little change in energy gap when the number of shoots increases.

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